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Discussions

Interactive comment on "The submarine groundwater discharge as a carbon source to the Baltic Sea" *by* B. Szymczycha et al.

B. Szymczycha et al.

pempa@iopan.gda.pl

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Biogeosciences Discuss., 10, C1948–C1950, 2013 www.biogeosciences-discuss.net/10/C1948/2013/ "The submarine groundwater discharge as a carbon source to the Baltic Sea" by B. Szymczycha et al. Authors reply to Anonymous Referee #1 comments: General comment: 1. The lack of scientific rigor is remarkable, and lends large uncertainties in the results presented. See specific issues to follow below. Moreover, the attempt to scale up largely unverified results to the greater Baltic Sea system and even the entire world's oceans is incredibly premature for this work. I think that the authors would have been better suited preparing one complete and scientifically sound paper from their data on this project rather than dividing their data set up into a number of small papers as they seem to be doing. In my opinion, this

dilutes the quality of each paper and therefore the impact they have on the scientific community. In this case, I just don't think there is enough in this manuscript (data or interpretations) to merit publication. Answer: The main aim of our report was to present dissolved carbon concentrations in the groundwater impacted area in the Bay of Puck and associated dissolved carbon fluxes. Moreover we used the literature data (SGD fluxes) for scaling up the obtained results. Extrapolating, results to the entire ocean is not a part of the results section. It is a part of discussion, and serves the purpose of showing the possible importance of the phenomenon of DIC/DOC delivery to the marine environment via SGD. Surly, establishing carbon loads delivered to the marine environment via SGD accurately would require much effort. Thus the purpose of scaling up is to resolve the problem: 'is extensive study covering more locations worth spending the effort?'; the message from our manuscript is the following 'yes, it is worth taking the burden' since the carbon load is substantial, and not really accounted for. It is clearly stated in the manuscript that uncertainty is large, nevertheless the SGD delivered carbon load is significant. We did not described all the afford that was made to obtain the results. Thus, the additional descriptions might be added in certain parts of the manuscript. Moreover Figure 1 and 2 might be changed with regard to Referee's suggestion. Moreover additional Figure 3 might be implemented for clarification the DIC and DOC profiles. Chemical constituents analyzed in sediment pore water samples cover a range of ecologically and biogeochemistry relevant substances. Combining results in one complex manuscript would make it overloaded with data and with topics as was already pointed out on submitting manuscripts accepted for publication (nutrients, mercury). The common feature of the separate manuscripts is sampling. This is described briefly in each of manuscripts, while the extensive description is provided in the paper reporting nutrients loads. Thus repetitions are avoided by presenting strategy and details of sampling in the first paper of the series (Szymczycha et al., 2012). We are sorry to have failed to convince the reviewer about the usefulness of our approach to indicate the importance of SGD as the carbon delivery to the marine environment. We do believe that there is a basic misunderstanding regarding the purpose of the manuscript. Apart from actual measurements and 2 characterizing SGD in the Bay of Puck, there is an attempt to indicate whether the SGD is a significant phenomenon in relation to the 'world ocean' We can modify the manuscript as regards referee specific suggestions, still we stick to the main message 'SGD is an important source of carbon to the ocean' Specific comments: 1. The authors MUST do a more complete job at demonstrating the representativeness of their data. Where were the seepage meters and groundwater lances deployed? These locations are not even shown in Figure 1, nor is there any discussion on position and depth of deployment relative to the beach/seepage face, etc. How well do these samples represent the greater area and region? Where is the subterranean estuary with respect to the lances? At what point in the tide were the lances sampled? Santos et al. (2008) demonstrate the spatial and temporal variability of groundwater DOC concentrations within the subterranean estuary. The authors offer no insight or justification into the representativeness of their samples in this regard. Until this is done with scientific rigor, the rest of the manuscript (comparison to other sources, upscaled fluxes, etc) is meaningless. Answer: The details and strategy of sampling and analytical measurements used are given in Szymczycha, B., Vogler, S., and Pempkowiak, J.: Nutrients fluxes via submarine groundwater discharge to the Bay of Puck, Southern Baltic, Sci. Total Environ., 438, 86–93, 2012. In this manuscript we did provide description of these analytical procedures that were not provided by Szymczycha at al., 2012, while sampling is described shortly- to avoid repetition. This approach can be modified, for example as follows (a section between the dashed lines): ——————————— Materials and methods 2.1 Study area The study area is situated in the Bay of Puck, a shallow part of the Gulf of Gdańsk, the Southern Baltic Sea (Figure. 1). The Bay of Puck is separated from the open sea by the Hel Peninsula which developed during the Holocene. Its coast is basically of recent alluvial and littoral origin. The bottom of the bay is covered by Holocene sediments from 10 to 100 m thick (Kozerski, 2007; Korzeniewski, 2003). The groundwater discharge zone of the Puck Bay is a part of the Gdańsk hydrological system which is

