<u>**Response to Referee #1**</u>

We would like to thank referee 1 for the comments on our manuscript and agree on most of the mentioned suggestions. A point by point answer to the specific comments and the modifications we plan to do in the revised manuscript are given thereafter.

General comments.

We appreciate the comments pointing out that our data represent a *"coherent set of sedimentary facies"* and that *"our interpretations are largely sounds".* While a few studies have shown that OM quality of sediments can strongly vary across a single lake, our study was designed to determine what are the spatial patterns of a large set of organic compounds and compounds classes without discarding any lake location types (as pointed out by the referee, our study *"analyses a large array of surface sediments samples"*). Combined with elemental inorganic geochemistry data, we aimed at comprehensively investigating how OM molecular composition varies within the sediments of an entire lake basin and thereafter what factors and processes are involved in the spatial distribution of OM molecular composition (e.g., catchment sources, transport pathway, degradation…). Our study was not designed to get insights into specific mechanisms controlling the spatial distributions of sediments geochemistry and OM composition. Such an objective would require additional or others types of information (e.g., sediment ages, detailed catchment input) and a different sampling strategy, i.e. sediment sampling at higher spatial resolution and thus by focusing on some lake locations (e.g., the main south basin) to be a feasible research study.

While our interpretations may thus appear as "*mostly descriptive explanations for the observed patterns"*, our study clearly demonstrates that the spatial distribution of OM molecular composition is well explained by general/common factors and processes of lake ecosystems (i.e. sediment focusing, macrophytes, catchment input, mineralization). Our results give for the first time information on the OM molecular composition – as a whole matrix rather than only specific compounds or classes – that can be found in different locations of a lake in relation to such common factors. Hence, our study provide insights into the locations where it would be relevant to determine and compare the fate of C, nutrients and trace elements within a single lake, especially regarding the reactions for which OM molecular composition play a critical role, such as OC mineralization, mercury methylation, phosphorus mobility. As an example, our data indicate that the rates of OC mineralization and Hg methylation, two reactions strongly dependent on bacteria activity that are controlled by C and electron donor sources, should not only be investigated in the deeper sediments (rich in fresher algal OM) as often done, but also in, e.g., shallower sediments associated with macrophyte growth (rich in fresher higher plant and algal OM) as well as in the near-shore sheltered bays where there is accumulation of terrestrial OM including fresh carbohydrates. Thus, we believe that our study is not restricted to *"that care must be taken in using a single (or few) sediment sample(s) to characterize sediment composition of an entire lake".*

"*Quantitative exploration of how far off the mark would be to study a single sediment sample from the deep hole – as might be sampled in a more typical lake survey or paleolimnological study.*" rather than studying multiple lake locations, has been done in previous studies focused on inorganic elements such as Hg or P to assess the errors made by calculating lake budgets or reconstructing past atmospheric pollution from data collected in the deeper sediments. However, it is difficult to apply such an approach to the OM molecular composition, which in our study includes 42 groups of organic compounds. Also, the aim of our study is not to show *"that care must be taken in using a single (or few) sediment sample(s) to characterize sediment composition of an entire lake",* but rather that for studies interested in assessing key biogeochemical processes related to, for example, carbon cycling or mercury methylation, care must be taken in scaling up to a whole lake basin from a limited number of sites. It is fully possible that a limited sampling strategy might overlook critical sites. Key aspects of our study are to: i) highlight that OM molecular composition, a key parameter of reactions controlling the fate of element of major concern, spatially vary and thus not only between-lake, but also within-lake, spatial variability of those reactions should be investigated and ii) provide a baseline work/ detailed information for the relevant lake locations to study.

Specific comments.

(1) Rewording the title

We agree with referee 1 that "sediments" is a key word of our study, and thus the title of our manuscript will be changed to "*Spatial variability of organic matter molecular composition and elemental geochemistry of sediments in a small boreal Swedish lake*".

(2) A short methods description for sample collection and processing is needed.

The 44 studied surface sediments (0-10cm) samples were collected as follow:
"*Short sediment cores (0-25 cm) were taken with a gravity corer from the ice-covered lake in winter 1997 and 1998, and were sectioned into an upper sample (0-10 cm) and a lower sample (10-25 cm; not studied here) on-site. In the laboratory, the samples were weighed, freeze-dried, and reweighed to determine the water content and dry mass of the sediment. The freeze-dried samples have been stored in plastic containers within closed boxes shielded from light and at room temperature since winter 1997-1998. Before further analysis in this study, the samples were finely ground at 30 Hz for 3 min using a stainless steel Retsch swing mill.*"
This paragraph which includes additional information about the sample collection and processing will replace the third paragraph in the sub-section "2.1 Study site and samples".

