

Reply to Frank Poitrasson

We thank Dr Poitrasson for his helpful review of our manuscript. Dr Poitrasson raises a number of issues that we would categorize as follows: 1) lack of general information on Baltic Sea hydrography and particle flux; 2) concerns related to the general redox structure of the Eastern Gotland Basin (in comparison to the Black Sea and Norwegian Fjords); 3) the sources of Fe; 4) the distribution of Fe<sup>2+</sup> and Fe<sup>3+</sup>; and 5) analytical issues regarding reproducibility and blanks. There are additional specific comments.

We quote all references in addition to the ones in our manuscript in full.

### 1) Concerning the general information on Baltic Sea hydrography and particle flux in the Eastern Gotland Basin (EGB)

In order to accommodate reviewers requests for more general information on the Baltic Sea, we rewrote the respective chapter for the revised manuscript:

#### **“2 Baltic Sea hydrography, general redox zonation and state of Fe redox cycling in fall 2005”**

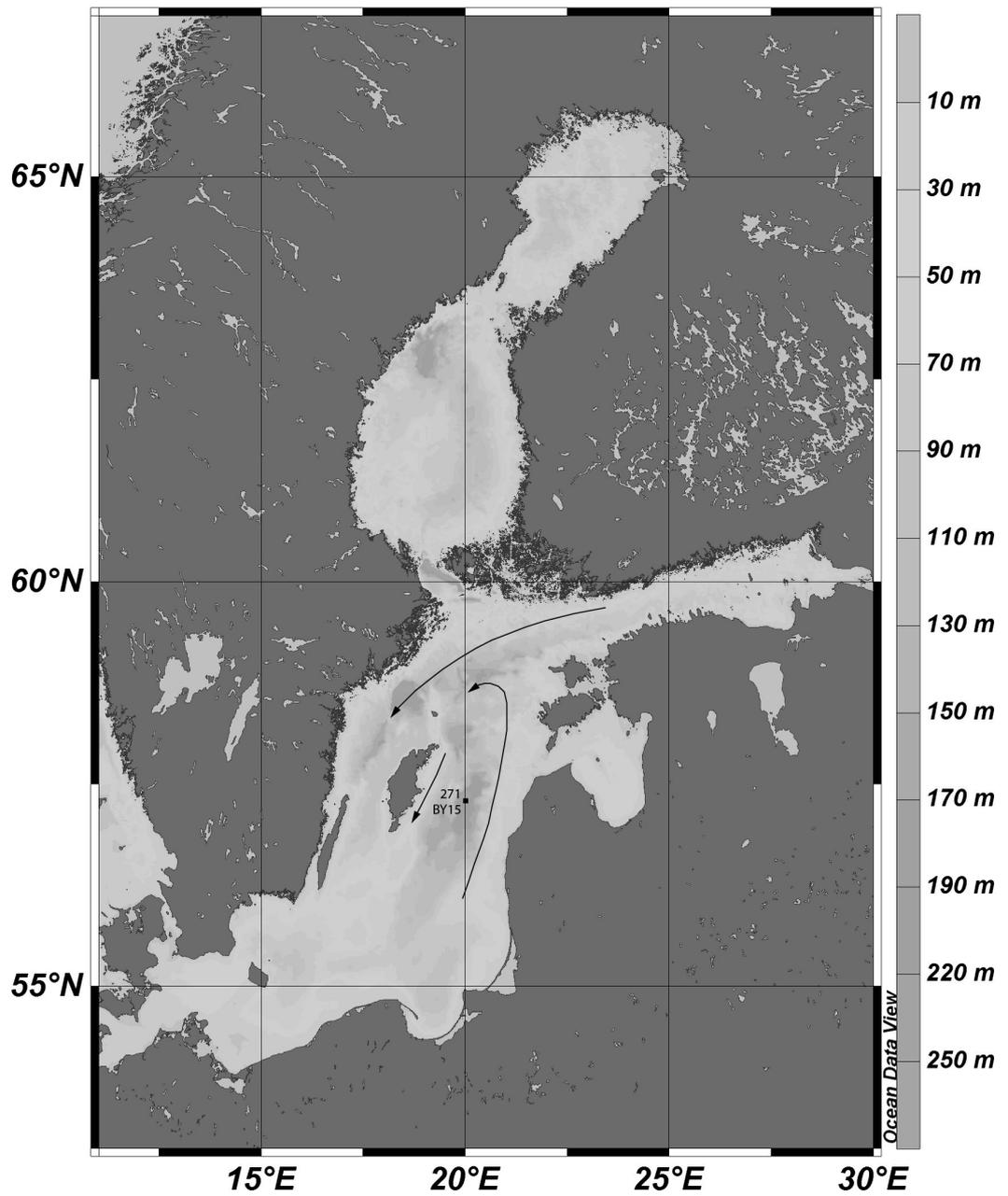
The Eastern Gotland Basin (EGB) is the largest of a series of anoxic basins in the Baltic Sea with a maximum depth of 250 m (see figure below). Anoxic conditions in the Gotland Deep result from an estuarine type circulation pattern in the Baltic Sea, stable stratification with a pronounced pycnocline due to strong gradients in temperature and salinity between approximately 60 and 90 m (Fig. 2a, b) and limited exchange of deep water with the adjacent North Sea by a series of shallow sills (Meier et al. 2006, Matthäus et al. 2008 “*The inflow of highly saline water into the Baltic Sea*” In: *State and evolution of the Baltic Sea*, 265-309, edited by Nausch et al.). Small-volume intrusions of warm but saline water in summer prevent oxygen concentration to drop to zero below the pycnocline between approximately 80 and 125 m (Neretin et al. 2003 “*Manganese cycling in the Gotland Deep, Baltic Sea*” *Marine Chemistry*, 82, 125-143; Matthäus et al. 