Biogeosciences Discuss., 10, 2069–2091, 2013
www.biogeosciences-discuss.net/10/2069/2013/
doi:10.5194/bgd-10-2069-2013

Biogeosciences Discussions Open Access

The submarine groundwater discharge as a carbon source to the Baltic Sea

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Received: 25 December 2012 – Accepted: 14 January 2013 – Published: 5 February 2013

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Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Submarine Groundwater Discharge (SGD) is an important, yet poorly recognized pathway of material transport to the marine environment. This work reports on the results of dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) concentrations in the groundwater seeping to the Bay of Puck. The loads of carbon via SGD were quantified for the Baltic Sea sub-basins and the entire Baltic Sea.

The annual averages of DIC and DOC concentrations in the groundwater were equal to $64.5 \pm 10.0\,\mathrm{mg\,C\,L^{-1}}$ and $5.8 \pm 0.9\,\mathrm{mg\,C\,L^{-1}}$. The DIC and DOC fluxes via SGD to the Baltic Sea were estimated at $283.6 \pm 66.7\,\mathrm{kt\,yr^{-1}}$ and $25.5 \pm 4.2\,\mathrm{kt\,yr^{-1}}$. The SGD derived carbon load to the Baltic Sea is an important component of carbon budget, which turns the status of the sea into firmly heterotrophic.

The carbon load to the World Ocean, which was calculated basing on few reports on groundwater discharges and the measured carbon concentrations, amounts to- (142–155) $\times 10^3\,\mathrm{kt\,yr^{-1}}$ (DIC), and (13–14) $\times 10^3\,\mathrm{kt\,yr^{-1}}$ (DOC). The carbon flux via SGD amounts to some 25 % of the riverine carbon load, and should be included into the World Ocean carbon budget.

1 Introduction

The carbon cycle is one of the most significant biogeochemical cycles concerning the flow of matter and energy in the environment. The major constituent of the carbon cycle is carbon dioxide (CO_2). In recent decades an important increase of carbon dioxide in the atmosphere, due to fossil fuel burning, has been observed, resulting in global warming and seawater acidification (Chen and Borges, 2009; IPCC, 2007).

Takahashi et al., (2009) estimated that almost 35 % of anthropogenic CO_2 emission is absorbed by seas and oceans, while almost 1/3 of this load is absorbed by shelf seas. It has been projected that shelf seas, including the Baltic Sea, are responsible for approximately 20 % of marine organic matter production and about 80 % of the total organic matter load deposited to marine sediments (Borges, 2005). However, recent findings question earlier estimations regarding carbon dioxide sequestration, at least for selected coastal seas. One of the reasons is that important pathway of material exchange between land and ocean-SGD is neglected. Although data concerning carbon concentrations and fluxes via SGD are limited (Cai et al., 2003; Santos et al., 2009; Moore, 2010, Liu et al., 2012); it is clear that SGD must be considered as an important carbon source for the marine environment. It is especially important for shelf seas, which play a significant role in the global matter and energy transfer between land, ocean and atmosphere (Thomas et al., 2009).

The Baltic Sea is an example of such a sea. The Baltic used to be characterized as an autotrophic semi-enclosed brackish sea (Thomas et al., 2004). Substantial amounts of nutrients, mostly from agriculture and industry, enter the sea from rivers, making the Baltic one of the most productive marine ecosystems (Emelyanow, 1995; Thomas et al., 2004). Primary production, river run-off and import from the North Sea are the major sources of organic matter in the Baltic Sea (Wasmund et al., 2003; Kulinski and Pempkowiak, 2012). At the same time the Baltic Sea is a net source of organic matter for the North Sea (Kuliński and Pempkowiak, 2011). Recent study by Kuliński and Pempkowiak (2011) revealed that the Baltic is marginally heterotrophic. It was estimated that rivers are the largest carbon source for the Baltic Sea (10.90 $\mathrm{Tg\,C\,yr^{-1}}$ with 37 % contribution of organic carbon). At the same time, carbon is effectively exported to the North Sea (7.67 $\mathrm{Tg\,C\,yr^{-1}}$) and also buried in seabed sediments (2.73 $\mathrm{Tg\,C\,yr^{-1}}$). The net CO_2 emission from the Baltic Sea to the atmosphere was estimated at 1.05 $\mathrm{Tg\,C\,yr^{-1}}$. On the other hand, slight shifts in hydrological conditions can switch the carbon fluxes in such a way that the sea turns autotrophic (Kuliński and Pempkowiak, 2012). The estimates were based on a carbon budget comprising major 3 sources and sinks of carbon to the sea. The budget did not include carbon loads delivered to the Baltic via submarine groundwater discharges (SGD), as no studies on SGD chemistry had been available.