(3) Better clarity on OM sources

In order to avoid confusion with the term "plants", we will clarify this term by using instead "higher plants and mosses" or "higher plant" in the revised manuscript.

(4) Discussion of the decreasing bSi with depth (lines 438-441)

We agree with the reviewer that the lower bSi content in deeper than in shallower sediments is related to light limitation with increasing water depth. For us, this was meant by our explanation that diatom production in this clear, acidified lake is mostly benthic.

For better clarity, we will replace the corresponding paragraph (lines 438-441 in the initial manuscript) by:

"The bSi decline, from ~15 to 4 %, indicates a decrease of diatom production with depth due to increasing light attenuation and thus suggests that the diatom assemblage is dominated by benthic species as shown for many acidified lakes, such as surrounding lakes in Svartedalen (e.g., Andersson, 1985; Anderson and Renberg, 1992)."

(5) Discussion of the depth-linked trend in algal OM degradation (lines 449-453)

We agree that higher rate of sediment burial can favor OM preservation (although the sedimentation rates in the deeper basins of Härsvatten shown in studies of past atmospheric Pb pollution are nonetheless very low with >500 yr for the upper 30 cm). Thus higher mineralization of algal OM in the shallow and intermediate water depth sediments with respect to the deeper sediments could be related to lower accumulation rates in addition to oxic conditions, this latter hypothesis being supported by the elemental inorganic geochemistry. We will thus modify the corresponding sentence (lines 449-453 in the initial manuscript) as follows:

"Although our results are based on the top 10 cm of sediment and thus account for different sediment ages, we suggest that the higher proportions of decomposed algal material, based on N-compound and chlorophyll composition (Table 1), at shallower and intermediate water depths (<21m) than at the deepest sites (23.5–24.5 m) reflect higher mineralization rates of OM in shallow/intermediate areas. Higher OM mineralization rates in these areas than at deeper sites are most probably due to more oxic conditions and lower sedimentation rates (i.e. longer exposition time of sediment OM at the sediment-water interface)."

(6) and (7) Discussion of the spatial distribution of Fe, Mn and Al

We fully agree with the reviewer that the spatial distribution of Fe, Al and Mn contents in lakes, including our study lake, is not restricted to the formation and/or preservation of Fe, Al and Mn (oxy)hydroxides, but depends on others factors and processes such as the discharge of groundwater, diffusion in the sediment or sediment diagenesis (comment 6). However, the main aim of our study

was not to describe and comprehensively understand the spatial distribution of the sediment inorganic fraction, for which there are a number of published studies addressing this. Our study was focused on the spatial distribution of the sediment OM molecular composition as clearly stated in the introduction. Thus, we did not, and do not want to, discuss in detail the spatial distribution of the inorganic elements because we know the limitations of using only elemental contents to describe inorganic geochemistry, and more specifically that Fe, Al and Mn are not confined only to one mineral phase and they may reflect both detrital material and/or dissolved or amorphous phases (as pointed out by the referee 1 in comment 7).

The main/more significant trends for Fe, Al and Mn highlighted by the PCA and cluster analyses are i) Fe, Al contents together with As, P and Fe:Al, indicative of Fe, Al (oxy)hydroxides, are high or low in certain sediment locations and ii) Mn content together with Co, Pb and Mn:Fe, indicative of Mn (oxy)hydroxides are high in certain sediment locations. Hence, we use this information to discuss the relationship between OM composition and redox conditions which have evidences from others sediments parameters (such as sediment depth, epilimnion depth and/or sediment bottom type), have support from previous studies and appeared to the referee 1 as **"quite reasonable, as far as it goes"** (cf. comment 6).

Therefore, in the revised manuscript, we agree to follow the suggestion of comment 7 and add information on the limitations of using Fe, Al and Mn contents to describe inorganic geochemistry in the sub-section "*3.1.2. Principal components of the elemental geochemistry*" where we present and interpret PCA results (lines 229-237 in the initial manuscript), as follows (the new sentences are in bold):