2008, Pohl and Turnewitsch 2010 “*An estimate of the efficiency of the iron- and manganese-driven dissolved inorganic phosphorus trap at an oxic/euxinic water column redoxcline*” *Global Biogeochemical Cycles*, 24, art. no. GB4024). Deeper water is replaced by major intrusions on average only about once in a decade by storm-induced entrainment of salty water from the North Sea. Water column ventilation by winter convection varies but is confined to the upper ~ 70 m. (Fig. 2b). Below the pycnocline a manganoous, a ferruginous, and a sulfidic (euxinic) redox zone are observed down the water column (for terminology see Canfield and Thamdrup 2009 *Geobiology*, 7, 385-392). The zones are each confined at the top by the respective redox boundary and overlapping with each other (Neretin et al. 2003; Pohl et al. 2004, 2008; Pohl and Turnewitsch 2010; Dellwig et al. 2010 “*a new particulate Mn-Fe-P shuttle at the redoxcline of anoxic basins*”, *Geochim. Cosmochim. Acta* 74, 7100-7115). During anoxic intervals redox boundaries shoal with progressing time and the ferruginous zone becomes somewhat compressed as the sulfidic boundary rises. All redox boundaries vary on a seasonal scale with an amplitude of approximately 10 m (Pohl et al. 2004). The last major inflow prior to this study occurred in winter 2003. Monthly monitoring of chemical properties in the EGB show that by the time of this study’s sampling campaign in October 2005, anoxic conditions had returned below 125 m depth (Nausch et al. 2008). Euxinic conditions with moderate concentrations of total sulfide (0 – 60  $\mu\text{M}$   $\Sigma \text{H}_2\text{S}$ ) prevailed below 150 m.

Vertical particle flux through the pycnocline in the EGB is strongly seasonal and dominated by a maximum flux of biogenic organic matter in late summer and fall (Pohl et al. 2004). Vertical flux in winter has a lower magnitude and is dominated by lithogenic alumo-silicates. Lithogenic particles originate from rivers and are distributed by turbulent transport in the