Since then a major study regarding loads of chemical constituents delivered with the seepage inflows to the Baltic Sea have been completed (Szymczycha et al., 2012). Among several chemical constituents quantified dissolved inorganic and organic carbon were included and the results are used in this paper to improve the carbon budget for the Baltic Sea.

This work reports on the results of a study on quantification of carbon flux and concentrations in the Bay of Puck, Southern Baltic. Estimates of both DIC and DOC concentrations and loads delivered to the study area are presented. The data are then scaled up to the entire Baltic Sea using the measured carbon concentrations and SGDs derived from earlier publications. Possible significance of SGD to the entire World Ocean is also discussed.

2 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 (Fig. 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 $L\,d^{-1}\,m^{-2}$, while average concentrations of nutrients are equal to 60.6 ± 5.9 $\mu mol\,L^{-1}$ (PO_4), and 119.4 ± 42 $\mu mol\,L^{-1}$ ($NH_4 + NO_2 + NO_3$). 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 3500 $m^3\,h^{-1}$. Peltonen (2002) estimated the total volume of SGD entering the Baltic Sea to be 4.4 $km^3\,yr^{-1}$ – 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 $m^3\,h^{-1}$. Kozerski (2007) estimated the rate of SGD to the Gulf of Gdańsk including the Bay of Puck to be 6700 $m^3\,h^{-1}$. Uścinowicz (2011) concluded that SGD in the Bay of Puck/Gulf of Gdańsk exceeds, by far, SGDs in other regions of the Baltic.

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 August–3 September 2009, 2–6 November 2009, 28 February–1 March 2010, 5–7 May 2010. Seepage water sampling points were selected at sites characterized by low salinity of sediment porewater, close to the sediment-water interface. The sites were selected based on the results of salinity surveys (Szymczycha et al., 2012). 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 seepage meters and groundwater lances were installed and used to measure SGD rates and collect porewater 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, 35 mL 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. 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 0.1 °C 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 0.1 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 mixtures of sea-water and ground-water. Since the collected porewater 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 – Fig. 1) and from land based groundwater wells (Reda I (RI), Reda II (RII), Reda III (RIII), Hel (H1), Władysławowo (W1) – Fig. 1) were also collected. RI is a Tertiary aquifer at 41 m depth RII is a Quaternary aquifer at 15.7 m depth, RIII is a Craterous aquifer at 178 m 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 Fig. 1. Carbon fluxes via river run-off were established as a product of the based on earlier research regarding

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rivers flows (Korzeniewski, 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 5 °C 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 CO_2-free air. DOC concentrations in the analysed samples were derived 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 ± 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 $HgCl_2$ 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 CO_2 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 Na_2CO_3 standard solutions. The recovery was equal to 97.5 ± 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 and concentrations of DIC and DOC. 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 and groundwater flux derived from available publications were used. A groundwater flux ($0.03\,km^3\,yr^{-1}$) 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 Bay of Puck. 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 the study site 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.