one of the richest in groundwater in Poland. It consists of three aquifers: Cretaceus, Tertiary and Quaternary (Kozerski, 2007). Piekarek-Jankowska et al. (1994) proved that the seepage of fresh groundwater occurring in the Bay of Puck comes from the Tertiary and Quaternary aquifers and suggested that the discharge of Cretaceous water ascending through the sediments overlying the aquifer is possible. It may be concluded that the bulk of groundwater discharge originates from the lakelands on the moraine upland along the southern coast of the Baltic Sea. The groundwater seepage in the study area has been a subject of several studies recently (Pempkowiak et al., 2010, Kotwicki et al., 2012, Szymczycha et al., 2012). It has been established that groundwater outflow varies seasonally ranging from 3.6 to 21.3 l d-1 m-2. Groundwater seepage results can be divided into two groups: lower fluxes in February and May, 2010 and higher fluxes measured in September and November, 2009. The groups of fluxes are well correlated with average monthly precipitation characteristic of the area (Korzeniowski, 2003). The average concentrations of nutrients are equal to 60.6$\pm$5.9 3 μmol l-1 (PO4), and 119.4$\pm$42 μmol l-1(NH4 + NO2 + NO3). The SGD phenomenon at the study site apparently is a major factor behind the abundance of biota there (Kotwicki et al., 2012). The seepage rate in the study site is influenced by several factors including: sea level, wave action, precipitation, sea bottom relief and movement. Storm events seem to be the most significant factors impacting the groundwater run-off and resistance time of pore water in the study area (Szymczycha et al, 2012). Assessment of SGD into the Baltic Sea was the aim of several research studies and projects. Piekarek-Jankowska (1994) projected that the groundwater seepage to the Puck Bay reached 3,500 m3 h-1. Peltonen (2002) estimated the total volume of SGD entering the Baltic Sea to be 4.4 km3 yr-1 - a value equal to about 1% of the total river run-off. Kryza et al. (2006) calculated that the volume of SGD to the Polish coastal zone of the Baltic Sea was equal to 16,568 m3 h-1. Kozerski (2007) estimated the rate of SGD to the Gulf of Gdańsk including the Bay of Puck to be 6,700 m3 h-1. Uścinowicz (2011) concluded that SGD in the Bay of Puck/Gulf of Gdańsk exceeds, by far, SGDs in other regions of the Baltic. This is a reason why the present study area can be characteristic example of regional SGD, especially for the Southern Baltic Sea. 2.2 Sampling and measurements The reported study is a continuation of earlier investigations reported by Pempkowiak et al. (2010) and Szymczycha et al. (2012). Four sampling campaigns were carried out in September 2009, November 2009, February 2010 and May 2010, during the following periods respectively: 31.08-3.09.2009, 2-6.11.2009, 28.02-1.03.2010, 5-7.05.2010. Seepage water sampling points were located off the Hel Peninsula (covering about 9200 m2) at selected sites characterized by low salinity of sediment pore water, close to the sediment-water interface. The sites were selected based on the results of salinity surveys (31.08.2009). The salinity surveys were obtained by salinity profiles measurements (at two depths: 5cm and 25 cm in the sediment). The profiles were performed along parallel transects that extended seaward from the beach. Seawater depth along the salinity profiles ranged from 0.5 to 2 m in accordance with distance from the shore. The pore water salinity profiles of the study area were measured before each of the sampling campaigns to confirm sampling points selection. At the selected points both: seepage meters and groundwater lances were installed and used to measure SGD rates and collect pore water samples. Seepage rates were measured by means of seepage meters (Pempkowiak et al., 2010). Groundwater lances described by Beck et al. (2007) were used to collect pore water samples for salinity and carbon analysis. After 24 h, from inserting the device into sediment, 35ml of pore water were collected from several depths (0, 4, 8, 12, 16, 24, 30 cm) below sediment- water interface. Two groundwater lances (groundwater lance I – GL I and groundwater lance II-GL II) were used to collect samples at two groundwater seepage locations simultaneously. For comparison groundwater lance (groundwater lance G') and seepage meter were deployed in the area without apparent impact of groundwater seepage The seawater depth at the sites was equal to 0.5 m. Water properties like salinity, pH and temperature of the collected water samples were measured with a salinometer (WTW Multi 3400i Multi-Parameter Field Meters) having 0.02 psu and 0.1oC accuracies. At the sampling points several types of water samples

