

## ***Interactive comment on “Changes in mobility and solubility of the redox sensitive metals Fe, Mn and Co at the seawater-sediment interface following CO<sub>2</sub> seepage” by M. V. Ardelan and E. Steinnes***

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Journal: BG Title: Changes in mobility and solubility of the redox sensitive metals Fe, Mn and Co in seawater - sediment interface following CO<sub>2</sub> seepage Author(s): M. V. Ardelan and E. Steinnes MS No.: bg-2009-69 Special Issue: The ocean in the high-CO<sub>2</sub> world II

Reply to Reviewers Comments: We thank the editor and both reviewers for taking the time to read our paper and for their constructive comments. We have now made changes to the manuscript to make it publishable in Biogeosciences

In the following, we listed our responses to each of the referee's comments.

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Reviewer #1

Specific Comments

1- “How do you completely de-couple the seepage signal from that induced by the resuspension? How long after the resuspension event did you take your sample? From the figures it is not clear when this resuspension took place. How much material was resuspended?”

We explained how we tried to de-couple the CO<sub>2</sub> seepage signals from that induced by resuspension in page 5628, lines 11- 27. To make this section more apparent we add a sub-title for this section as “Testing the sediment re-suspension effects on trace metal solubility and transport” Weakness of proper control on re-suspension during the experiment has been discussed in the text. We assumed that amount of re-suspension was the same between control and co<sub>2</sub> chamber, since flux of the seepage of both gases (CO<sub>2</sub> and N<sub>2</sub> in control) was same (section 2.1 page 5628 lines 11-27. We did not attempt to measure the amount of re-suspended sediment. The seepage was not so powerful and did not lasted not so long time (about 3 min for each day). Therefore CO<sub>2</sub> and N<sub>2</sub> did not re-suspend entire sediment column. Only tiny portion of the sediment has been re-suspended. All of these points (2.1, page 5628, lines 11-27) and the effect of re-suspension has been discussed in the text in sections, 3.2, 3.2.1 (pages 5635, 5636 and 5637) and 3.2.2 (pages 5639, 5641 and 5646).

2-“How fast were the DGT units moving? They will be affected by limited flow and have an increased diffusive boundary layer, thus affecting the calculations. How did the authors overcome this and did they measure/estimate the DBL and is 12cms-1 fast enough?”

Total thickness of diffusive gel and filter is about 1.34 mm. If diffusive boundary layer (DBL) is less than % 20 (around 0.2 mm) of the total thickness of gel+ filter in the DGT unit, error due to DBL has to be considered minimal (Warnken et al. 2006). In Warnken et al (2006), threshold flow and high flow rates during DGT deployment have

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been given as 2cm s<sup>-1</sup> and 10 cm s<sup>-1</sup>, respectively. Garmo et al (2003) also used flow rates of 10 cm s<sup>-1</sup>. Our flow rate (12 cm s<sup>-1</sup>) is higher than these values. Therefore we can safely assume that DBL did not effect our calculation.

3- “What are the biological implications of the change in metal concentrations due to the CO<sub>2</sub> seepage? The last paragraph of the conclusions could be very informative. Are the concentrations seen after CO<sub>2</sub> seepage above OSPAR designated concentrations, would these conditions have a detrimental effect to the benthic community?”

We have added the following paragraph in the conclusion section to address these questions : “Our results show that level of the dissolved and DGT labile concentrations of Fe, Mn and Co in CO<sub>2</sub> chamber (DFe: 100-150 nM, FeDGT: 250-400 nM; DMn: 600-1900 nM, MnDGT: 350; DCo: 8 nM CoDGT: 2.5 nM are much higher than the highest background concentration of OSPAR convention for the protection of the marine environment of the North-east Atlantic (DFe: 10.7 nM, DMn: 2.7 nM and DCo: 0.4 nM) (OSPAR 2006). Our study indicates that “Fe-Mn shuttle” (diffusion of reduced and dissolved Mn and Fe oxyhydroxides from suboxic-anoxic zone of sediment into oxic sediment-water interface and subsequent precipitation Fe and Mn as oxyhydroxides) in surface sediment and sediment-water interface has been disturbed by CO<sub>2</sub> leakage and acidification. Fe-Mn shuttle is an important mechanism for i) removal of many toxic elements and trace metals from water into sediment (Ardelan et al, 2009) and, ii) microbial stratification in sediment and sediment-water interface (Burdige, 2006). Disturbed Fe-Mn shuttle mechanisms will cause enhanced concentrations of toxic heavy metals and trace elements in the seawater. Natural bacterial stratification may have also been affected due to disturbed Fe-Mn shuttles. Any changes in the processes taking place in the upper section of marine sediments have a intense effect on the local and global cycling of many elements. CO<sub>2</sub> leakage and acidification can significantly alter these biogeochemical processes occurring in surficial marine sediment and may have profound impact on bacterial processes and other biological activities in surface sediment. Especially coastal sediments subjected to elevated anthropogenic inputs of

