Nutrient fluxes via submarine groundwater discharge to the Bay of Puck, southern Baltic Sea

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HIGHLIGHTS

► SGD fluxes were measured, and seepage water collected, by means of seepage meters.
► Both groundwater and recirculated seawater end-members were quantified.
► Nitrogen (N) and Phosphorus (P) loads were scaled up to the Puck Bay and Baltic Sea.
► N and P loads to the Puck Bay were significant at the background of other sources.
► SGD contributed significant P proportion of Baltic Sea nutrient budget.

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ABSTRACT

Submarine groundwater discharge (SGD) has been recognized as an important exchange pathway between hydrologic reservoirs due to its impact on biogeochemical cycles of the coastal ocean. This study reports nutrient concentrations and loads delivered by SGD into the Bay of Puck, the southern Baltic Sea. Measurements were carried out between September, 2009 and October, 2010 at groundwater seepage sites identified by low salinity of pore water. Groundwater fluxes, measured using seepage meters, ranged from 3 to 22 L m⁻² day⁻¹. Average concentrations of nutrients in groundwater samples collected were as follows: 0.4 μmol L⁻¹ nitrate (NO₃), 0.8 μmol L⁻¹ nitrite (NO₂), 18.2 μmol L⁻¹ ammonium (NH₄) and 60.6 μmol L⁻¹ orthophosphate (PO₄). Levels of NH₄ and PO₄ were significantly higher in samples from SGD sites than in seawater. Seawater and SGD samples showed similar NO₂ concentrations but SGD samples exhibited lower NO₃ levels than those observed in seawater samples. Measured seepage water fluxes and nutrient concentrations were used to calculate nutrient loads discharged into the study area while the literature groundwater flux and the measured nutrient concentrations were used to estimate nutrient loads discharged into the Bay of Puck. The estimates suggest that SGD delivers a dissolved inorganic nitrogen (DIN) load of 49.9±18.0 t yr⁻¹ and a PO₄ load of 56.3±5.5 t yr⁻¹ into the Bay of Puck. The projected estimates are significant in comparison with loads delivered to the bay from other, well-recognized sources (705 t yr⁻¹ for DIN and PO₄). Nutrient discharge input loads were projected to the entire Baltic Sea. The extrapolated values indicate SGD contributes a significant proportion of phosphate load but only an insignificant proportion of DIN load. Further studies are necessary to better understand SGD contributions to the nutrient budget in the Baltic Sea.

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1. Introduction

Submarine groundwater discharge (SGD) is a one of the water pathways of exchange between marine and continental water reservoirs that strongly influences the hydrogeochemistry of coastal zones (Rokuniewicz, 1992; Burnett et al., 2006; McCoy and Corbett, 2009). In comparison with easily quantified and typically large point sources of surface water inputs (e.g., rivers and streams) which are easily quantified, groundwater inputs are harder to evaluate due to difficulties in gauging fluxes from these sources and accuracy of discharges estimates is limited by the spatial and temporal variability in groundwater discharges. Burnett et al., 2003; Mulligan and Charette, 2009). Groundwater from many areas is enriched with chemical constituents and thus may serve as a substantial source of nutrients, trace metals and organic compounds entering the marine reservoir and influencing marine biota. SGD is thus likely to contribute to marine geochemical cycles and may cause environmental perturbations in coastal zones. Numerous studies have documented the ecological impact of groundwater flow into coastal areas. The scale of SGD nutrient loads can also affect coastal eutrophication (Valiela et al., 2002; Slomp and...
Van Cappellen, 2004; Andersen et al., 2007). As such, SGD poses a critical threat to biodiversity around the world (Carlton, 2006; Eamus et al., 2006). Quantifying groundwater transport of nutrients and their fate in coastal environments can enhance understanding of the hydrogeochemical processes in these areas.