were collected. These included sea-water (above the seafloor; salinity: 7.1), and sediment pore- water (interstitial water; salinity in the range of 1 to 6.9). In general, it was assumed that pore-water samples characterized by salinity smaller than 1 were actually ground-water, while pore-water samples characterized by salinities in the range from 1 to 6.9 were 4 mixtures of sea-water and ground-water. Since the collected pore water samples were characterized by salinity larger than these typical of groundwater, the groundwater contribution to the seepage-water samples was calculated using the end member approach (Szymczycha et al., 2012). In May, 2010 water samples from streams and rivers discharging to the Bay of Puck (Gizdepka, Zagórska Struga, Płutnica, Reda - Figure 1) and from land based groundwater wells (Reda I (RI), Reda II (RII), Reda III (RIII), Hel (H1), Władysławowo (W1) - Figure 1) were also collected. RI is a Tertiary aquifer at 41m depth RII is a Quaternary aquifer at 15.7 m depth, RIII is a Craterous aquifer at 178m depth, H1 and W1 are Pleistocene aquifers at 170 m and 122.5 m depth respectively. Locations of the river-water and ground-water sampling sites are presented in Figure 1. Carbon fluxes via river run-off were established as a product of the based on earlier research regarding rivers flows (Korzeniowski, 2003) and measured, in the course of the reported study, DIC and DOC concentrations. Upon collection samples for DOC analysis were passed through 0.2 μm pre-combusted glass-fibre filters. A total of 10 ml of the filtrate was acidified with 150 μl of concentrated HCl and stored, in the dark, at 5C until analysis was performed at a laboratory. This was carried out by means of a'HyPerTOC'analyser using the UV/persulphate oxidation method and NDIR detection (Kuliński and Pempkowiak, 2008). In order to remove inorganic carbon from samples before DOC analysis they were purged with CO2-free air. DOC concentrations in the analysed samples were derivered from calibration curves based on analysis of potassium hydrogen phthalate aqueous solutions. Quality control for DOC analysis was performed using CRMs seawater (supplied by the Hansell Laboratory, University of Miami) as the accuracy tracer with each series of samples (average recovery was equal to 96 $\pm$ 3%). The precision described as Relative Standard Deviation (RSD) of triplicate analysis was no worse than 3%. Samples for DIC analysis were collected into 40 ml glass vials, each poisoned with 150 μl of saturated HgCl2 solution. The analysis was carried out with a 'HyPerTOC' analyser (Thermo Electron Corp., the Netherlands), using a modified method based on sample acidification and detection of the evolving CO2 in the non-dispersive infrared (NDIR) detector (Kaltin et al., 2005). The DIC concentrations in the samples were calculated from the calibration curve obtained using aqueous Na2CO3 standard solutions. The recovery was equal to 97.5 $\pm$ 1 %. Each sample was analysed in triplicate. The precision assessed as RSD was better than 1.5%. DIC and DOC loads via SGD to the study area were calculated as a product of measured groundwater fluxes (seepage meters results) and concentrations of DIC and DOC measured in the groundwater samples. To quantify the annual DIC and DOC loads delivered to the Bay of Puck, the DIC and DOC concentrations measured at the study site in the groundwater samples (collected by mean of groundwater lances) and groundwater flux derived from available publications were used. A groundwater flux (0.03 km3 yr-1) was adopted from Korzeniewski (2003). The estimate was based on hydrogeological and oceanographical methods and allowed to evaluate the role of SGD in the water balance of the entire Puck Bay. This is yet another reason why the authors decided to use fluxes characteristic of the entire Puck Bay not only those measured for the study site. Given the absence of previous SGD carbon load estimates, we scaled up the carbon inputs observed here to the entire Baltic Sea using the same approach. This scaling up assumed that SGD along the Baltic Sea coast contains DIC and DOC at concentrations similar to those observed in seepage water from the Bay of Puck site and combined these estimates with groundwater flow estimates from earlier sources (Peltonen, 2002; Uścinowicz, 2011). The error envelopes of the estimates were calculated from standard deviations of the average yearly carbon species concentrations observed at the study site. 5 ——————————— 2. The authors make very little attempt to interpret their data. The data are presented and the numbers are listed in the text, but there is little attempt to discuss WHY the DIC and DOC concentrations are different during one

