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Could submarine groundwater discharge be a significant carbon source to the southern Baltic Sea?*

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Abstract

Submarine Groundwater Discharge (SGD) is an important yet poorly recognised 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 and loads in the groundwater seeping into the southern Baltic Sea. Most of the research was carried out in the Bay of Puck (2009–2010), while in 2013

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the study was extended to include several other groundwater seepage impacted areas situated along the Polish coastline. The annual average concentrations of DIC and DOC in the groundwater were equal to 64.5 ± 10.0 mg C L^{-1} and 5.8 ± 0.9 mg C L^{-1} respectively. The carbon specific flux into the Bay of Puck was estimated at 850 mg m^{-2} yr^{-1}. The loads of carbon via SGD were scaled up for the Baltic Sea sub-basins and the entire Baltic Sea. The DIC and DOC fluxes via SGD to the Baltic Sea were estimated at 283.6 ± 66.7 kt yr^{-1} and 25.5 ± 4.2 kt yr^{-1}. The SGD derived carbon load to the Baltic Sea is an important component of the carbon budget, which gives the sea a firmly heterotrophic status.

1. Introduction

The carbon cycle is one of the most significant biogeochemical cycles as regards the flow of matter and energy in the environment. A major constituent of the carbon cycle is carbon dioxide (CO_2). In recent decades the amount of CO_2 in the atmosphere has increased significantly as a consequence of fossil fuel combustion, which has resulted in global warming and seawater acidification (IPCC 2007, Chen & Borges 2009). Takahashi et al. (2009) estimated that almost 35% of anthropogenic CO_2 emissions are absorbed by seas and oceans, while almost 1/3 of this load is absorbed by shelf seas. It has been estimated 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 estimates regarding CO_2 sequestration, at least in selected coastal seas (Kuliński & Pempkowiak 2012, Omstedt et al. 2014). One of the possible reasons is that the important pathway of material exchange between land and ocean– Submarine Groundwater Discharge (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 an important carbon source for the marine environment. It is especially important for shelf seas, which play a significant role in the global transfer of matter and energy between land, ocean and atmosphere (Thomas et al. 2009). The Baltic is an example of such a sea.

The Baltic used to be characterised as an autotrophic semi-enclosed brackish sea (Thomas et al. 2004). Substantial amounts of nutrients, mostly from agriculture and industry, enter this sea from rivers, making the Baltic one of the most productive marine ecosystems in the world (Emelyanov 1995, Thomas et al. 2004). Primary production, river run-off and import from the North Sea are major sources of organic matter in the Baltic Sea (Thomas et al. 2003, Wasmund et al. 2003, Kuliński & Pempkowiak 2012). At the same time the Baltic is a net source of organic matter for the North Sea (Kuliński & Pempkowiak 2011). A recent study by Kuliński

& Pempkowiak (2011) found the Baltic to be marginally heterotrophic. It was estimated that rivers are the largest carbon source for the Baltic Sea (10.90 Tg C yr^{-1} with a 37% contribution of organic carbon). At the same time, carbon is effectively exported to the North Sea (7.67 Tg C yr^{-1}) and also buried in seabed sediments (2.73 Tg C yr^{-1}). The net CO_2 emission from the Baltic Sea to the atmosphere was estimated at 1.05 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 becomes autotrophic (Kuliński & Pempkowiak 2012). These estimates were based on a carbon budget comprising the major sources and sinks of carbon to the sea. The budget did not include carbon loads delivered to the Baltic Sea via SGD, however, no studies on SGD chemistry were available.

Since then a major study of SGD rates and concentrations of chemical constituents delivered with the seepage inflows to the Baltic Sea has been completed (Szymczycha et al. 2012, 2013, Kotwicki et al. 2013). Dissolved