3 Results

3.1 DIC and DOC concentrations

Pore water depth profiles for salinity, pH, DIC and DOC in the groundwater impacted area (GIA) are shown in Fig. 2. In general, salinity and pH decreased with depths while DIC and DOC concentrations increased with depths in the sediments. The salinity profiles are explained by intrusion of seawater into the sediments (Szymczycha et al., 2012). The seawater percolation depth depends on hydrodynamic conditions at the time of sampling. The salinity decrease towards the subsurface sediment layer was caused by groundwater–seawater mixing, the granulometric properties of the sediments, water depth, sea bottom relief and wave action. The deepest seawater intrusion was observed in November 2009 resulting in a salinity decrease from 7.2 to 2.1 in profile GL I 5.11.2009. The largest shallow seawater intrusions into the sediments were observed in February 2010 and May 2010. The highest DIC and DOC concentrations were characteristic of the low salinity porewater classified here as groundwater. DIC and DOC concentrations in porewater collected from depths 15 cm, or greater, below sediment- water interface, characterized by salinity not greater than 1 were used as characteristic of groundwater. The annual averages of DIC ($n = 13$) and DOC ($n = 13$) concentrations in groundwater were equal to $64.5 \pm 10.0\,\mathrm{mg\,C\,L^{-1}}$ and $5.8 \pm 0.9\,\mathrm{mg\,C\,L^{-1}}$, respectively. The highest DIC concentration was observed in November 2009 ($80.5 \pm 23.9\,\mathrm{mg\,C\,L^{-1}}$), while the smallest DIC concentration – in February 2010 ($45.0 \pm 4.2\,\mathrm{mg\,C\,L^{-1}}$). The highest DOC concentration was measured in May 2010 ($6.8 \pm 0.4\,\mathrm{mg\,C\,L^{-1}}$), while the smallest – in September 2009 ($4.5 \pm 0.2\,\mathrm{mg\,C\,L^{-1}}$). The DIC and DOC concentrations in groundwater were also measured in samples of other provenience: seawater, groundwater from wells located at the coast of the Bay of Puck and in rivers and streams discharging to the Bay of Puck. The highest DIC concentration was observed in groundwater ($64.5\,\mathrm{mg\,C\,L^{-1}}$), while seawater had the smallest DIC concentration ($21.2\,\mathrm{mg\,C\,L^{-1}}$). The DIC concentrations in wells were ranged from 41.9 to $55.6\,\mathrm{mg\,C\,L^{-1}}$. Run-off was characterized by variable DIC concentrations ranging from 38.0 to $51.1\,\mathrm{mg\,C\,L^{-1}}$. The highest DOC concentration was measured in the Płutnica river ($5.9\,\mathrm{mg\,C\,L^{-1}}$). In groundwater samples collected at the study site DOC concentration was equal to $5.8\,\mathrm{mg\,C\,L^{-1}}$ and in groundwater samples from RII DOC was equal to $5.0\,\mathrm{mg\,C\,L^{-1}}$, while in groundwater from Hel DOC concentrations were lowest and equal to $0.03\,\mathrm{mg\,C\,L^{-1}}$.

The DIC and DOC concentrations measured in this study are well within ranges reported earlier for the specific water types: seawater (Kuliński i Pempkowiak, 2012; Pempkowiak, 1983), groundwater (Cai et al., 2003; Moore et al., 2006; Santos et al., 2009; Liu et al., 2012), river water (Korzeniewski, 2003), and porewater (Bełdowski i Pempkowiak, 2003).

3.2 The DIC and DOC fluxes to the study area via SGD

Since the samples of porewater collected by means of both the seepage meter and groundwater lances comprised mixtures of groundwater and seawater, the end-members approach was used to derive the actual concentrations of DIC and DOC in groundwater, and actual flows of groundwater (Szymczycha et al., 2012). The results are presented in Table 1. The highest DIC fluxes were observed