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certain toxic metals (Burdige, 2006), after CO<sub>2</sub> leakage and acidification sediment will be source for some toxic metals after CO<sub>2</sub> leakage. There is a potential that these contaminants may be taken up in the food chain.

4- “What about speciation – you have used DGT probes which give an indication of speciation compared to total values from the sea water.”

DGT-labile metal distributions has been discussed under different metal sub-heading. In this study the main focus are how CO<sub>2</sub> would effect the solubility and mobility of some trace metals. That is why we believe that to discuss DGT more than we did would cause the manuscript i) moves the attention from the main focus (CO<sub>2</sub> effects on trace metal mobility) ii) will be longer than to be acceptable as a focused research paper.

Nevertheless, we follow the suggestion of reviewer 1 to include relevant discussion on DGT-labile fractions of studied metals as a separate sub-section:

3.2.5 DGT-labile fractions of trace metals The fraction of a metal present as free cation or bound in labile complexes are likely to be in the DGT-labile fraction in seawater, given that the metal has affinity to the Chelex-100 resin. These fractions of metals may be also most bioavailable forms of metlas for biological organisms. The capturing of DGT-labile metals by Chlex-100 depends on the dissociation kinetics of the metal species at the surface. The metals in seawater that are strongly complexed with large organic ligands (such as Fe) would be considerably underestimated by using average diffusion coefficient for calculation of DGT-labile concentration due to the diffusion coefficients of organic-metal complexes are about one or two orders of magnitude lower than the free metal ion diffusion coefficients in the gel under the same conditions (Zhang and Davison, 1999; Li et al., 2005). However, during the CO<sub>2</sub> seepage, the dissociation ability of some organic-metal complexes (both soluble and solid surface–metal complexes) and their dissociation kinetics may be changed. Our results indicate that it is likely some organically complexed and particulate-bound metal, such as Fe, is rapidly

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dissociated by CO<sub>2</sub> seepage and subsequently able to diffuse through the gel and be collected by the DGT chelating resin. Therefore, not only dissolved fractions but also total suspended metal concentrations are important to elaborate the real metal mobilization under CO<sub>2</sub> seepage. On the other hand, if the metal ions are present as inert complexes they will not be released and subsequently will be bound to Chelex-100. Based on these facts, the results of DGT-labile fractions in the present work potentially did not only give information about the time average concentration of existing DGT-labile metals in the studied environment but also on kinetics of the transformation of possible non-bioavailable forms of metal into easily bioavailable fractions.

#### Technical Corrections

5-"The figures Fig 3, 4 and 5, make the scales bigger (text) or produce more figures so they can be easily viewed."

All of these figs have been re-drawn with bigger text.

6-Regarding the legend for Figure 3, 4 and 5:

The legends for Figs 3, 4 and 5 re-written (please see at the end of this document)

#### Reviewer #2

##### Specific Comments

1- "The comments of Anonymous Reviewer 1 are valid and should be addressed. With regard to resuspension, the paragraph at the bottom of pg. 5628 of the methods section appears to say that "resuspension" samples were taken during the time that CO<sub>2</sub> or N<sub>2</sub> were being bubbled through the sediment. "No-resuspension" samples were taken 6 hours after the bubbling ceased. This detail is lost in the subsequent discussion, creating some confusion. Also, the authors state that an increase in turbidity was seen during bubbling. Was turbidity measured?"

We agree with Reviewer 2, therefore we separate the section (page 5628 lines 11-27)

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which explain how re-suspension de-coupled from CO<sub>2</sub> seepage. A sub-title has been added for that section. (please see comment no 1 for Reviewer 1).

Unfortunately we did not measured turbidity, however, during the gas seepage in both control and CO<sub>2</sub> chamber turbidity was visible, especially at the bottom of the containers. In both treatments, after about 2 hr there was no visible turbidity in both chambers. In order to be sure, we waited 5-6 hr after the daily gas seepage (seepage was ca 3 min/day) to take samples which represent "no-resuspension".

