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Interactive comment on “Fractionation of iron species and iron isotopes in the Baltic Sea euphotic zone” by J. Gelting et al.

Anonymous Referee #2

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The authors present a study of the speciation and isotope composition of Fe in the euphotic zone of the Baltic sea, during spring and summer. The prospect of using Fe-isotopic and Fe-speciation techniques to investigate particulate and colloidal Fe cycling in coastal waters is interesting and this topic is principally well suited for publication in Biogeosciences. That said, I'm not convinced that the authors provided compelling interpretations of the Fe-isotope data, especially regarding the distinction between various Fe-sources and the importance of water-column cycling. Although those Fe-isotope data are worthwhile of publication, I unfortunately found too many erroneous statements or reasoning that precluded me to recommend publication at this point. Hence, I don't think this paper should be accepted, unless major clarifications and revisions are being made. I think the paper could be largely improved if the data were presented with more careful considerations of alternate interpretation and proper

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credit to other publications.

specific comments: 1) First, the text needs careful editing for grammar and spelling. In several places, the text is really difficult to read - and understand.

2) The introduction is too long and way too technical for what it has to say. It does not present the paper in a concise way nor give a clear overview of the sites selected for this study. More importantly, it does not give a justification and perspective for using Fe-isotopes, which is rather a new tracer. The sentence L14, p6494 “This will lead to an enrichment of heavy Fe in the aggregated fraction” will not resonate in most reader mind, unless a presentation (even succinct) of the Fe-isotope systematics is given upfront.

3) The description of the analytical methods is insufficient and, in some case, poses questions about the reliability of the data. I understand that dissolved Fe concentrations (<0.22um) in the water samples is determined by ICP-MS without any matrix separation. Using a dilution factor of only 4, matrix effects are certainly problematic even with the use of internal standards. Please give the limit of determination and analytical precision on certified water standards with this technique. The presentation of the Fe-isotope technique is also insufficient. The reference to Ingri et al., 2006 does not give a clear idea about the overall external precision of the d56Fe measurements. For example, precisions of 0.01 per mil (2STD) reported by Ingri et al. is probably related to internal precisions of a single measurement, not the external precision of the method. Please explain how the errors bars in Figures 6 and 11 have been obtained. Also, please report the d56Fe values and other ancillary data in the form of tables.

4) A major issue of this paper is that the variations of d56Fe values in particulate Fe in the Baltic sea is quite small (between -0.1 to 0.2 per mil) compared to the overall variations of d56Fe in rivers (between -0.9 to +0.4 per mil, see reference below). Hence, I'm absolutely not convinced by the interpretation of Fe-isotope signatures as reflecting a mixing between river-borne colloids or particles and Fe-oxyhydroxides derived from

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oxidation of dissolved Fe(II) in the euphotic zone. Basically, everything could be explained by the input of riverine Fe without the need of water-column redox processes. What do we know about the variability of Fe-isotope composition of freshwater source to the Baltic Sea? Fantle, M.S. and DePaolo, D.J., 2004. Iron isotopic fractionation during continental weathering. *Earth Planet. Sci. Lett.*, 228, 547-562. Escoube, R., Rouxel, O., Sholkovitz, E. and Donard, O., 2009. Iron Isotope Systematics in Estuaries: The case of the North River, Massachusetts (USA). *Geochim. Cosmochim. Acta.*(73), 4045–4059. Bergquist and Boyle, 2006 (reference cited).

5) The authors assume throughout the paper that average continental crust $\delta^{56}\text{Fe}$ values is 0 per mil (relative to IRMM-14). This is not true. Beard et al.2003 and many other studies (none cited!) have dealt with the variations of $\delta^{56}\text{Fe}$ in crustal rocks and the accepted $\delta^{56}\text{Fe}$ value for the bulk crust is about 0.09 per mil \pm 0.05 relative to IRMM-14. This distinction is really important considering the small range of $\delta^{56}\text{Fe}$ values discussed in this paper. Hence, “positive” $\delta^{56}\text{Fe}$ at around 0.2 per mil as presented in Figure 6 are only 0.1 per mil heavier than the bulk crust. Considering the analytical precision and potential variability of $\delta^{56}\text{Fe}$ in various crustal materials, it is very speculative to explain such “positive” values solely by the occurrence of Fe-oxyhydroxides.

6) I’m puzzled by the comparison between Fe/Ti and $\delta^{56}\text{Fe}$ values. Although a correlation is actually observed in Figure 6 (please, report error bars for both Fe/Ti and $\delta^{56}\text{Fe}$ values in this diagram), a two-component mixing line should be observed between $\delta^{56}\text{Fe}$ and Ti/Fe, not Fe/Ti. On the other hand, in figure 11, the authors report a range of $\delta^{56}\text{Fe}$ values between -0.1 and -0.25 while Fe/Ti remains practically unchanged near crustal values. Those two conflicting observations are not sufficiently discussed in the paper. Also, while Al can be also affected by organic compounds, such as Fe, it would have been interested to also report Al/Fe ratios together with Ti/Fe ratios.

7) P6511, the references related to the importance of redox cycling in generating light Fe-isotope fluxes from coastal sediments are not appropriate. Severmann et al., 2006

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initially reported Fe-isotope compositions of several margin sediment porewaters and suggested the importance of diagenetic reactions in producing isotopically light benthic Fe fluxes. This study was also confirmed by Staubwasser et al., 2006 and Rouxel et al., 2008. Staubwasser, M., Blanckenburg, F.v. and Schoenberg, R., 2006. Iron isotopes in the early marine diagenetic iron cycle. *Geology*, 34, 629–632. Severmann, S., Johnson, C.M., Beard, B.L. and McManus, J., 2006. The effect of early diagenesis on the Fe isotope compositions of porewaters and authigenic minerals in continental margin sediments. *Geochimica et Cosmochimica Acta*, 70, 2006-2022. Rouxel, O., Sholkovitz, E., Charette, M. and Edwards, K., 2008. Iron Isotope Fractionation in Subterranean Estuaries. *Geochem. Cosmochim. Acta*, 72, 3413-3430.

8) P6506, L20, the statement that the aggregation of colloidal Fe during estuarine mixing should remove heavy isotopes is misleading. In fact, Bergquist and Boyle (2006) reported river water-seawater mixing experiments and found that precipitated colloids have $\delta^{56}\text{Fe}$ values up to 0.2 per mil heavier than than dissolve Fe. Since this value is close to the analytical precision, those results should be used with caution. More recently, Escoube et al., 2009 (see reference above) reported dissolved and particulate Fe-isotope composition along the North River estuary and didn't observe any significant Fe-isotope fractionation during colloid flocculation.

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