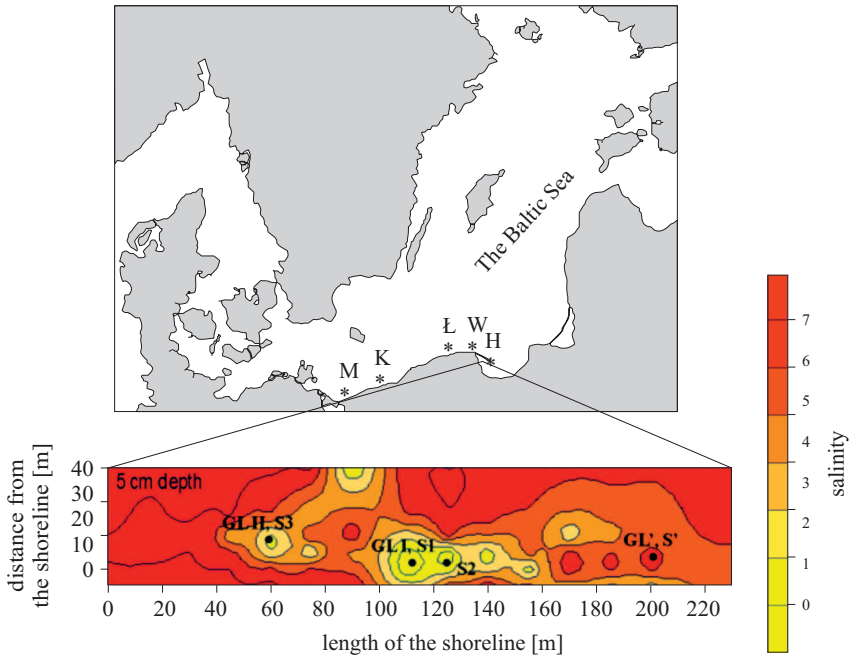

Figure 1. A map of the southern Baltic Sea. H corresponds to the location of the main study area situated in the Bay of Puck, while the points M (Międzyzdroje), K (Kołobrzeg), Ł (Łeba), W (Władysławowo) correspond to the locations of other groundwater impacted areas sampled. The salinity survey (31.08.2009) based on Szymczycha et al. (2012) represents the positions of groundwater lances (GL) and seepage metres (S)

inorganic and organic carbon were included among the chemical constituents quantified, and the results are used in this paper to recalculate the carbon budget for the Baltic Sea. This research is supplemented by measurements that were carried out along the Polish coast of the Baltic Sea in 2013. Thus, this paper reports on the results of a study to quantify DIC and DOC concentrations at a number of study sites: the Bay of Puck (H), Międzyzdroje (M), Kołobrzeg (K), Łeba (Ł), Władysławowo (W) (Figure 1) and fluxes to the Bay of Puck, southern Baltic Sea. The data are then scaled up to the entire Baltic Sea using the measured carbon concentrations and SGD rates derived from earlier reports.

To our knowledge, this is the first evaluation of DIC and DOC delivered to the Baltic Sea via SGD and its impact on the carbon budget of the sea. The possible significance of SGD as a carbon source to the entire World Ocean is also discussed, as SGD-associated carbon fluxes cannot be neglected in the overall carbon cycle.

2. Material and methods

2.1. Study area

The main study area is situated in the Bay of Puck (H), a shallow part of the Gulf of Gdańsk in 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. The bay's 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 (Korzeniewski 2003, Kozerski 2007). The Gulf of Gdańsk hydrological system is thought to be a significant SGD area in the southern Baltic. It consists of three aquifers: Cretaceous, Tertiary and Quaternary (Kozerski 2007). Piekarek-Jankowska et al. (1994) demonstrated that fresh groundwater seeps into the Bay of Puck from the Tertiary and Quaternary aquifers and suggested that the discharge of Cretaceous water ascending through the sediments overlying the aquifer is possible. It was concluded that the bulk of the groundwater discharge to the Baltic Sea originates from the lakelands on the moraine upland along the southern coast of the Baltic Sea (Peltonen 2002, Kryza & Kryza 2006). Groundwater seepage in the study area has been the subject of several recent studies (Pempkowiak et al. 2010, Szymczycha et al. 2012, 2013, Kotwicki et al. 2013). It has been established that the groundwater outflow varies seasonally from 3.6 to 21.3 L d^{-1} m^{-2}. Groundwater rates were lower in February and May (2010) and higher in September and November (2009) and correlated well with the average monthly precipitation characteristic of the area (Korzeniewski 2003). The average concentrations of nutrients

were calculated at 60.6 ± 5.9 μmol L^{-1} (PO_4) and 119.4 ± 42 μmol L^{-1} ($NH_4 + NO_2 + NO_3$). SGD at the study site is apparently a major factor behind the abundance of biota there (Kotwicki et al. 2013). The seepage rate in the study site is influenced by several factors, including sea level, wave action, precipitation, sea bottom relief and dynamics. Storm surges seem to be the most significant factor influencing the groundwater seepage rate and the residence time of pore water in the study area (Szymczycha et al. 2012).

The additional study sites were situated along the Polish coast at Międzyzdroje (M), Kołobrzeg (K), Łeba (Ł) and Władysławowo (W). These locations were selected in accordance with literature reports indicating areas that were expected to be impacted by groundwater (Kryza & Kryza 2005). This additional sampling campaign was carried out in order to investigate DIC and DOC concentrations in seeping water collected at locations other than the main study area – the Bay of Puck.