in September and November 2009 and equalled $1303.9 \pm 109.9\,\mathrm{mg\,C\,d^{-1}\,m^{-2}}$ and $1480.8 \pm 440.4\,\mathrm{mg\,C\,d^{-1}\,m^{-2}}$, respectively. The lowest DIC fluxes were observed in February 2010 at $135.1 \pm 24.0\,\mathrm{mg\,C\,d^{-1}\,m^{-2}}$. In May 2010 DIC fluxes were equal to $256.0 \pm 24.0\,\mathrm{mg\,C\,d^{-1}\,m^{-2}}$. Similarly to DIC, the highest DOC fluxes observed in September and November 2009 are due, primarily, to increased SGDs and were equal to $95.5 \pm 3.7\,\mathrm{mg\,C\,d^{-1}\,m^{-2}}$ and $111.8 \pm 13.5\,\mathrm{mg\,C\,d^{-1}\,m^{-2}}$, respectively. The lowest DOC fluxes were observed in February 2010 at $17.6 \pm 1.6\,\mathrm{mg\,C\,d^{-1}\,m^{-2}}$. In May 2010 DOC fluxes were equal to $24.4 \pm 1.4\,\mathrm{mg\,C\,d^{-1}\,m^{-2}}$. The large carbon fluxes in September and November 2009 can be attributed to increased SGD due to precipitation. Kozerski (2007) proved that the Gdansk hydrological system is recharged mainly by precipitation. In the Puck Bay a significant role is also played by storms.

3.3 The DIC and DOC fluxes to the Baltic Sea sub-basins and to the Baltic Sea

The obtained DIC and DOC concentrations in the groundwater and the earlier measured (Korzeniewski, 2003) SGD fluxes which were used to calculate carbon fluxes to the Baltic Sea Sub-Basins and the entire Baltic Sea are presented in Table 2. The DIC fluxes via SGD to the Puck Bay were equal to $1.9 \pm 0.2\,\mathrm{kt\,C\,yr^{-1}}$ while DOC fluxes were equal to $0.2 \pm 0.002\,\mathrm{kt\,C\,yr^{-1}}$. SGD carbon fluxes are an important carbon source in comparison with riverine carbon fluxes. The most significant carbon source for the Puck Bay is the river Reda with DIC and DOC loads equal to $5.4\,\mathrm{kt\,C\,yr^{-1}}$ and $0.5\,\mathrm{kt\,C\,yr^{-1}}$, respectively. The Gizdepka river ($0.25\,\mathrm{kt\,C\,yr^{-1}}$ DIC, $0.03\,\mathrm{kt\,C\,yr^{-1}}$ DOC) and Zagórska Struga ($0.73\,\mathrm{kt\,C\,yr^{-1}}$ DIC, $0.08\,\mathrm{kt\,C\,yr^{-1}}$ DOC) are smaller carbon source compared with SGD. DIC and DOC fluxes via SGD equaled approximately 30 % of the river runoff discharges to the Bay of Puck. The DIC and DOC fluxes via SGD into other Baltic Sea sub-basins are also presented in Table 2.

The DIC and DOC fluxes via SGD to the Baltic Sea were estimated at $283.6 \pm 66.7\,\mathrm{kt\,C\,yr^{-1}}$ and $25.5 \pm 4.2\,\mathrm{kt\,C\,yr^{-1}}$ (Table 2). Thus the DIC fluxes were approximately 11 times higher than DOC fluxes. The total carbon flux to the Baltic

Sea (sum of DIC and DOC) amounts to $0.3\,\text{Tg}\,\text{C}\,\text{yr}^{-1}$. DIC and DOC fluxes via SGD are significant compared to other carbon sources for the Baltic Sea, presented by Kuliński and Pempkowiak (2011). They were slightly lower than atmospheric deposition ($0.57\,\text{Tg}\,\text{C}\,\text{yr}^{-1}$) and higher than point sources ($0.04\,\text{Tg}\,\text{C}\,\text{yr}^{-1}$).

There are few reports devoted to carbon loads delivered to the coastal seas via SGD (Table 2). These showed that SGD fluxes of both dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) are important carbon pathways from land to coastal ocean. Cai et al. (2003) estimated DIC fluxes as- 20 to $170 \times 10^9\,\text{mol}\,\text{yr}^{-1}$ and concluded it to exceed river inputs in South Carolina. Moore et al. (2006) calculated SGD fluxes of DIC and DOC from the marshes around the Okatee estuary, South Carolina, $1400 \times 10^3\,\text{mol}\,\text{d}^{-1}$ and $120 \times 10^3\,\text{mol}\,\text{d}^{-1}$, respectively. These carbon fluxes were comparable with river inputs to the marsh. Liu et al. (2012) estimated that DIC load carried by SGD to the East China Sea equaled $153–347 \times 10^9\,\text{mol}\,\text{yr}^{-1}$, a value representing 23–53 % of DIC contributions from the Pearl River to the sea. The source of SGD was mostly recirculated seawater and it was equivalent to 12–21 % of the Pearl River discharge.