water column above the pycnocline. Within the water column a substantial flux of internally redox-cycled authigenic  $\text{MnO}_x$  and  $\text{FeOOH-PO}_4$  is observed across the redox boundaries (Neretin et al. 2003, Dellwig et al. 2010). These minerals are formed by oxidative precipitation and result in significant suspended Mn ( $\text{Mn}_{\text{SPM}}$ ) and moderate Fe ( $\text{Fe}_{\text{SPM}}$ ) maxima (Neretin et al. 2003; Pohl et al. 2004, 2008, Pohl and Turnewitsch 2010). The high  $\text{Mn}_{\text{SPM}}$  and  $\text{Fe}_{\text{SPM}}$  zones may show as variable turbidity maxima in sensor profiles. The steep Fe concentration gradient generally found across the ferruginous zone – with Fe concentration reaching up to micromolar concentration – may sustain an eddy-diffusive upwards flux of dissolved Fe of up to  $\sim 10 - 15 \mu\text{mol m}^{-2} \text{d}^{-1}$  (Pohl and Hennings, 2005). In addition to vertical particle flux, there is considerable lateral lithogenic flux by near bottom nepheloid transport, with a composition typical for the shallow basin margins (Leipe et al. 2008 "*Sedimentary records of environmental changes and anthropogenic impacts during the past decades*" In: *State and evolution of the Baltic Sea, 395-439, edited by Nausch et al.*). This lateral nepheloid flux exceeds vertical flux. Average sedimentation rates in the EGB are almost 1 mm/year and much too high to allow for a significant contribution by atmospheric deposition. Some trace elements in the water column are affected by atmospheric deposition (mostly antropogenic), but this is not the case for the elements discussed here (Mn and Fe).

The water column in the EGB in fall 2005 displays the typical Fe profile of marine anoxic basins with intense Fe redox cycling across the ferruginous zone (Fig 1c). Concentrations of dissolved Fe ( $\text{Fe}_{\text{dis}}$ ) of less than 10 nM in the oxic surface layer increase to almost 400 nM in the sulfidic water (as to the depth level sampled). At the top of the ferruginous zone oxidative precipitation results in a maximum concentration of  $\text{Fe}_{\text{SPM}}$ , predominantly with iron oxyhydroxides ( $\text{Fe}_{\text{IOH}}$ ) comprising mixed a  $\text{MnO}_x\text{-FeOOH-PO}_4$  phase at the top and  $\text{FeOOH-PO}_4$  inside the sulfidic zone (Dellwig et al. 2010). This  $\text{Fe}_{\text{SPM}}$  maximum broadly overlaps with a general suspension maximum in the turbidity sensor profile (Fig. 2b, c). The  $\sim 10$  m discrepancy in depth is most likely due to the 2 days difference between Fe sampling and acquisition of the turbidity profile.

A comparison of the fall 2005 profile data of  $\text{Fe}_{\text{dis}}$  and  $\sum\text{H}_2\text{S}$  to the penultimate anoxic period studied in detail during 1981 and 1985 by Dyrssen and Kremling (1990) shows that both  $\text{Fe}_{\text{dis}}$  and  $\sum\text{H}_2\text{S}$  at 180 m are at the low end of concentrations measured in the euxinic waters. The 2005 EGB data are well below the equilibrium concentrations of FeS indicative of sulfide precipitation and determined for the euxinic profiles in 1981 and 1985. No FeS was detected in the sulfidic water column by SEM scanning of suspended matter by Dellwig et al. (2010) in a study of the 2006 and 2007 water column at practically equal redox conditions. FeS precipitation below the sampled depth in 2005, however, may have occurred.



New Figure: A map of the Baltic Sea, with bathymetry and surface currents for the central Baltic Sea. Bottom currents are similar. Data Profile (Station 271 / BY 15) as indicated.

## 2) Concerning the general redox structure of the EGB in comparison to the Black Sea and Norwegian (Framvaaren) Fjord shown in Millero's textbook (Millero 2006)