sampling compared to another, or to put any context to their data. Could the increased DIC/DOC concentrations with depth be due simply to sediment compaction, thereby concentrating all dissolved solutes into a smaller volume? Instead, they simply take an average value of their data and calculate fluxes, which they then upscale to larger areas. Answer: The possible reasons for differences in DIC and DOC concentrations in pore water profiles between the study campaigns are described in part 4.1 of the manuscript. The increased DIC/DOC concentrations with depths are caused by high concentrations of DIC and DOC in groundwater percolating through sediments. A suitable paragraph and figure to the Results section (3.1) can be added to substantiate the thesis (a section between the dashed lines).: —————————- Results 3.1 Line 7 Page 2077 Figure 3 presents the pore water profiles for salinity, pH, DIC and DOC in the area without apparent impact of groundwater seepage. Salinity oscillates around 7.1 while pH subtly decrease from 8.1 to 7.9. DIC concentrations decrease from 17.6 mg C L-1 to 15.5 mg C L-1 while DOC concentrations decline from 4.6 mg C L-1 to 3.5 mg C L-1. ——————————— 3. It is also not clear whether the authors are reporting DIC/DOC concentrations from the seepage meters, or just from the lances. One side effect of installing a seepage meter in the seabed is that the benthic autotrophs no longer receive sunlight and die, potentially enhancing bacterial remineralization of that organic matter. If DOC samples were collected from the seepage meter, they likely overestimate DOC concentrations due to this effect. Answer: We presented the DIC concentrations and DOC concentrations measured in the groundwater collected by means of groundwater lances. A clarification was made in the materials and method section above. Seepage meters were used for the purpose of establishing the SGD rates. 4. The authors cite a number of other studies for SGD rates to use in calculating fluxes. There needs to be a description of each study's methodology in determining SGD rates to determine whether they are truly comparable or not. Answer: We used DIC and DOC concentrations in groundwater samples (collected by means of groundwater lances) in order to calculated the DIC and DOC fluxes via SGD. The SGD rates calculated by Peltonen, 2002, Kozerski, 2007; Piekarek-Jankowska, 1994; Viventsowa and Voronow used the hydrodynamic method combined with hydrogeological method. Thus, the authors used the measured DIC and DOC concentrations and literature SGD rates that were calculated using similar methods. 6 More precise description may be added to the Results part 3.3, if neccessary ————————: Line 15 Page 2078 The methods used to calculated SGD rates to the Baltic Sea Sub-Basins and the entire Baltic Sea came from the same group of method: hydrodynamic method combined with hydrogeological method. Thus the comparison between the obtained results is appropriate. - Figure 3. Pore water depth profiles for dissolved organic carbon (DOC) dissolved inorganic carbon (DIC), pH and salinity in the groundwater not impacted area (G'). ——————————————————— 5. Scaling up to the entire world's ocean (section 4.3) is completely inappropriate in this case. Please remove this section entirely. Answer: We intend to provide the 'order of magnitude' carbon fluxes via SGD to the marine environment.. There are, of course, certain limitations of the used methods. Thus the estimates of SGD derived dissolved carbon input into the World Ocean is primarily intended to draw attention to the significance of SGD in hydrologic carbon cycles. 6. Figure 1 needs refinement. The regional base map is hard to read and hard to interpret land from sea. The area map must also include a better layout of the study site with respect to locations of seepage meters and groundwater lances. Answer: The appropriate map with regard to Referee's suggestions might be implemented to the manuscript.We did not want to repeat data presented in Szymczycha et al., 2012 and this was a reason for using more general map. 7 7. Figure 2 is very hard to read. There is too much presented. I suggest breaking this up into individual figures. Answer: Figure 2 might be broaken up into 4 figures named: Figure 2a, Figure 2b, Figure 2c, Figure 2d. 8 Figure 2a Pore water depth profiles for dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), pH and salinity in the groundwater impacted area. GLI indicates groundwater lance I, while GL II - groundwater lance II. Figure 2b Pore water depth profiles for dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), pH and salinity in the groundwater impacted area. GLI indicates groundwater