4 Discussions

4.1 Carbon loads in the seepage water of the study area

Relatively high concentrations of DIC compared to, for example, rivers that discharge in the region were measured in the groundwater at the study site. The content of carbonates within geological structures of the Baltic Sea continental drainage area is much higher than in the drainage area covering the Scandinavian Peninsula. The Baltic Sea is a land locked sea, and thus covers an area of geological structures similar to the land surrounding it (Uścinowicz, 2011). The south-western part of the Baltic Sea, where the study is located, lies on the Paleozoic West European Platform separated from the East European Platform by the Teisseyre-Tornquist Fault Zone. The northern part of

the Baltic Sea lies within the Baltic Shield, while the southern part is situated on the East European Platform. The study area is located on the sediment layer consisting of dolomites, calcites, limestones, syrrulian clays, and silts with dolomites abundant with carbonates. The reason for a higher DIC concentration in groundwater and, as a result, high loads of DIC via SGD can thus be contributed to the geological structure of the southern Baltic Sea. Other possibilities here are reduction-oxidation processes of the system. The groundwater is anoxic (Szymczycha et al., 2013) so the organic matter oxidation pathways are both sulphate reduction and methane production. Both these processes lead to carbonate increase in the system (Schulz and Zabel, 2006). This also explains higher alkalinity and carbon concentrations in "continental" rivers entering the sea along the southern coast compared with rivers draining the Scandinavian Peninsula.

4.2 The carbon budget of the Baltic Sea

In a recent paper Kuliński and Pempkowiak (2011) quantified major sinks and sources of carbon to the Baltic. In a constructed carbon budget, CO_2 exchange through the air-seawater interface was used as a closing term. The results obtained identify the entire Baltic Sea as a source of CO_2 to the atmosphere amounting to $-1.05 \pm 1.71\,\text{Tg}\,\text{C}\,\text{yr}^{-1}$. The accuracy of CO_2 exchange between seawater and atmosphere depended on uncertainties of each component of the budget. Despite the uncertainties significance, the CO_2 exchange through the air-seawater interface, categorized the Baltic Sea as basin with a near neutral balance of annual CO_2 exchange, with slight skewness towards the emissions. However, the seepage carbon flow (FSGD) was not included in the budget. When the budget is supplemented with FSGD ($0.31\,\text{Tg}\,\text{C}\,\text{yr}^{-1}$, Table 2) the new mass balance of carbon in the Baltic Sea is obtained:

$$\text{Fe} + \text{Fi} + \text{Fo} + \text{FCO}_2 + \text{Ff} + \text{Fp} + \text{Fr} + \text{Fm} + \text{Fs} + \mathbf{FSGD} = 0 \quad (1)$$

$$\text{FCO}_2 = \text{Fe} + \text{Fi} + \text{Fo} + \text{Ff} + \text{Fp} + \text{Fr} + \text{Fm} + \text{Fs} + \mathbf{FSGD} \quad (2)$$

where Fe – export to North Sea, Fi – import from the North Sea, Fo – atmospheric deposition, FCO_2 – net CO_2 exchange between seawater and the atmosphere, Ff – fisheries, Fp- point sources, Fr – river input, Fm – return flux from sediments to the water column, Fs – accumulation in the sediments, FSGD – submarine groundwater discharge.