Although Millero (2006) does not show profile data from the Baltic Sea for dissolved metals concentration, but the general similarity in chemical properties between the (central) Baltic Sea anoxic basins and other marine anoxic basins is well established (and shown in earlier chapters of Millero 2006). We will limit this discussion to relevant elements, which are Mn, Fe and S. The similarity has been noted many times in original papers such as Lewis and Landing (1991), or in recent comparisons, such as Dellwig et al 2010. Differences exist most visibly in the extent of sulfidic (euxinic) conditions. Because the EGB is flushed episodically, the sulfide inventory varies on the time scale of a few years. After flushing of the basin, inventories of dissolved Mn, Fe and sulfide build up. The precipitation of Mn-oxides and Fe-oxyhydroxides is evident shortly after the flushing due to very low solubility. The ion activity product of dissolved Fe and sulfides apparently exceeds the solubility constant of relevant Fe-sulfides only several years after flushing. The last flushing event previous to the time of our 2005 cruise occurred in 2003. Inventories have built up steadily thereafter (Turnewitsch and Pohl 2010), but Fe-sulfides were not detected in the water column of 2006 and 2007 (Dellwig et al. 2010). As we discussed, the concentrations in 2005 were lower than at saturation conditions during the penultimate sulfidic interval. In summary, the EGB resembles the Black Sea profile down to ~ 150 m. In Norwegian Fjords the redox sequence from manganous to ferruginous is much compressed within ca. 10-20 m, but principally similar to the EGB.

## 3) Concerning the sources of iron

Average sedimentation rates in the EGB are almost 1 mm/year and much too high to allow for a significant contribution by atmospheric deposition. Atmospheric deposition is not relevant for Fe (Pohl et al. 2004). Most of the detrital material originates from rivers, but there are no Fe-isotope data available. It is clear from suspended matter analysis by SEM that authigenic particles dominate the particle spectrum between ~80 and 180 m is dominated by authigenic particles (Neretin et al. 2003; Dellwig et al. 2010). With respect to the shape of the profile indicating possible bottom efflux of  $Fe_{diss}$ , we would like to point out that our profile does not reach to the bottom and hence is not conclusive. As we discussed in detail in our response to the same concern raised by Dr Severmann, it is not likely that sulfidic sediments at the bottom of the EGB are significantly contributing Fe to the water column. The generally much higher concentration of sulfide in pore water can sustain much less  $Fe_{diss}$  than the water column. For details we would like to refer to our response to Dr Severmann's comments.

## 4) Concerning the distribution of $Fe^{2+}$ and $Fe^{3+}$

Unfortunately, marine DOC is only poorly constrained simply because the entire spectrum of masses often is undifferentiated (Millero 2006). In the Baltic Sea, the majority of DOC originates from terrestrial sources (Stedmon et al. 2007). To our knowledge there are no studies of natural organic Fe binding ligands in the Baltic Sea available.

The analysis of Fe(II) in anoxic seawater is not trivial (see Breitbarth et al. 2009) and was not done during our 2005 cruise. In addition to analytical obstacles, operational difficulties such as the separation of colloidal Fe (Lewis and Landing 1991) must be considered. The formation of colloidal Fe(III) during oxidative precipitation will be significant in the zone of Fe(II) oxidation (Pham & Waite 2008). Unfortunately, there is no published data available regarding the concentration of organic ligand bound  $Fe_{dis}$ . As such, the system is too poorly constrained to calculate the  $Fe^{2+}/Fe^{3+}$  ratio. Although it could be done, we would not like to calculate  $Fe^{2+}/Fe^{3+}$  ratios by using the simple reaction scheme that was applied to model Fe isotope fractionation between inorganic  $Fe^{2+}$  and  $Fe^{3+}$  species (Beard & Johnson 2004). As we cannot quantify oxidation and precipitation rates in the redox transition layer, the calculation would be meaningless. Such data will have to come from

future measurements. Our profile data suggest that Fe isotope fractionation during oxidative precipitation is dominated by kinetic effects, but we are unable to provide any meaningful analysis or argument towards a specification of the ligands involved in that reaction process beyond a discussion in the most general terms for that poorly constrained system.