lance I, while GL II - groundwater lance II. 9 Figure 2c Pore water depth profiles for dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), pH and salinity in the groundwater impacted area. GLI indicates groundwater lance I, while GL II - groundwater lance II. 10 Figure 2d Pore water depth profiles for dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), pH and salinity in the groundwater impacted area. GLI indicates groundwater lance I, while GL II - groundwater lance II.

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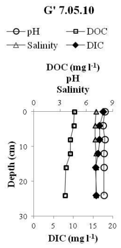


Fig. 1. 3

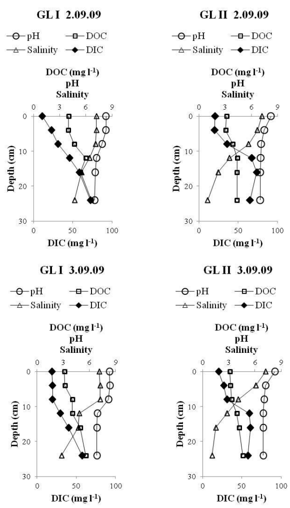


Fig. 2. 2a

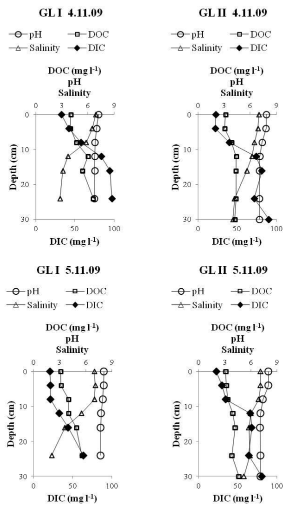


Fig. 3. 2b

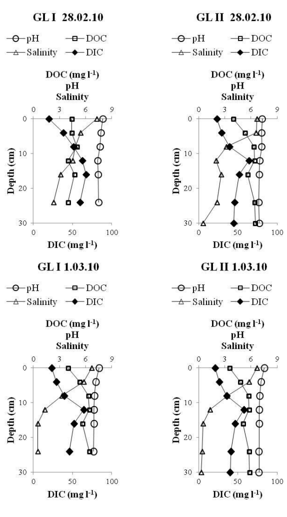
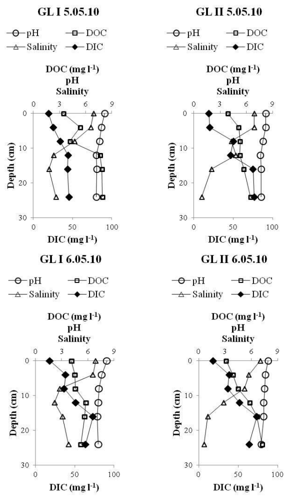


Fig. 4. 2c


GL I 5.05.10
GL II 5.05.10
GL I 6.05.10
GL II 6.05.10
pH
DOC
Salinity
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DOC (mg l-1)
pH
Salinity
Depth (cm)
DIC (mg l-1)

Fig. 5. 2d