2-"The figures are indeed much too small to be clearly seen on the screen without enlargement and the printed figures are nearly illegible."

Figs 3, 4 and 5 have been improved, please see comments no 5 and 6 for Reviewer 1

3-"The conclusions section adequately summarizes the main findings of the experiment. I do, however, agree with Reviewer 1 that the authors should elaborate on the potential environmental impact of CO<sub>2</sub> seepage. Given a realistic estimate of the amount of CO<sub>2</sub> released and the area of sediment affected, what might be the geochemical and biological consequences?"

We agree that the conclusion section should be elaborated. Therefore, we have added a paragraph to address the suggestions from both Reviewer 1 and Reviewer 2 (please see comment no 3 for Reviewer 1, above)

#### Conclusion

Our results give some information about how CO<sub>2</sub> leakage may have effects on the mobility and solubility of redox sensitive metals in transient condition. It is apparent that longer CO<sub>2</sub> leakage experiments with more realistic experiments (under continuous water flow and various pressure) will better provide the conditions for a possible leakages from CO<sub>2</sub> storage zones

Sincerely

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Murat Van Ardelan,

On behalf of Eiliv Steinnes

#### References

Ardelan M.V., Steinnes E., Lierhagen, S. and Linde, S. 2009. Effects of experimental CO<sub>2</sub> leakage on solubility and transport of seven trace metals in seawater and sediment. In print, Science and Total Environment )

Burdige, D.J. 2006. Geochemistry of Marine Sediments, Princeton Univ. Press, 630 pp.

OSPAR 2006. Convention for the Protection of the marine Environment of the North-East Atlantic-Quality Agreement on Background Concentrations for Contaminants in Seawater, Biota and Sediment (OSPAR Agreement 2005-6)

Warnken, K. W., Zhang, H., and Davison, W.: Accuracy of the Diffusive Gradients in Thin-Films Technique: Diffusive Boundary Layer and Effective Sampling Area Considerations, Anal.Chem., 78, 3780–3787, 2006.

Figure 3: Concentrations of total acid-leachable Fe (TFe), dissolved Fe(DFe) and DGT labile Fe (FeDGT) in water during the first (a, c, and e) and second (b, d and f) phases of the experiment in CO<sub>2</sub> seepage (full triangles) and in the control (open circles) chambers. Note that scales of TFe are logarithmic (a, b). The amounts of Fe collected in the DGT units are shown by columns (e and f): light columns for control, dark columns for CO<sub>2</sub> chamber. Flux of FeDGT from the sediment into DGT units in the first (g) and second (h) phases of the experiment in CO<sub>2</sub> (full triangles) and control chamber (open circles). The time average flux of FeDGT in the sediment, for CO<sub>2</sub> and control chambers were indicated by a broken line and dotted line, respectively. Figure 4: Concentrations of total acid-leachable Mn (TMn), dissolved Mn(DMn) and DGT labile Mn (MnDGT) in water during the first (a, c, and e) and second (b, d and f) phases in CO<sub>2</sub> seepage (full triangles) and in the control (open circles) chambers. Note that

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scales of TMn and DMn in the first phase of the experiment (a and b) are logarithmic. The amounts of Mn collected in the DGT units are shown by columns (e and f): light columns for control, dark columns for CO<sub>2</sub> chambers. Flux of MnDGT from the sediment into DGT units in the first (g) and second (h) phases of the experiment are shown in CO<sub>2</sub> (full triangles) and control chamber (open circles). The time average flux of MnDGT in the sediment, for CO<sub>2</sub> and control chambers were indicated by a broken line and dotted line, respectively.

Figure 5: Concentrations of total acid-leachable Co (TCo), dissolved Co(DCo) and DGT labile Co (CoDGT) in water during the first (a, c, and e) and second (b, d and f) phases of the experiment in CO<sub>2</sub> seepage (full triangles) and in the control (open circles) chambers. The amounts of Co collected in the DGT units are shown by columns (e and f): light columns for control, dark columns for CO<sub>2</sub> chambers. Flux of CoDGT from the sediment into DGT units in the first (g) and second (h) phases of the experiment are shown in CO<sub>2</sub> (full triangles) and control chamber (open circles). The time average flux of CoDGT in the sediment, for CO<sub>2</sub> and control chambers were indicated by a broken line and dotted line, respectively.

Interactive comment on Biogeosciences Discuss., 6, 5623, 2009.

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