As the outcome of calculations, similarly to Kuliński and Pempkowiak (2011), net emissions of CO_2 to the atmosphere were calculated and amounting to $1.36 \pm 1.71\,\mathrm{Tg\,C\,yr^{-1}}$. The mean CO_2 emission reached $-3.5\,\mathrm{g\,C\,m^{-2}\,yr^{-1}}$ ($-12.9\,\mathrm{g\,CO_2\,m^{-2}\,yr^{-1}}$). Thus, the Baltic Sea's status as a source of CO_2 to the atmosphere was confirmed. Moreover, when the SGD carbon loads are supplemented to the Baltic carbon budget, the status of the sea defined to date as "marginally heterotrophic" turns into firmly heterotrophic.

The projected estimates of dissolved carbon input into the Baltic Sea via SGD should draw attention to the significance of SGD in hydrologic carbon cycles. The projections demonstrate that SGD sites may transport substantial loads of carbon to the coastal areas. One immediate consequence of this is the modification of biodiversity in the seepage affected areas.

4.3 The carbon fluxes to the world ocean

The global carbon cycle involves processes among the major global reservoirs: atmosphere, ocean and land. The fundamental element of carbon cycling is CO_2. Ocean carbonate chemistry has a great impact on CO_2 partial pressure in the atmosphere. So far no carbon fluxes via SGD to the World Ocean were considered in the global carbon cycle. However, as indicated, the SGD derived carbon load constitutes a significant portion of a carbon budget in entire coastal basins (Table 2). Moreover, it has been estimated that the total flux of SGD to the Atlantic Ocean is comparable, in volume, to the riverine flux (Moore, 2010). For this reason in this study the authors attempted to calculate carbon fluxes via SGD to the World Ocean. There are very few reports

on carbon concentrations in the groundwater impacted areas (Cai et al., 2003; Moore et al., 2006; Liu et al., 2012) (Table 2), and few- on global groundwater discharge (Zekster and Loaiciga, 1993; Zekster et al., 2007; Moore, 2010) (Table 3). Since the carbon concentrations obtained in this study are comparable to those in other study areas (Table 2), it was decided to use DIC and DOC concentrations measured in this study and the literature derived SGD to World Ocean to establish the load of carbon that might enter the marine environment with SGD (Table 3). The calculated carbon fluxes are in the ranges: $(142\text{–}838) \times 10^3\,\mathrm{kt\,C\,yr^{-1}}$ (DIC), and $(13\text{–}75) \times 10^3\,\mathrm{kt\,C\,yr^{-1}}$ (DOC). Carbon load delivered to the sea with the river run-off is also presented. It follows from the data included in Table 3 that the SGD load, and the load delivered with riverine discharge are comparable. Thus the carbon flux associated with groundwater discharge might well prove to be an important component of carbon cycle and have a potential to significantly change the projected CO_2 absorption by the ocean from the atmosphere.

5 Conclusions

The DIC and DOC fluxes carried via SGD into the Bay of Puck are significant compared to other carbon sources. The DIC and DOC fluxes via SGD to the Baltic Sea were equal to $283.6 \pm 44.0\,\mathrm{kt\,C\,yr^{-1}}$ and $25.5 \pm 2.2\,\mathrm{kt\,C\,yr^{-1}}$, respectively. It is concluded that SGD derived carbon loads represent some 10 % of the load discharged to the sea with river run-off. When the SGD carbon loads are supplemented to the Baltic carbon budget, the status of the sea that had been set as "marginally heterotrophic" turns into firmly heterotrophic. The average CO_2 emission to the atmosphere was quantified at $1.9\,\mathrm{g\,C\,m^{-2}\,yr^{-1}}$ after including carbon load carried by SGD. To our knowledge, this is the first evaluation of DIC and DOC fluxes via SGD and its impact on the budget of carbon in the Baltic Sea. There is a substantial uncertainty originating from both uncertain groundwater flow and carbon concentration in groundwater. Despite these uncertainties, however, we contend that SGD-associated carbon fluxes cannot be neglected in regional carbon budgets.

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This study indicates that, when projected to the entire World Ocean, submarine groundwater discharge might well prove to be a significant source of carbon.

Acknowledgements. The study reports the results obtained within the framework of the following projects: statutory activities of the Institute of Oceanology Polish Academy of Sciences theme 2.2, research projects: 3837/B/P01/201039 and 2012/05/N/ST10/02761 sponsored by the Polish Ministry of Science and Higher Education.