Assessment of SGD into the Baltic Sea was the aim of several research studies and projects. Piekarek-Jankowska (1994) estimated the groundwater seepage to the Bay of Puck to be 3500 m^3 h^{-1}. Kryza & Kryza (2006) calculated that the volume of SGD to the Polish coastal zone of the Baltic Sea was equal to some 16 570 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}. Peltonen (2002) estimated that the total volume of SGD entering the Baltic Sea was 4.4 km^3 yr^{-1} accounting for some 1% of the total river run-off volume. It was estimated that around 75% of the groundwater discharge enters the Baltic along its southern coast (Peltonen 2002). Uścinowicz (2011) concluded that SGD in the Bay of Puck/Gulf of Gdańsk exceeds by far the SGDs in other regions of the Baltic. Thus the study area can be regarded as representing the most important southern Baltic Sea groundwater seepage area.

2.2. Sampling and measurements

This study is a continuation of earlier investigations by Pempkowiak et al. (2010), Szymczycha et al. (2012) and Szymczycha et al. (2013). Five sampling campaigns were carried out during the following periods: 31.08–3.09.2009, 2–6.11.2009, 28.02–1.03.2010, 5–7.05.2010 and 10–17.07.2013. The study area in the Bay of Puck (H) covers about 9200 m^2 and is shown on Figure 1. Seepage water sampling points were selected at sites characterised by a low sediment pore water salinity. Site selection was based on the results of sediment pore-water salinity survey (Figure 1). The survey included salinity measurements (at two depths: 5 cm and 25 cm in the sediment) along parallel transects, spaced 10 m from each other, that

extended seawards from the beach for some 50 m. Seawater depths ranged from 0.5 to 2 m in accordance with distance from the shore. The sediment pore water salinity surveys of the study area were performed before each of the sampling campaigns to confirm the sampling point locations. Seepage meters and groundwater lances were installed at the selected points.

Seepage rates were measured by means of seepage meters applying the end member approach (Szymczycha et al. 2012). In short, seepage water flowing through the sediment displaces water trapped in the chamber forcing it up through the port into the PTE bag. The change in volume of water in the bag, over a measured time interval, provides the seepage water flux. The measured salinity of the samples varied from 3.7 to 6.5 (Szymczycha et al. 2012). The groundwater fraction in the samples was calculated using the end-member method (Burnett et al. 2006, Szczepańska et al. 2012), and finally the groundwater flux was calculated as the ratio of the collected groundwater volume to the device's surface area and to time.

Groundwater lances, described by Beck et al. (2007), were used to collect pore water samples for salinity and carbon analysis. 24 h after the device had been inserted into the sediment, 35 mL of pore water were collected from several depths (0, 4, 8, 12, 16, 24, 30 cm) below the sediment-water interface (Szymczycha et al. 2012). Two groundwater lances (groundwater lance I – GLI and groundwater lance II – GLII) were used to collect samples at two groundwater seepage locations simultaneously. For comparison, a groundwater lance (groundwater lance G′) and a seepage meter were additionally deployed in an area without apparent impact of groundwater seepage.

The properties of the groundwater samples, including salinity, pH and temperature, were measured with a multimeter (WTW Multi 3400i Multi-Parameter Field Meters) with accuracies of 0.02 PSU and 0.1°C. Several types of water samples were collected at the sampling points. These included seawater (above the seafloor; salinity ≥ 7.0) and sediment pore water (interstitial water; salinity 0.1–6.9). Sediment pore water samples of salinity ≤ 0.5 were assumed to represent groundwater, while pore water samples with salinities from 0.6 to 6.9 were assumed to be mixtures of seawater and groundwater. Since the salinities of the collected sediment pore water samples were characterised by salinity larger than these typical of groundwater, the groundwater contribution to the collected 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) and from land based groundwater wells (Reda I – RI, Reda II – RII, Reda III – RIII, Hel – H1, Władysławowo – W1) 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. In July 2013 groundwater samples were collected via push-point lances, in each of the study sites indicated in Figure 1.

After collection, the water 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 conc. HCl to remove carbonates and to prevent mineralisation of dissolved organic matter (Pempkowiak 1983), then stored in the dark at 5°C until analysis. This was carried out by means of a 'HyPerTOC' analyser (Thermo Electron Corp., The Netherlands), using the UV/persulphate oxidation method and non-dispersive infrared (NDIR) detection (Kuliński & 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 the analysis of aqueous solutions of potassium hydrogen phthalate. 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 the Relative Standard Deviation (RSD) of triplicate analysis, was no worse than 3%.