The Baltic Sea receives a relatively high loads of material originating from anthropogenic sources. SGD represents a source of inputs into the Baltic Sea that has not been rigorously quantified. Peltonen (2002) estimated the total volume of SGD entering the Baltic Sea to be 4.4 km$^3$ yr$^{-1}$, or about 1% of total river run-off. SGD studies conducted along the Baltic Sea coastline over the years have mostly focused on groundwater fluxes in the Gulf of Finland, the Eckernförde Bay, the Gulf of Gdansk and the Bay of Puck (Zekster, 1973; Piekarek-Jankowska et al., 1994; Piekarek-Jankowska, 1996; Bussmann and Süss, 1998; Falkowska and Piekarek-Jankowska, 1999; Kaleris et al., 2002; Peltonen, 2002; Viventsova and Voronov, 2003; Korzeniowski, 2003; Schlüter et al., 2004; Kryza and Kryza, 2006; Pempkowiak et al., 2010). Groundwater discharge into the Gulf of Finland (surface area equal to 29,500 km$^2$) was estimated to be 0.6 km$^3$ yr$^{-1}$, whereas the discharge rate into the Eckernförde Bay (171 km$^2$) ranges from 0.04 to 0.4 km$^3$ yr$^{-1}$ (Schlüter et al., 2004). Piekarek-Jankowska et al. (1994) estimated groundwater discharge of 0.03 km$^3$ yr$^{-1}$ into the Bay of Puck (359.2 km$^2$). Uścinowicz (2011) concluded that SGD into the Bay of Puck and Gdansk Bay significantly exceeded SGD levels in other regions of the Baltic Sea.

Despite greater recognition of the role of SGD in coastal ecosystems and land-locked seas, uncertainties remain concerning the chemical composition of groundwater seeping into the Baltic Sea. Anomalous nutrient concentrations for the Gulf of Gdansk water column have been attributed to SGD (Falkowska and Piekarek-Jankowska, 1999). No studies up to this point have attempted to quantify nutrient concentrations and loads delivered by known SGD sites or input into the Baltic Sea as a whole. This work reports nutrient concentrations and load estimates as well as overall groundwater volume discharged into the study area and the Bay of Puck. The results allowed us to project nutrient loads to the entire Baltic Sea in order to assess the potential scale of nutrients delivered by SGD relative to other sources. Thus the results of this study contribute to understanding of the role of SGD in Baltic Sea nutrient budgets.

2. Description of the study area

The Bay of Puck (Fig. 1) is the eastern part of the Gulf of Gdansk, along the southern Baltic Sea coast. A narrow spit known as the Hel Peninsula separates the bay from the open waters of the Baltic. The bay has a total area of 359.2 km$^2$ and consists of an outer southeastern region with an average depth of 20.5 m, and an inner northwestern region with an average depth of 3.1 m. The basin slopes downward in a northeasterly direction reaching a depth of 54 m near the tip of the Hel Peninsula (Nowacki, 2003). Salinity in the Bay of Puck is around 7, similar to that of the open Baltic Sea. Relatively uniform salinity of seawater throughout the bay reflect limited river run-off as well as exchange between its inner and outer regions (Korzeniowski, 2003).

The Hel Peninsula developed during the Pleistocene and Holocene epochs. Geomorphic landforms surrounding the Bay of Puck consist of wave-dominated sedimentary plains and dune deposits forming in micro tidal zones. Coastal erosion is the dominant source of sediments within the study area. Waves, storm surges, currents and winds drive erosion, transport, accumulation and redeposition of sediments in the coastal zone. The average river run-off into the Bay of Puck equals to 0.25 km$^3$ yr$^{-1}$ and the average precipitation amounts to 0.20 km$^3$ yr$^{-1}$ (Cyberski, 1992).

Seismic–acoustic investigations of the study area have imaged permeable layers of Holocene to Pleistocene sands and silts and underlying Tertiary silt layers (Piekarek-Jankowska et al., 1994). Groundwater appears within Quaternary and Tertiary units that include interbedded sands and glacial clays with peripheral fluvial (sand and gravel) deposits. Beneath the weakly permeable Cretaceous layers of the aquifer, occasional SGD seepage sites are confined to near-shore, coarse-grained aquifers (Falkowska and Piekarek-Jankowska, 1999).