"Positive loadings on $PC3_{geo}$, which explains 16 % of the total variance, are found for Al and Fe along with As, P and Y (Fig. 2b). ***Compared to elements such as Mg, Na and K that are mostly confined to the silicate fraction of sediments, Fe and Al may reflect both detrital material and dissolved or amorphous phases. However, the fact that As and P contents as well as Fe:Al ratio plot with Fe and Al contents on the positive side of $PC3_{geo}$, but not S content, strongly suggest that sediments with high $PC3_{geo}$ scores are associated with*** *higher content of Fe and Al (oxy)hydroxides known* ***to strongly*** *bind both As and P (Mucci et al., 2000; Plant et al., 2005; Zhu et al., 2013). $PC4_{geo}$ captures 12 % of the total variance and separates Mn, Co, Pb and to a lesser extent Fe (positive loadings) from OM and Br (negative loadings; Fig. 2b).* ***Although Mn, as Fe and Al, is not confined to a specific mineral phase and can reflect both detrital or dissolved and amorphous phases,*** *the positive loadings are interpreted as reflecting Mn (oxy)hydroxides, which bind Pb, especially when they contain cobalt (Co) (Yin et al., 2011). This interpretation is supported by the positive loadings on $PC4_{geo}$ of the ratio Mn:Fe, often used as a paleolimnological proxy for bottom water oxygenation (Naeher et al., 2013). The negative loadings could indicate a terrestrial OM fraction that is rich in Br (Leri and Myneni, 2012)."*

However, we prefer to not include further discussion on the factors and processes involved in the spatial distribution of Fe, Al and Mn, because it would lead to more emphasis in our discussion

on the spatial distribution of inorganic geochemistry, which is not our objective, and our data based on total concentrations are not precise enough to do so.

(8) High concentrations of S and trace metals, Hg, Pb, Zn in sheltered bays (lines 536-541).

We think that our explanation for the high concentrations of S along with trace metals (Hg, Pb, Zn) in the sediments of near-shore sheltered bays of Härsvatten (sites N1-2 and S23) has been misunderstood. Hence, we have clarified the corresponding paragraph (lines 536-541 in the initial manuscript). Indeed, we do not ascribe the high concentrations of S and trace metals to accumulation of atmospheric pollutants directly. As pointed by the referee, this would have "**invoked very localized deposition for which there is not much evidence or theoretical mechanism**". We ascribe the high S and trace metals contents to the accumulation of terrestrial organic matter derived from the coniferous-forested catchment in theses sediments (enrichment in lignin). Indeed, the OM fraction of boreal terrestrial ecosystems (i.e. forest soils and wetlands) is well known to be enriched in S and trace metals because it retains atmospheric S and trace metals since the industrial revolution (Johansson et al., 2001). Also, there are strong evidences that the transport of terrestrial OM to boreal aquatic ecosystems is associated to significant input of trace metals (Grigal et al., 2002; Rydberg et al., 2008).

However, we cannot rule out that accumulation of metal sulfide due to specific redox conditions or near-shore groundwater gradients is involved in the accumulation of S, Hg, Pb and Zn in the sediments of two near-shore sheltered bays of Härsvatten. We have thus added these hypotheses in the manuscript.

The corresponding paragraph (lines 536-541 in the initial manuscript) will be thus re-written as follows:

"*The sediments found in a small number of near-shore locations (cluster$_{geo}$ 4 and cluster$_{OM}$ 5; n=4), three of which being located in two more-sheltered bays at the northwestern corner and the southern end of the lake and thus more protected from wind circulation (Bindler et al. 2001, Abril et al. 2004), predominantly accumulate terrestrial OM as indicated by the abundance in lignin oligomers and the ratio indicative of in-lake:terrestrial plant OM that are respectively above and below 10% of whole-lake average (Table 3). Accumulation of OM coming from the coniferous-forested catchment most probably explained the high OM content (i.e. 52-58%, which is as high as in the deeper sediments of the main south basin) as well as the high concentrations of S and trace metals (i.e., Hg, Pb and Zn) in these near-shore sediments (Table 1). Indeed, boreal forest soils are known to be enriched in S and trace metals because their organic fraction retains atmospheric S and trace metals since the industrial era (Johansson and Tyler, 2001). Also, there are evidences that the transport of terrestrial OM to boreal aquatic ecosystems is associated to significant input of trace metals (Grigal et al., 2002; Rydberg et al., 2008). Alternatively, high S and trace metal*

contents could also be linked to accumulation of metal sulfides due to near-shore groundwater gradients and/or anoxic conditions or redox cycling related to the large input of terrestrial OM."

This new paragraph will bring two additional references in the revised manuscript, which are:

Johansson, K. & Tyler, G. Impact of atmospheric long range transport of lead, mercury and cadmium on the Swedish forest environment. Water, Air Soil Pollut. 425 279–297 (2001).

Grigal, D. F. Inputs and outputs of mercury from terrestrial watersheds: a review. Environ. Rev. 10, 1–39 (2002).

Technical corrections.

All technical corrections have been considered.