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Table 1. Specific DIC and DOC concentrations and fluxes to the study area via SGD.

Sampling campaign	Carbon concentrations		SGD	Carbon fluxes	
	DIC ± SD[*]	DOC ± SD		DIC ± SD	DOC ± SD
	$mg\,L^{-1}$		$L\,d^{-1}\,m^{-2}$	$mg\,d^{-1}\,m^{-2}$	
Sep 2009	61.2 ± 5.2	4.5 ± 0.2	21.3	1303.9 ± 109.9	95.5 ± 3.7
Nov 2009	80.5 ± 23.9	6.1 ± 0.7	18.4	1480.8 ± 440.4	111.8 ± 13.5
Feb 2010	45.0 ± 4.2	5.9 ± 0.5	3.0	135.1 ± 12.6	17.6 ± 1.6
May 2010	71.1 ± 6.7	6.8 ± 0.4	3.6	256.0 ± 24.0	24.4 ± 1.4
Annual average	64.5 ± 10.0	5.8 ± 0.5	11.6	793.9 ± 146.7	62.3 ± 5.0

[*] Standard deviation.

Table 2. Submarine groundwater discharge and associated carbon fluxes to the Baltic Sea Basins and the Baltic Sea. SGD derived carbon fluxes to other coastal areas are presented for comparison.

Study area	SGD ± SD $km^3\,yr^{-1}$	Carbon concentrations ± SD $mg\,L^{-1}$		Carbon fluxes ± SD $kT\,yr^{-1}$		References
		DIC	DOC	DIC	DOC	
The Baltic Sea:	4.40 ± ND[*]	64.5 ± 15.0	5.8 ± 0.5	283.8 ± 44.0	25.5 ± 2.2	This study (SGD rate based on Peltonen, 2002)
The Polish and German coast	1.90 ± ND	64.5 ± 15.0	5.8 ± 0.5	122.6 ± 19.0	11.0 ± 1.0	This study (SGD rate based on Peltonen, 2002)
The Gulf of Gdańsk	0.06 ± ND	64.5 ± 15.0	5.8 ± 0.5	3.9 ± 0.6	0.3 ± 0.03	This study (SGD based on Kozerski, 2007)
The Puck Bay	0.03 ± ND	64.5 ± 15.0	5.8 ± 0.5	1.9 ± 0.2	0.2 ± 0.002	This study (SGD based on Piekarek-Jankowska, 1994)
The Gulf of Finland	0.60 ± ND	64.5 ± 15.0	5.8 ± 0.5	38.7 ± 6.0	3.5 ± 0.3	This study (SGD based on Viventsova and Voronow, 2003)
North Inlet, South Carolina	12.6 ± 5.9	60.0 ± 114.0	–	1140.0 ± 1272.8		Cai et al. (2003)
Okatee Estuary, South Carolina	0.94 ± ND	192.0 ± ND	16.0 ± ND	184.0 ± ND	15.8 ± ND	Moore et al. (2006)
South China Sea	3230.0 ± 1161.0	60.6 ± 51.8	–	3000.0 ± 1646.0		Liu et al. (2012)
West Ireland	–		5.4 ± 0.5	–		Smith and Cave (2012)

[*] ND – no data.

Table 3. SGD rates, rivers flow rates and associated carbon fluxes to the World Ocean.

Surface discharge to the World Ocean	Flow rate $m^3 yr^{-1}$	$L s^{-1}$	Carbon Fluxes ± SD $kT yr^{-1}$ DIC	DOC	References
SGD	$(0–13) \times 10^{12}$	$(0–13.7) \times 10^6$	$(0–838) \times 10^3$	$(0–75) \times 10^3$	This study (SGD flux based on Moore, 2010)
	$(2.2–2.4) \times 10^{12}$	$(3.2–2.5) \times 10^6$	$(142–155) \times 10^3$	$(13–14) \times 10^3$	This study (SGD flux based on Zekster et al., 2007)
	2.4×10^{12}	2.5×10^6	155×10^3	14×10^3	This study (SGD flux based on Zekster and Loaiciga, 1993)
Rivers	35×10^{12}	37×10^6	402×10^3	–	Emerson and Hedges (2008)
	–	–	384×10^3	324×10^3	Chen et al. (2003)[a]
	–	–	320×10^b	205×10^3	Ludwig et al. (1996)

[a] Carbon flux to the continental margins from rivers, ground water, ice.
[b] Bicarbonate ions (HCO_3).