Pempkowiak et al. (2010) identified a submarine groundwater discharge site located off the Hel Peninsula covering about 9200 m$^2$. At the study area medium or moderately well sorted, mostly symmetrical sand occurs. The site is located in shallow, sandy, wave-dominated areas, and hosts irregular groundwater seepage. The sediments of the study area are influenced by three major processes: seepage of groundwater, percolation of seawater into the surface layer of sediments and sedimentary processes including mineralization of deposited organic matter in the sediments. The last process is limited to the uppermost layer of the sediments, while seawater can be forced into the sediments to the depth of few decimeters. Therefore the study on groundwater chemical composition needs to concentrate on pore-water residing on the depth where no salinity increase caused by groundwater–seawater mixing actually occurs. This depth depends on several factors: seepage intensity, the granulometric properties of the sediments, water depth, sea bottom relief and wave action. Thus there are several water types to be dealt with: seawater (occurring above the seafloor) and pore water (water in sediments–interstitial water). Pore water can be unaffected groundwater (salinity equal to zero), or mixed groundwater and seawater (seepage water; salinity less than that of seawater). The extent of the water types is specific to both particular section within the study area and hydrodynamic conditions at the time of sampling.

This report continues earlier investigations by Pempkowiak et al. (2010) and describes the chemical composition of discharge from the previously identified SGD site.

3. Materials and methods

Four sampling campaigns were carried out near the shoreline of the Hel Peninsula during the following periods: 31.08 to 3.09.2009, 2 to 6.11.2009, 28.02 to 1.03.2010 and 5 to 7.05.2010. Seepage water sampling points were selected based on a salinity survey of the study area carried out in August, 2009 (31.08.2009).

3.1. Salinity survey

On 31st August, 2009 salinity profiles were recorded along parallel transects that extended seaward from the beach. Along each of the 20 transects, samples were collected from 15 sampling points spaced about 15 m apart (Fig. 2). Moreover in the periods: 2 to 6.11.2009, 28.02 to 1.03.2010 and 5 to 7.05.2010 less extensive salinity measurements (4–6 sampling stations) in the study area were performed using seepage meters and groundwater lances.
Seawater depth along the transects ranged from 0.5 to 2 m in accordance with distance from the shore.

Push-point lances (see Beck et al., 2007b) equipped with 50 ml polyethylene syringes were used to sample pore water at depths of 5 cm and 25 cm within the sediment. Salinity and temperature measurements of sediment pore water and seawater were performed with a salinometer (WTW Multi 3400i Multi-Parameter Field Meters) having 0.02 and 0.1 °C accuracy.

3.2. Pore water sampling for nutrient analysis

Groundwater lances were used to collect pore water for salinity and nutrient analysis. After a 24 h equilibration period following insertion, the devices were used to withdraw 35 ml of pore water at depths of 0, 4, 8, 12, 16, 24 and 30 cm below sediment–water interface. Groundwater measuring less than 0.5 often occurred at depths greater than 15 cm below the sediment–water interface. Pore water at this depth was thus interpreted as groundwater seepage into the surroundings.

3.3. Seepage water fluxes to the study area

Seepage meters (Pempkowiak et al., 2010) were used to measure seepage water fluxes to the study area. This method is acceptable at sites where the outflow is controlled by small scale geological heterogeneity (Andersen et al., 2007). However, in geologically heterogeneous areas SGD results may vary as they depend upon the exact seabed selection for deployment of the seepage meter (Burnett et al., 2006). Seepage meters consisted of a polyethylene (PTE) chamber (surface: 0.785 m²) with an inlet at one end and a sample port with a PTE collector at the other end. Groundwater seeping through the sediment was trapped in the PTE collector. The volume of collected over a measured time interval provided the seepage flux rate.

The PTE chambers were deployed one day before actual sampling of seepage water. Than the PTE collector was installed and seepage water rate was collected over the following time periods: on 2.09.09 and 4.11.09 the PTE collectors were left for 45 min, on 28.02.10 – 145 min, and on 5.04.2010 — 60 min.

Salinity of the collected samples varied from 2 to 4. The groundwater fraction for each sample was calculated using the end-member method (Burnett et al., 2006; Szczepańska et al., 2012). Groundwater flux was calculated as the ratio of groundwater volume plus device surface area divided by the observation time interval. Briefly, the end-member method is based on the following mass balance relationships:

\[ V_S = V_G + V_{SW} \]
\[ S_S V_S = S_G V_G + S_{SW} V_{SW} \]

where \( S \) and \( V \) are salinity and volume. Subscripts \( S, G \) and \( SW \) represent the sample, groundwater and seawater fractions, respectively. The two unknowns \( (V_G, V_{SW}) \) were calculated using the above equations and the measured values for \( S_S, S_G, S_{SW} \) and \( V_S \).