Samples for DIC analysis were collected in 40 ml glass vials, each poisoned with 150 μl of saturated $HgCl_2$ solution. The analysis was carried out with a 'HyPer-TOC' analyser (Thermo Electron Corp., The Netherlands), using a modified method based on sample acidification and detection of the evolving CO_2 in the NDIR detector (Kaltin et al. 2005). The DIC concentrations in the samples were calculated from the calibration curve obtained using standard aqueous solutions of Na_2CO_3. The recovery was $97.5 \pm 1\%$. 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 the product of the measured groundwater fluxes 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 (salinity ≤ 0.5) and in the groundwater taken from Piekarek-Jankowska et al. (1994) (0.03 $km^3\ yr^{-1}$) were used. The estimate was based on hydrogeological and oceanographic methods and enabled us to evaluate the role of SGD in the water balance of the entire Bay of Puck (Piekarek-Jankowska 1994, Kozerski 2007). Given the lack of previous SGD carbon load estimates, we scaled up the carbon inputs obtained at the study site to

the entire Baltic Sea using the same approach, that is, by taking SGD rates from the available publications and carbon concentrations measured in the Bay of Puck. The methods used to evaluate SGD rates in the Bay of Puck, Gulf of Gdańsk and the entire Baltic Sea were all based on hydrodynamic measurements combined with a hydrogeological method (Peltonen 2002, Kryza & Kryza 2006, Kozerski 2007). Thus the incompatibility of the SGD estimates as a source of error can be excluded. The error envelopes of the estimates were calculated from the standard deviations of the average yearly carbon DIC and DOC concentrations measured at the study site.

Carbon fluxes via river run-off were established as the product of the literature-derived river flows (Korzeniewski 2003) and the DIC and DOC concentrations, measured in the course of the this study.

3. Results

3.1. DIC and DOC concentrations

Pore water depth profiles for salinity, pH, DIC and DOC in the groundwater seepage impacted area (GIA) are shown in Figure 2. In general, salinity and pH decreased with depth while DIC and DOC concentrations increased with depth in the sediments. The salinity profiles are explained by the intrusion of seawater into the sediments (Szymczycha et al. 2012). The seawater percolation depth depends on the hydrodynamic conditions at the time of sampling. The decrease in sediment pore water salinity towards the subsurface sediment layers was caused by groundwater-seawater mixing, governed by the granulometric properties of the sediments, water depth, sea bottom relief and wave action. The deepest seawater intrusion was observed on November 2009 resulting in a salinity decrease from 7.2 to 2.1 in profile GL I 5.11.2009. The shallowest seawater intrusions into the sediments were recorded in February 2010 and May 2010. The highest DIC and DOC concentrations were characteristic of the low-salinity pore water, classified here as groundwater. The annual averages of DIC ($n = 13$) and DOC ($n = 13$) concentrations in the groundwater were 64.5 ± 10.0 mg C L^{-1} and 5.8 ± 0.9 mg C L^{-1} respectively. The highest DIC concentration was recorded in November 2009 (80.5 ± 23.9 mg C L^{-1}) and the smallest in February 2010 (45.0 ± 4.2 mg C L^{-1}). The highest DOC concentration was measured in May 2010 (6.8 ± 0.4 mg C L^{-1}), the smallest in September 2009 (4.5 ± 0.2 mg C L^{-1}). The DIC and DOC concentrations measured in the groundwater samples (salinity ≤ 0.5) collected in July 2013 were comparable to those measured earlier in the Bay of Puck and were equal to 70.6 ± 1.1 mg C L^{-1} and 8.1 ± 0.4 mg C L^{-1} (M), 64.7 ± 0.9 mg C L^{-1} and 8.1 ± 0.2 mg C L^{-1} (K), 54.6 ± 0.8 mg C L^{-1} and 6.9 ± 0.2 mg C L^{-1} (Ł),