#### 5) Concerning the blanks and reproducibility

The overall external reproducibility for samples calculated from the four anoxic samples replicate measurements (Miller & Miller 2007, p.57) is 0.16 ‰ (2sd). Our maximum blank is about twice the average blank of Lacan et al. (2008). We attribute this to the fact that the Mg coprecipitation method we used for Fe-separation comprised two precipitation steps and two passes through an exchange column. Concerning the blank issue, we would like to note that the 200-400 ng Fe quoted by us was the amount of Fe loaded into the mass spectrometer's autosampler. The amount of Fe per sample during chemical separation was at minimum two times higher. As we said, yields were variable and not as high as in Lacan et al (2008), which is another flaw in the Mg-coprecipitation method. The blank to sample ratio in our worst case (20 ng blank for 200 ng of sample) is comparable to Lacan et al. (2008), whose worst case is an ~ 8 ng blank for a 80 ng sample (their tab. 2, sample B10: 0.16 nM Fe or ~ 90 ng of total out of a 10 L sample according to methods description). At the time of the measurements we were unaware of the method used by Lacan et al (2008). The bottom line is that we would not recommend the use of the Mg-coprecipitation method for isotope work, particularly because with the larger volume samples commonly required the amount of precipitate becomes too large to handle.

#### Concerning specific comments:

We will check the manuscript once more for spelling and linguistics. Responses to specific comments regarding the content of the manuscript as follows:

- CTD stands for Conductivity-Temperature-Depth profiling and is standard sensor log procedure on scientific ship cruises.
- Concerning request to check particles by SEM: we cannot do this in retrospect as the filters have been digested for MS analysis. However, the issue is covered in detail by Dellwig et al (2010) for the EGB for cruises one and two years later at practically equal redox conditions.
- "*Where was Fe<sup>2+</sup> concentration data presented?*": we originally cited Breitbarth et al 2009 in Biogeosciences Discussion. However, the section we were referring to was significantly altered in the final paper. Since there is no Fe<sup>2+</sup> data available for the EGB in the redox transition layer of interest here, we will skip this reference. See also above.
- Comment to page 4807, 110-13. Dissimilatory Fe reduction within the water column is not at variance with sulfidization within the underlying sediments (see Canfield et al. 2005; *Aquatic Microgeobiology*). We claim that dissimilatory Fe reduction expresses itself in the  $\delta^{56}\text{Fe}_{\text{SPM}}$  of the water column based on results from our previous studies in sediments. The low  $\delta^{56}\text{Fe}$  efflux mentioned above did refer to the  $\delta^{56}\text{Fe}$  in fluid efflux (initially Fe(II)aq) from surrounding sediments above the euxinic water column. Because of the fractionation factor  $\Delta^{56}\text{Fe}_{\text{Fe(II)aq-Fe(III)s}} = -1.3\text{‰}$  (Johnson and Beard 2004), such efflux should have a much lower isotopic value than reactive Fe in the sediment (which may originate in parts from Fe<sub>SPM</sub>).
- Note on HCl leaching: we agree, which is why we say that this procedure applied by Fehr et al (2010) represents only a crude approximation of reactive Fe.
- Concerning the confusion on chapter 4.3: We refer all aspects of the mixed layer (where plankton resides) to Gelting et al (2010). We discuss the lower part of the oxic layer in terms of the Severmann et al (2008) benthic shuttle model for Fe isotopes. The model suggests that the water column should be dominated by low  $\delta^{56}\text{Fe}$  from diagenetically derived Fe-efflux from the sea-floor sediments within the oxic zone of the water column. Here, supposedly

high TOC fuels early marine diagenesis and dissimilatory Fe reduction occurs near enough underneath the sediment surface that significant amounts can diffuse back into the water column along the concentration gradient of Fe in the sedimentary pore water. We do not observe the expected a low  $\delta^{56}\text{Fe}$  value and explain what it means with respect to the Severmann model.

- Suggested use of Poitrasson reference for crustal average instead of Beard et al (2003): There is a  $< 0.1$  ‰ difference in  $\delta^{56}\text{Fe}$  between the IRMM-14 and the Beard-scale. That minor difference should be meaningless in the context of our argument. We will report a crustal average value of  $\sim 0.1$  ‰ on the IRMM-14 scale and refer to Beard and Johnson (2004), where both scales are given.
- Concerning the figure: practical salinity units (psu) rather than g/l are routinely used in oceanography (Millero 2006). There is also no useful indicator for the overall redox state in the aquatic environment (see Lindberg 1984, *Science* 225, 925-927). We will add the info for the turbidity sensor (it is measured by another sensor using back-scattered light, measurements are uncalibrated). And of course we will adjust error bars according to the above response.