3.4. Nutrient analysis

Water samples (sediment pore water and seawater; 35 ml volume) were passed through 0.45 μm syringe-driven membrane filters and transferred into polyethylene bottles. The sample bottles were initially washed in 2 M nitric acid and then rinsed with MilliQ water until the measured background nutrients were below detection limits (5 times×30 ml). The bottles were also rinsed with a small volume of the collected sample water prior to the final sample collection. The collected samples were then transported to the laboratory and analyzed for nutrient concentrations within 48 h. The samples were refrigerated at 4 °C between transport and analysis stages.

Nutrients were analyzed using colorimetric methods described by Strickland and Parsons (1967) and Salley et al. (1986). Repeated analyses of both sediment pore water and seawater samples \( (n=7 \) for each) using internal and external (spike) standards established the accuracy and precision of nutrient analyses. The standards included 0.5, 1.5, 2.0 mg L\(^{-1}\) for NO\(_3\), NH\(_4\), PO\(_4\) and 0.005, 0.05, 0.5 mg L\(^{-1}\) for NO\(_2\). The average relative standard deviations (precisions) were 0.4% for NO\(_3\), 1.4% for NO\(_2\), 0.3% for NH\(_4\) and 1.4% for PO\(_4\). Analyses indicated recoveries of 96.2% for NO\(_3\), 101.4% for NO\(_2\), 98.3% for NH\(_4\) and 99.1% for PO\(_4\).

4. Results

4.1. Salinity concentrations in pore water samples

Pore water salinity was used to locate SGD sites within the study area. Previous studies have used this method to identify SGD locations and measure seepage rates (Zohdy and Jackson, 1969;
Millham and Howes, 1994; Rapaglia, 2007). Fig. 2 shows the pore water salinity distribution within the study area in August, 2009 with clearly distinguished areas of higher and lower salinity. The groundwater salinity distribution is rather variable. This can be attributed to the granulometric properties of the sediments, sea bottom relief, wave action and hydrodynamic conditions at the time of sampling. A groundwater impacted area (site G) and an area without apparent groundwater impact (site G’) were selected from the salinity distribution map (Fig. 2). Fig. 3 shows the salinity profiles for both G and G’ sampling points. Pore water salinity of the G profile (measured on 3.09.09, 5.11.09, 28.02.10, 5.05.10) decreases with depth from about 7 to about 0.2. In November, 2009 the lowest observed salinity (2.1) occurred at 30 cm depth. The G salinity profiles show two distinct segments. The first segment extends from the surface to about 15 cm below the sediment–water interface and represents a mixing zone between seawater and groundwater. This zone is affected by wave-induced seawater intrusion into the sediment (Li et al., 1999; Ullman et al., 2003; Beck et al., 2007a, 2010; Pempkowiak et al., 2010). In addition to heterogeneities within the aquifer, coastal seepage sites host a recirculated seawater component. Seepage fluxes from Great South Bay, New York for example reached values of 150 L m⁻² d⁻¹. Discharge measurements of 50 L m⁻² d⁻¹ for near-shore environments decreased to 30 L m⁻² d⁻¹ at sites located 100 m offshore. Secondary convection due to instabilities in the water density structure at the sediment–water interface can thus obscure the seepage distribution. Marine water can penetrate seepage sites to depths of tens of centimeters due to thermohaline density effects (Bokuniewicz, 1992). The end member approach provides a seepage flux interpretation that recognizes potential contribution from recirculated seawater.

The groundwater-seawater mixing zone gradually grades into fresh groundwater without a sharp boundary between zones. Previous studies of SGD sites have reported salinity profiles similar to those described here (Ullman et al., 2003; Beck et al., 2007a, 2010; Pempkowiak et al., 2010). In contrast to SGD sites, pore water salinity profiles of the G’ site showed nearly constant salinity of around 7. At reference point G’ also a seepage meter was deployed. The measured salinity at the PTE collector was 7.2 and the nutrient concentrations were similar to those characteristic of seawater: nitrate (NO₃⁻) 0.76–1.34 μmol L⁻¹, nitrite (NO₂⁻) 0.13–0.98 μmol L⁻¹, ammonium (NH₄⁺) 0.56–1.98 μmol L⁻¹, orthophosphate (PO₄³⁻) 1.91–4.21 μmol L⁻¹, thus samples collected at the G site can be regarded as containing traces of groundwater at the most.