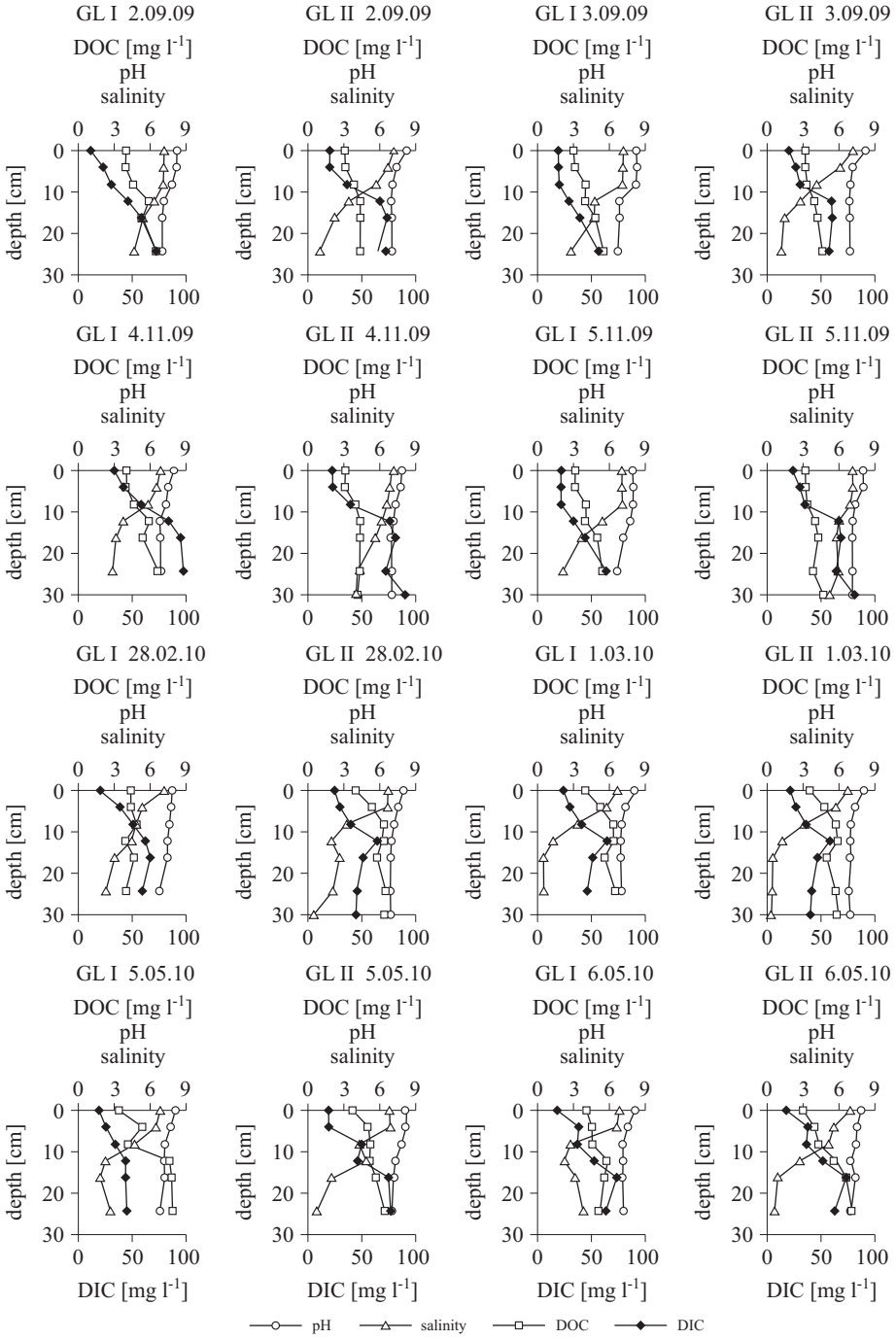

Figure 2. Pore water depth profiles for dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), pH and salinity in the groundwater impacted area. GLI and GLII stand for groundwater lances I and II respectively. The error bars as given by the standard deviations of the average values are smaller than the size of the signs indicating them

60.2 ± 0.9 mg C L^{-1} and 5.9 ± 0.2 mg C L^{-1} (W), and 70.2 ± 1.0 mg C L^{-1} and 5.4 ± 0.1 mg C L^{-1} (H) respectively. DIC and DOC concentrations were also measured in samples of other origin: seawater, groundwater from wells situated near the shore of the Bay of Puck and in rivers and streams discharging into the Bay of Puck. The highest DIC concentration was measured in groundwater (64.5 mg C L^{-1}), while seawater had the smallest DIC concentration (21.2 mg C L^{-1}). The DIC concentrations in well water ranged from 41.9 to 55.6 mg C L^{-1}. River run-off was characterised by variable DIC concentrations ranging from 38.0 to 51.1 mg C L^{-1}. The highest DOC concentration was measured in the River Płutnica (5.9 mg C L^{-1}). The average DOC concentration was 5.8 mg C L^{-1} in the groundwater samples collected at the study site, 5.0 mg C L^{-1} in groundwater samples from RII, and 0.03 mg C L^{-1} in groundwater from Hel (the lowest value recorded). Figure 3 presents the pore water profiles for salinity, pH, DIC and DOC in the area without apparent impact of groundwater seepage. The salinity fluctuated around 7.1 while pH decreased slightly from 8.1 to 7.9. DIC concentrations decreased from 17.6 mg C L^{-1} to 15.5 mg C L^{-1} while DOC concentrations declined from 4.6 mg C L^{-1} to 3.5 mg C L^{-1}.