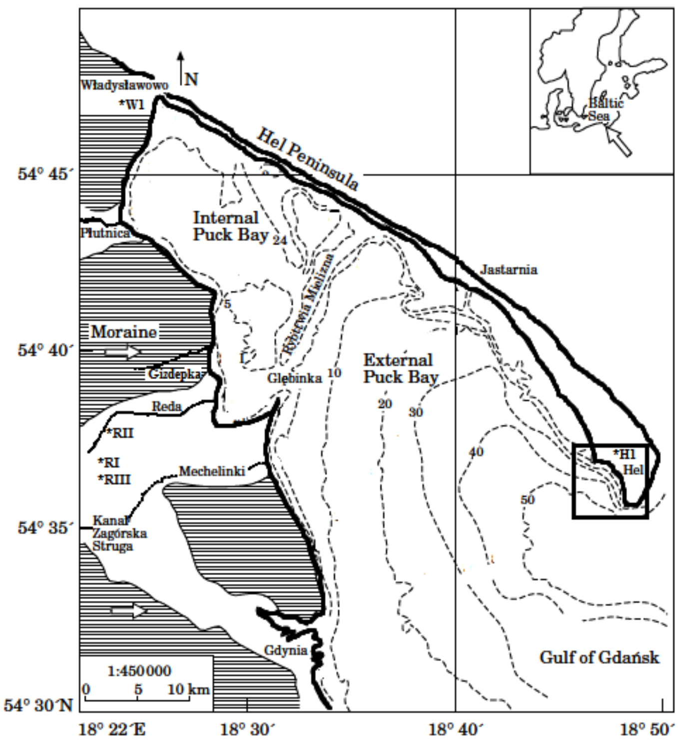

Fig. 1. A map of the Puck Bay and the Gulf of Gdańsk showing the location of the study area and sampled rivers: Gizdepka, Zagórska Struga, Płutnica, Reda. Points: RI (Reda I), RII (RedaII), RIII (Reda III), H1 (Hel), W1 (Władysławowo) correspond to the locations of groundwater wells.

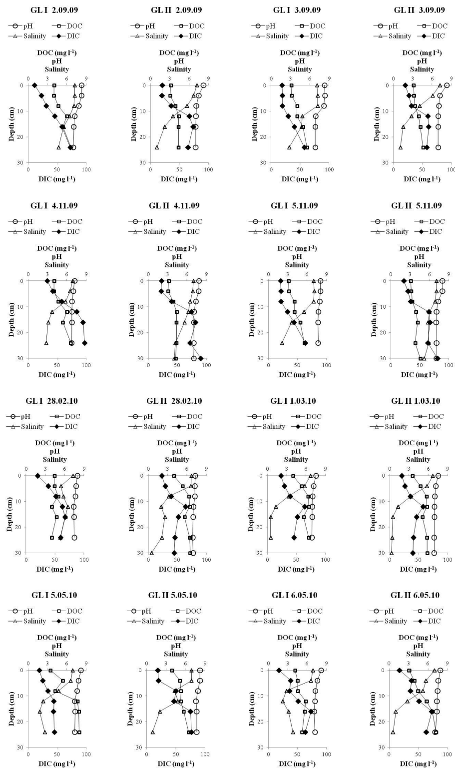

Fig. 2. Pore water depth profiles for dissolved organic carbon (DOC) dissolved inorganic carbon (DIC), pH and salinity in the groundwater impacted area. GLI indicates groundwater lance I, while GL II – groundwater lance II.