4.2. Nutrient concentrations from SGD sites in the study area

Fig. 4 shows characteristic pore water nutrient profiles (samples collected on 3.09.2009, 5.11.2009, 28.02.2010 and 5.05.2010). In September 2009, NO₃ decreased with depth from 1.03 to 0.36 μmol L⁻¹ while and NO₂ decreased from 0.26 to 0.1 μmol L⁻¹. Measured NH₄ and PO₄ concentrations followed opposite trends with NH₄ increasing from 5.6 to 367.5 μmol L⁻¹ and PO₄ increasing from 0.09 to 56.5 μmol L⁻¹. In November 2009, the NO₂ concentration profile showed decreases with depth from 0.5 to 0.3 μmol L⁻¹, and NO₃ concentrations decreased with depth from 0.9 to 0.2 μmol L⁻¹. Both NH₄ and PO₄ concentrations were higher in pore water collected from deeper sediment layers (43.1 and 57.9 μmol L⁻¹, respectively) than from surface layers (0.9 and 1.05 μmol L⁻¹, respectively). Profiles measured in February, 2010 resembled those measured in November, 2009. Profiles collected in May, 2010 resembled those collected in September, 2009. The NH₄ concentration maxima varied significantly with time. The lowest NH₄ concentration was measured from samples collected in February, 2010 and the highest NH₄ concentrations (<300 μmol L⁻¹) occurred in samples collected in September, 2009. The other nutrients analyzed showed less variation in their concentrations as a function of time.

Fig. 5 shows inverse relationships between salinity and both NH₄ and PO₄ concentrations. The PO₄ profile exhibits a nonlinear decrease with salinity. The apparently non-conservative behavior of PO₄ suggests diagenetic processes taking place on ground- and sea-water mixing. Relative to phosphates, NH₄ concentrations exhibit more conservative behavior.

The patterns observed in NH₄ and PO₄ data resemble those reported in Ullman et al. (2003) wherein nutrient concentrations in sediment pore waters from Cape Henlopen, Delaware (a sandy beach face) showed signs of dispersive mixing between saline and groundwater end-members, as well as a diagenetic contribution (or removal).

In many coastal environments, groundwater discharge represents only a small proportion of freshwater flux into the ocean and thus may not be a significant input pathway of dissolved chemical substances. If nutrient concentrations are sufficiently high however, SGD can deliver substantial input loads. Table 1 shows average concentrations of nutrients in groundwater and seawater samples collected from the study area. Nutrients concentrations in pore water collected from the depths of 15 cm, or deeper, below sediment–water interface (salinity smaller than 0.1) were used as characteristic of groundwater. Derivation of these values assumed that groundwater salinity ranged from 0 to 1 (except samples collected in November, 2009 when salinity ranged from 1 to 2.1) and seawater salinity ranged from 6.9 to 7.2. Pore water samples having salinities ranging from 1 to 6.9 (or 2.1 to 6.9 for November, 2009) were assumed to represent mixed groundwater–seawater samples. We used groundwater flux measures to calculate weighted average values for concentrations of each species. Table 1 shows the yearly average concentration values calculated as arithmetic means of the average seasonal concentrations.

Variations in nutrient concentrations over the course of the year indicate pronounced seasonal changes in groundwater nutrient content. Ammonia reached its highest average value in samples collected during the summer months (239 μmol L⁻¹) and its lowest value (55 μmol L⁻¹) in samples collected during the spring. The highest average PO₄ concentration was observed in samples collected during the autumn (76.6 μmol L⁻¹) and the lowest PO₄ concentrations occurred in samples collected during the spring (49 μmol L⁻¹). Concentrations of NO₂ and NO₃ were less temporally variable. Average NH₄ and PO₄ concentrations measured from seawater were lower than those measured from groundwater. Concentrations of NO₂ were higher than those observed in seawater whereas NO₃ concentrations were equal to those observed in seawater.