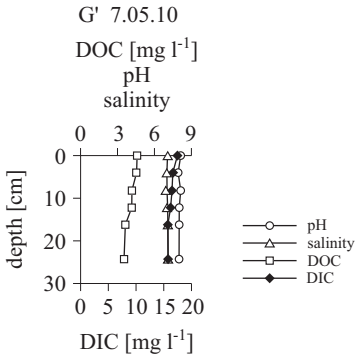

Figure 3. Pore water depth profiles for dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), pH and salinity in the groundwater non-impacted area. The error bars as given by the standard deviations of the average values are smaller than the size of the symbols representing them

The DIC and DOC concentrations measured in this study are well within the ranges reported earlier for specific water types: seawater (Pempkowiak 1983, Kuliński & Pempkowiak 2008), groundwater (Cai et al. 2003, Moore et al. 2006, Santos et al. 2009, Liu et al. 2012), river water (Korzeniewski 2003) and sediment pore water (Bełdowski & Pempkowiak 2003).

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

Groundwater fluxes and the dissolved carbon concentrations measured in groundwater were used to calculate the carbon loads delivered into the

study area via SGD (see Table 1). DIC fluxes were the highest in September and November 2009 – 1303.9 ± 109.9 mg C d^{-1} m^{-2} and 1480.8 ± 440.4 mg C d^{-1} m^{-2} respectively. DIC fluxes were the lowest in February 2010 (135.1 ± 24.0 mg C d^{-1} m^{-2}), while in May 2010 they were 256.0 ± 24.0 mg C d^{-1} m^{-2}. Like DIC, the highest DOC fluxes were measured in September and November 2009 – 95.5 ± 3.7 mg C d^{-1} m^{-2} and 111.8 ± 13.5 mg C d^{-1} m^{-2} respectively. DOC fluxes were the lowest in February 2010 – 17.6 ± 1.6 mg C d^{-1} m^{-2} – while in May 2010 they were 24.4 ± 1.4 mg C d^{-1} m^{-2} . The large carbon fluxes in September and November 2009 can be attributed to increased SGD caused by precipitation, as Kozerski (2007) showed that the Gulf of Gdańsk hydrological system is recharged mainly by precipitation. A close relation between SGD and precipitation was reported by Smith & Cave (2012) and Cable et al. (1997), who indicated that SGD rates from shallow aquifers can vary seasonally as a result of changes in precipitation. Hence, it can be assumed that groundwater is a more significant source of DIC and DOC to the study area during summer and autumn than in winter and spring.

Table 1. Specific DIC and DOC concentrations and fluxes to the Bay of Puck (H) 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}]	
September 2009	61.2 ± 5.2	4.5 ± 0.2	21.3	1303.9 ± 109.9	95.5 ± 3.7
November 2009	80.5 ± 23.9	6.1 ± 0.7	18.4	1480.8 ± 440.4	111.8 ± 13.5
February 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.

3.3. Carbon sources to the study area

DIC flux via SGD to the Bay of Puck (Table 2) is 1.9 ± 0.2 kt C yr^{-1} and the corresponding DOC flux is 0.2 ± 0.002 kt C yr^{-1}. The most significant riverine carbon source for the Bay of Puck is the River Reda with DIC and DOC loads of 5.4 kt C yr^{-1} and 0.5 kt C yr^{-1} respectively. The Rivers Gizdepka (0.25 kt C yr^{-1} DIC, 0.03 kt C yr^{-1} DOC) and Zagórska Struga (0.73 kt C yr^{-1} DIC, 0.08 kt C yr^{-1} DOC) are smaller carbon sources. DIC and DOC fluxes via SGD make up ca 30% of the carbon river runoff discharged into the Bay of Puck.

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 rate based on Kozerski 2007)
the Bay of Puck	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 rate based on Viventsova & Voronov 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 & Cave (2012)

*ND – no data.

4. Discussion

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

The Bay of Puck groundwater discharge makes up just a small proportion of the total SGD to the Baltic Sea. Moreover, little is known regarding DIC and DOC concentrations in SGDs at other Baltic locations. Thus, in July 2013 other SGD-impacted areas were identified, and groundwater samples were collected in order to measure DIC and DOC concentrations. The DIC and DOC concentrations in groundwater samples were comparable to those characteristic of the Bay of Puck. This supports the conclusion that not only the Bay of Puck is typical of most southern Baltic Sea seepage areas (Kozerski 2007, Uścinowicz 2011). Moreover, the groundwater discharge along the southern Baltic Sea coast exceeds by far the discharge along the Scandinavian coast (Peltonen 2002).