4.3. Nutrient fluxes into the study area

Seepage water fluxes and nutrient concentrations measured in groundwater was used to calculate nutrient load input via SGD. Seepage water flux was measured using a seepage meter. Seepage water...
percolating into the device from the sediment displaces water trapped in the chamber, forcing it up through a port into a PTE measurement bag. The change in the volume of water within the bag over a measured time interval equals the seepage flux. The contribution of groundwater to flux estimates was established using the end-member method. Thus this method uses sensitive and precise measurements of end-member compositions to receive groundwater and seawater components of seepage fluxes.

Salinity is often used as a tracer for SGD identification (Rapaglia, 2007). Table 2 shows salinity of seepage water samples, seepage water fluxes and groundwater fluxes. The highest flux (21.3 L d⁻¹ m⁻²) was observed on 2.09.09 and the lowest flux (3.0 L d⁻¹ m⁻²) on 28.02.10. Within the fluxes results we can observe lower fluxes in February, 2010 and May, 2010 whereas higher fluxes were measured in September, 2009 and November, 2009. The SGDs are well correlated with average monthly precipitation characteristic of the area (Korzeniowski, 2003).

The calculated average groundwater fluxes and the measured nutrient concentrations were used to derive nutrient fluxes at sampling points (Table 3).

5. Discussion

5.1. Nutrient fluxes to the Bay of Puck

Nutrient loads from SGD are usually calculated as the products of seepage water flux and concentration of chemical species measured in inland groundwater sources (Oberdorfer et al., 1999). This method assumes that nutrient concentrations from coastal and inland groundwater sources do not change. Due to the questionable nature of this assumption, the actual nutrient concentrations were measured in groundwater samples collected throughout the study by means of
groundwater lances and seepage meters. We assume a continuous supply of nutrients transported by groundwater migration through the sediment driven by the hydraulic gradient. Nienchesky et al. (2007) used a similar approach, measuring average nutrient concentrations in water samples collected from permanent land-based wells, beach groundwater, and samples from the surf zone, inner shelf and open ocean. However, still, there is limitation to the implemented method, since in the mixing layer biogeochemical transformations of the nutrients may substantially alter the true discharge of this nutrient species.

The sum of the measured NO3, NO2 and NH4 concentrations formed a substantial part of the nutrient inputs into the Bay of Puck SGD site described here. The SGD fluxes estimated in this study were characteristic of the active SGD site reported by Piekarek-Jankowska et al. (1994) and Korzeniowski et al. (2003). SGD may significantly affect the nutrient balance of the entire Puck Bay. The seepage discharge rates estimated during this study were characteristic of the active SGD at the study area and thus exceed those calculated by Piekarek-Jankowska et al. (1994).

Table 4 gives the loads calculated as products of fluxes and average yearly concentrations of nutrients. The NH4 concentration was 47 times higher in groundwater than in seawater and the PO4 concentration was almost 99 times higher. In their study along a coastal lagoon barrier in southern Brazil, Nienchesky et al. (2007) also reported similar DIN concentrations to those reported here. The PO4 concentrations in groundwater samples reported by Lee et al. (2009) study however were approximately ten times lower than those reported here (see Table 4). The SGD concentrations reported here also exceed those measured at seepage locations in other studies (Beck et al., 2007b; Lee et al., 2009; Lee et al., 2009). Piekarek-Jankowska et al. (2012) reported SGD amounting to 8000 m3 day−1 over a 20,000 m2 area as well as DIN and DP fluxes of 920 mol day−1 and 56 mol day−1 respectively. Street et al. (2008) described sites along the Hawaii coast with SGD fluxes ranging from 0.02 to 0.65 m3 m−2 day−1, delivering nitrogen loads of 0.04 to 40 mmol m−2 day−1 and phosphate loads of 0.01 to 1.6 mmol m−2 day−1. Given their scale relative to previous examples, the SGD site described here is interpreted as a major source of nutrient input into the surrounding coastal ecosystem.

5.2. Nutrient fluxes to the Baltic Sea

River transport from drainage basin networks delivers major loads of nutrients to marine environments (Bokuniewicz, 1992; Turner et al., 1999; Burnett et al., 2003). Analysis of inputs from major rivers allows relatively precise estimates of freshwater and nutrient inputs into the Baltic Sea (HELCOM, 2005). Non-point pathways in the subsurface are increasingly recognized as a major input mechanism for certain coastal areas (Beck et al., 2007b; Lee et al., 2009; Pempkowiak et al., 2010). Burnett et al. (2003) define "submarine groundwater discharge" as any and all water flow from the seabed to the ocean along coastal margins, regardless of fluid composition or driving force. SGD typically exhibits low specific flow rates that make detection and quantification difficult. These fluids transfer biogeochemically important inputs into the coastal marine environment. Slomp and Van Cappellen (2004) suggest that groundwater seeps may contribute to P limitation in the vicinity of SGD sources due to specific N/P ratios. The Bay of Puck SGD site exhibits small N/P ratios and thus would not contribute to P limitation.
in surrounding coastal environments. Gradual seepage of groundwater through sediments can occur anywhere given an aquifer with sufficient hydrologic pressure relative to sea level and a permeable coastal interface. The Baltic Sea sediments are mostly impermeable (Peltonen, 2002) but some locations along the southern Baltic coastline include sufficiently porous bottom layers that permit freshwater seepage (Peltonen, 2002; Uścinowicz, 2011).

Although a number of studies have addressed SGD along coastal areas of the Baltic Sea (Zełke, 1973; Piekaręk-Jankowska et al., 1994; Piekaręk-Jankowska, 1996; Bussmann and Suess, 1998; Falkowska and Piekaręk-Jankowska, 1999; Kalieris et al., 2002; Peltonen, 2002; Viventsova and Voronov, 2003; Korzeniowski, 2003; Schlüter et al., 2004; Kryza and Kryza, 2006; Uścinowicz, 2011), these earlier works did not report nutrient concentrations. Given the absence of previous SGD nutrient load estimates, we project the nutrient inputs observed here to the Baltic Sea nutrient budgets. Nutrient projections assumed that SGD along the Baltic Sea coast contains DIN and PO₄ concentrations similar to those observed in seepage water from the Bay of Puck site (Table 4) and combined these estimates with groundwater flow estimates from literature sources (Peltonen, 2002). The error envelopes of estimates were calculated from standard deviations of the average yearly concentrations observed at the study site. The projections indicated that nutrient input into the Baltic Sea amounts to a mean value of 7,320 t yr⁻¹ for DIN (1080 to 13,560 t yr⁻¹) and a mean value of 8,260 t yr⁻¹ for DP (6,430 to 10,080 t yr⁻¹).

The limitations of the data notwithstanding, the projected nutrient load calculations constrain SGD inputs to the Baltic Sea within an order of magnitude, rather than approximating actual loads. Several factors may influence the nutrient load projection. These include uncertainties in the representativeness of concentrations for a given sampling campaign, representativeness of concentrations over the entire year and whether the study area provides an accurate groundwater flux estimate for the entire Baltic Sea. The following paragraphs discuss shortly each of these uncertainties.

The campaigns for collecting sediment pore water samples and measuring seepage water flux in this study lasted several days. Both fluxes and nutrient concentrations were rather constant over the time span of each of the four campaigns (Table 1). On the other hand, both fluxes and nutrient concentrations varied in samples collected during subsequent seasons. Studies of groundwater collected with piezometers within two to three-month long periods from inland locations in the vicinity of the study area indicate that concentrations of major ions are relatively constant along the Bay of Puck coastline (Przewtołka, 2007). The sampling frequency on which nutrient load projections were based may thus be close to the limit necessary to provide reliable mean estimates.

Pomerania, the area surrounding the study site, resembles other agricultural areas along the southern Baltic Sea coast (Peltonen, 2002). Few studies have addressed the location or flux intensity of groundwater discharges along the Baltic Sea coastline but the sedimentary and geomorphic structure of the area indicate that seeps occur primarily along the densely populated southern and eastern coastal areas where land use patterns are dominated by agricultural activity. Uścinowicz (2011) suggested that the Bay of Gdańsk is the dominant source of groundwater discharge into the Baltic Sea. Located within the Bay of Gdańsk, the present study area can serve as a characteristic example of regional SGD. The sampling site selected for the study is a typical agricultural area with average fertilizer usage of 150 kg km⁻² anum⁻¹ nitrogen and 10 kg km⁻² anum⁻¹ phosphate. Nutrient concentrations measured in groundwater from the study area can thus be considered typical of agricultural areas prevalent along the Baltic Sea coast. Given these factors, we interpret the loads listed in Table 4 as representative of the upper limit of nutrient fluxes from individual SGD sites along the southern Baltic Sea coast.