The content of carbonates within the geological structures of the Baltic Sea's continental drainage area is much higher than in the drainage area covering the Scandinavian Peninsula. Being a land-locked sea, the Baltic 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 area is located, lies on the Palaeozoic West European Platform separated from the East European Platform by the Teisseyre Tornquist Fault Zone. The northern part of the Baltic Sea lies over the Baltic Shield, while the southern part is situated on the East European Platform. The study area is located on a sediment layer consisting of dolomites, calcites, limestones, syrrulian clays and silts with carbonate-rich dolomites. The higher DIC concentration in groundwater and, as a result, the high loads of DIC via SGD, can thus be attributed to the geological structure of the southern Baltic. Other possibilities here are the reduction-oxidation processes of the system. The groundwater is anoxic (Szymczycha et al. 2013), so the oxidation pathways of organic matter include both sulphate reduction and methane production. Both these processes lead to an increase in carbonates in the system (Schulz & Zabel 2006). This also explains the higher alkalinity and carbon concentrations in 'continental' rivers entering the sea along the southern coast compared with rivers draining the Scandinavian Peninsula.

The aim of extrapolating dissolved carbon loads via SGD to the Baltic Sea sub-basins and to the Baltic Sea is to establish the order of magnitude of carbon loads entering the sea with SGD rather than to indicate actual loads. There are several factors influencing the carbon loads obtained as a result of scaling up: concentrations representative of a given sampling

campaign, concentrations representative of the entire year, concentrations representative of the study area for the entire Baltic Sea and the accuracy of groundwater seepage estimates (Szymczycha et al. 2012). The DIC and DOC concentrations in the groundwater obtained here and the literature SGD fluxes that were used to calculate carbon fluxes to Baltic Sea subbasins and the entire Baltic Sea are listed in Table 2. The DIC and DOC fluxes via SGD to the Baltic Sea were estimated at 283.6 ± 66.7 kt C yr^{-1} and 25.5 ± 4.2 kt C yr^{-1}. Thus the DIC fluxes are approximately 11 times larger than the DOC fluxes. The total carbon flux to the Baltic Sea (sum of DIC and DOC) amounts to 0.3 Tg C yr^{-1}. DIC and DOC fluxes via SGD are significant compared to other carbon sources for the Baltic Sea (see Kuliński & Pempkowiak 2012). They are slightly lower than the atmospheric deposition (0.57 Tg C yr^{-1}) and higher than point sources (0.04 Tg C yr^{-1}). There are few reports of carbon loads delivered to the coastal seas via SGD (Table 2). These indicate that SGD fluxes of both dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) are important carbon pathways from land to coastal areas of oceans. Cai et al. (2003) estimated DIC fluxes at 20 to 170×10^9 mol yr^{-1}, which exceed riverine discharges in South Carolina. Moore et al. (2006) calculated SGD fluxes of DIC and DOC from the marshes around the Okatee estuary, South Carolina, to be 1400×10^3 mol d^{-1} and 120×10^3 mol d^{-1}, respectively. These carbon fluxes were comparable with river inputs to the marsh. Liu et al. (2012) estimated that the DIC load carried by SGD to the East China Sea was (153–347) $\times 10^9$ mol yr^{-1}, a value representing 23–53% of DIC input from the Pearl River to the sea. The SGD there consisted mostly of recirculated seawater and was equivalent to 12–21% of the Pearl River discharge.

4.2. The carbon budget of the Baltic Sea

In a recent paper Kuliński & Pempkowiak (2011) quantified major sinks and sources of carbon to the Baltic. In the carbon budget they constructed, CO_2 exchange through the air-seawater interface was used as the closing term. The results identify the entire Baltic Sea as a source of CO_2 to the atmosphere with a magnitude of 1.05 ± 1.71 Tg C yr^{-1}. The accuracy of this CO_2 exchange between seawater and the atmosphere depended on the uncertainties of each component. But despite the significance of these uncertainties, the CO_2 exchange through the air-seawater interface categorised the Baltic Sea as a basin with a near-neutral balance of annual CO_2 exchange, though skewed slightly towards the emissions. However, the seepage carbon flow (FSGD) was not included in the budget. When the

budget was supplemented with FSGD (0.31 Tg C yr^{-1}, Table 2), a new mass balance of carbon in the Baltic Sea was obtained:

$$\mathrm{Fe} + \mathrm{Fi} + \mathrm{Fo} + \mathrm{FCO_2} + \mathrm{Ff} + \mathrm{Fp} + \mathrm{Fr} + \mathrm{Fm} + \mathrm{Fs} + \mathbf{FSGD} = 0, \quad (1)$$

$$\mathrm{FCO_2} = \mathrm{Fe} + \mathrm{Fi} + \mathrm{Fo} + \mathrm{Ff} + \mathrm{Fp} + \mathrm{Fr} + \mathrm{Fm} + \mathrm{Fs} + \mathbf{FSGD}, \quad (2)$$

where Fe – export to the 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. The upshot was, as in Kuliński & Pempkowiak (2011), that the net CO_2 emissions to the atmosphere were calculated at 1.36 ± 1.71 Tg C yr^{-1}. The mean CO_2 emission was -3.5 g C m^{-2} yr^{-1} (-12.9 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 added to the Baltic carbon budget, the status of the sea defined to date as 'marginally heterotrophic' becomes minimally, yet definitely heterotrophic. The projected estimates of dissolved carbon input into the Baltic Sea via SGD should draw attention to the significance of SGD in hydrological carbon cycles. The projections demonstrate that SGD sites may transport substantial loads of carbon to coastal areas. One immediate consequence of this is a change in the biodiversity in seepage-affected areas (Liu et al. 2012, Kotwicki et al. 2013).

4.3. Carbon fluxes to the world ocean

The global carbon cycle involves processes among the major global reservoirs of this element: the atmosphere, ocean and land. The fundamental carrier in 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 have been considered in the global carbon cycle. As indicated, however, the SGD-derived carbon load constitutes a significant portion of the 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). Hence, in order to establish the order of magnitude of the SGD derived carbon load, we attempted to calculate carbon fluxes via SGD to the World Ocean. Global SGD rates and dissolved carbon concentrations are required for this purpose. There are few reports on carbon concentrations in groundwater impacted areas (Cai et al. 2003, Moore et al. 2006, Liu et al. 2012) (Table 2) and few on global groundwater discharges (Zekster & 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), we

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

Surface discharge to the World Ocean	Flow rate		Carbon fluxes ± SD [kT yr^{-1}]		References
	[m^3 yr^{-1}]	[l s^{-1}]	DIC	DOC	
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 & Loaiciga 1993)
rivers	35×10^{12}	37×10^6	402×10^3	–	Emerson & Hedges (2008)
	–	–	384×10^3	324×10^3	Chen et al. (2003)*
	–	–	$320 \times 10^{3**}$	205×10^3	Ludwig et al. (1996)

*Carbon flux to continental margins from rivers, ground water, ice.
**Bicarbonate ions (HCO_3^-).

decided to use the DIC and DOC concentrations measured in this study and literature derived SGDs to the 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 following ranges: (142–838) $\times 10^3$ kt C yr^{-1} (DIC) and (13–75) $\times 10^3$ kt C yr^{-1} (DOC). Reports define the carbon load delivered to the sea with river run-off with much better precision – see Table 3 (Ludwig 1996, Hen et al. 2003, Emerson & Hedges 2008). It follows from the data in Table 3 that the SGD-derived carbon load and the carbon load delivered with riverine discharge are comparable. Hence, the carbon flux associated with groundwater discharge may well prove to be an important component of the carbon cycle and have the potential to significantly change the projected absorption of CO_2 by the ocean from the atmosphere.

5. Conclusions

The concentrations of DIC and DOC in the groundwater samples collected in the Bay of Puck are comparable to those from the other SGD-impacted areas on the southern coast of the Baltic Sea (M, K, Ł, W) and are thus accepted as characteristic of the southern Baltic. 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 to the Baltic Sea via SGD were 283.6 ± 44.0 kt C yr^{-1} and 25.5 ± 2.2 kt C yr^{-1} respectively. It is concluded that SGD-derived carbon loads may represent some 10% of the carbon load discharged to the sea with river run-off. When the SGD carbon loads are added to the Baltic carbon budget, the original, 'marginally heterotrophic' status of the sea changes to 'firmly heterotrophic'. The average CO_2 emission to the atmosphere was quantified at 1.9 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 arising from estimates of both the groundwater flow and carbon concentrations in groundwater. Despite these uncertainties, however, we contend that SGD-associated carbon fluxes cannot be neglected in regional carbon budgets. Moreover, this study indicates that, when projected onto the entire World Ocean, submarine groundwater discharge might well prove to be a significant source of carbon. Thus, the calculated carbon fluxes via SGD to both the Baltic Sea and the World Ocean need to be taken into account in carbon budgets and models dealing with CO_2 cycling and future climate change.

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