The projected estimates of nutrient input into the Baltic Sea are primarily intended to draw attention to the significance of SGD in hydrologic nutrient cycles. The projections demonstrate that SGD sites may transport several thousand tons of DIN and DP into the Baltic Sea. Nutrient budgets for marine reservoirs however do not typically include SGD sources. The Baltic Sea water column is relatively eutrophic and groundwater seepage within the coastal zone is likely to enhance eutrophication. Because primary production in coastal marine environments is often limited by nitrate, groundwater derived nitrate may contribute significantly to eutrophication and harmful algal blooms (Andersen et al., 2007).

Our results and the nutrient projections based on them indicate that SGD contributes a major portion of nutrients to the Baltic Sea. Overall nutrient estimates for the Baltic Sea typically include inputs from direct atmospheric deposition to surface water, river inputs and point sources discharging directly into the sea. Table 5 lists DIN and PO₄ input to the Baltic Sea from these sources. Waterborne inputs contributed the greatest proportion of nitrogen (75%) and phosphorous (nearly 100%) to the Baltic Sea in 2000. These estimates do not include nutrient loads from SGD but they provide an important point of comparison for the projected estimates reported here. Compared to other sources, the projected SGD DIN load constitutes only a small fraction of total nitrogen delivered to the Baltic Sea. The projected SGD PO₄ load however is significant relative to loads delivered from other sources. Comparison among the sources indicates that SGD contributes around 20% of the PO₄ input but only around 1% of the DIN input relative to the total respective dissolved nutrient fluxes into the Baltic Sea (HELCOM, 2005). Given that coastal areas with permeable sediment layers are highly susceptible to groundwater impact, these values indicate that SGD discharge plays a significant role in the hydrogeochemistry of coastal ecosystems in the Baltic Sea.

### 6. Conclusions

This study provides initial estimates of SGD nutrient concentrations and fluxes into the Bay of Puck. The PO₄ and NH₄ concentrations from SGD sources entering the Bay of Puck are elevated relative to seawater concentrations whereas NO₂ and NO₃ concentrations are comparable to those observed in seawater. The SGD phosphate load is significant relative to loads entering the bay from the atmosphere and fluvial sources, whereas DIN load is less significant relative to these sources.

Nutrient loads observed at the SGD site studied here were projected to the entire Baltic Sea in order to establish overall SGD nutrient contributions within an order of magnitude. The projections

### Table 4

<table>
<thead>
<tr>
<th>Source</th>
<th>Fluxes into the Bay of Puck</th>
<th>Fluxes into the Baltic Sea</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PO₄ [t yr⁻¹]</td>
<td>DIN [kmol yr⁻¹]</td>
</tr>
<tr>
<td>Atmosphere²</td>
<td>18</td>
<td>485</td>
</tr>
<tr>
<td>Rivers and point sources²</td>
<td>70</td>
<td>220</td>
</tr>
<tr>
<td>Resuspension²</td>
<td>97</td>
<td>825</td>
</tr>
<tr>
<td>SGD³</td>
<td>56</td>
<td>50</td>
</tr>
</tbody>
</table>

² Korzeniowski (2003).
³ This study.

### Table 5

<table>
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<th>Source</th>
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</tr>
</thead>
<tbody>
<tr>
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<td>PO₄ [t yr⁻¹]</td>
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<tr>
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<td>&lt;1730</td>
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<tr>
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<tr>
<td>SGD³</td>
<td>8668</td>
</tr>
</tbody>
</table>

² Fluxes in 2000 (HELCOM, 2005).
³ This study.
indicated significant SGD contribution to overall phosphate input into the Baltic Sea. Further studies are critical to fully understand the apparently significant role of SGD nutrient inputs into the Baltic Sea marine ecosystem.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2012.08.058.

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