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The benthic-pelagic coupling affects the surface water carbonate system above groundwater-charged coastal sediments

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Submarine groundwater discharge (SGD) can be a significant source of dissolved nutrients, inorganic and organic carbon, and trace metals in the ocean and therefore can be a driver for the benthic-pelagic coupling. However, the influence of hypoxic or anoxic SGD on the carbonate system of coastal seawater is still poorly understood. In the present study, the production of dissolved inorganic carbon (DIC) and alkalinity (A_T) in coastal sediments has been investigated under the impact of oxygen-deficient SGD and was estimated based on the offset between the measured data and the conservative mixing of the end members. Production of A_T and DIC was primarily caused by denitrification and sulphate reduction. The A_T and DIC concentrations in SGD decreased by approximately 32% and 37% mainly due to mixing with seawater counterbalanced by reoxidation and CO_2 release into the atmosphere. Total SGD-A_T and SGD-DIC fluxes ranged from 0.1 to 0.2mol m^{-2} d^{-1} and from 0.2 to 0.3mol m^{-2} d^{-1}, respectively. These fluxes are probably the reason why the seawater in the Bay of Puck is enriched in A_T and DIC compared to the open waters of the Baltic Sea. Additionally, SGD had low pH and was undersaturated with respect to the forms of the aragonite and calcite minerals of $CaCO_3$. The seawater of the Bay of Puck also turned out to be undersaturated in summer (Inner Bay) and fall (Outer Bay). We hypothesize that SGD can potentially contribute to ocean acidification and affect the functioning of the calcifying invertebrates.

KEYWORDS

SGD, submarine groundwater discharge, CO_2 partial pressure, Baltic Sea, ocean acidification

1 Introduction

SGD is defined as any flow of water from the seabed to the ocean, regardless of the composition of the fluid or the driving force (Burnett et al., 2003; Taniguchi et al., 2019). It occurs in all permeable coastal aquifers; both unconfined and confined (Johannes, 1980). SGD includes meteoric and recirculated seawater; therefore, it contains water of any salinity (Taniguchi et al., 2019). Usually, the fresh component of SGD is significantly smaller than that of saline (Santos et al., 2009a; Luijendijk et al., 2020). Coastal SGD is mainly affected by waves, tides, currents and bioirrigation, while deeper SGD is often influenced by hydraulic gradients, convection, and tidal pumping (Santos et al., 2009a; Santos et al., 2009b; Arévalo-Martínez et al., 2022). Although global SGD rate assessments are difficult to establish, it is estimated that the magnitude of fresh SGD in the ocean is between 1 and 10% of annual river discharge (Burnett et al., 2003; Taniguchi et al., 2019). Moore (1996) determined that SGD, mainly saline SGD, to the ocean shelf must be about 40% of the river flux to the same area. In the Baltic Sea, fresh SGD represents ~4% of river runoff (Peltonen, 2002). However, total (fresh and saline - driven by seawater recirculation on varying timescales) SGD can be significantly higher. Kłostowska et al. (2020) indicated that the total SGD to the Bay of Puck, southern Baltic Sea, is two orders of magnitude higher than fresh SGD. Additionally, SGD ranged from 5 to 25 times more than river discharge in the area (Kłostowska et al., 2020).

Although SGD has been identified and quantified in many regions of the world, it is still necessary to improve our understanding of the proportion of the saline component of SGD; its spatial and temporal variability (Taniguchi et al., 2019; Santos et al., 2021); and the impact of biogeochemical conditions occurring in the subterranean estuary (STE - zone where groundwater mixes with seawater; Moore, 1999) on SGD composition (Taniguchi et al., 2019; Moosdorf et al., 2021). Groundwater and seawater mixing zones are strongly influenced by groundwater flow rates and the redox gradient between SGD and seawater (Slomp and Van Cappellen, 2004). Additionally, the steep biogeochemical gradient at the water-sediment interface where anoxic SGD meets oxic seawater can significantly modulate the composition of the discharged solution (Charette et al., 2001; Charette and Sholkovitz, 2002; Testa et al., 2002; Slomp and Van Cappellen, 2004; Donis et al., 2017).

In many parts of the world, SGD contributes to a significant loading of nutrients on coastlines (Valiela et al., 2002; Wang et al., 2015; Zhang et al., 2017; Taniguchi et al., 2019). For example, Cho et al. (2018) determined that SGD and the accompanying flux of dissolved inorganic nitrogen, phosphorus, and silica (DSi) are comparable to river inputs on a global scale. Rahman et al. (2019) projected that the load of DSi via saline SGD accounts for an increase of 25-30% in global estimates of net DSi to the ocean. The high concentration of nutrients in SGD is generally caused by the leakage of nitrogen and phosphorus to aquifers from agriculture or sewage plants (Bishop et al., 2007) and the decomposition of organic matter (OM) (Cai et al., 2003; Liu et al., 2012; Liu et al., 2014; Wang et al., 2018). As groundwater is in contact with sediments for a long period, during this time, the particulate organic matter (POM) in the sediments is decomposed (during recharge and in STE), releasing nutrients, DIC, and dissolved organic carbon (DOC) (Cai et al., 2003; Liu et al., 2012; Liu et al., 2014; Wang et al., 2018). Further degradation of DOC causes an additional increase in DIC and CO_2. Consequently, SGD could make the receiving coastal seawater a source of CO_2 for the atmosphere. On the other hand, the supply of nutrients derived from SGD can enhance primary productivity in coastal waters, which would reduce surface water pCO_2 (Wang et al., 2018). Therefore, SGD can potentially have wide-reaching consequences for the coastal marine environment, such as the development of coastal eutrophication; hypoxia/anoxia of bottom waters; the enhancement or buffering of ocean acidification (OA); positive or negative influence on primary productivity and the composition, activity and maintenance of the benthic community (Zeebe and Wolf-Gladrow, 2001; Slomp and Van Cappellen, 2004; Zipperle and Reise, 2005; Knee and Paytan, 2011; Kotwicki et al., 2014; Wang et al., 2014; Winde et al., 2014; Liu et al., 2017; Middelburg et al., 2020; Moosdorf et al., 2021).

Several studies indicated a large input of A_T and DIC through SGD into the ocean (Moore et al., 2011; Liu et al., 2012; Liu et al., 2014; Santos et al., 2015; Sadat-Noori et al., 2018), however, the production of A_T and DIC coupled to anaerobic biogeochemical processes is still an unresolved field of study that requires further research. In addition to poor knowledge of the impact of SGD on DIC and A_T generation in sediments, there is generally limited understanding of quantitative benthic A_T and DIC fluxes from shallow marine environments and the potential importance of coastal sediments for the global carbon cycle and climate (Krumins et al., 2013; Łukawska-Matuszewska and Graca, 2018). In addition, A_T generated through anaerobic processes and its release to the water column may be especially important for basins with low buffer capacity.

The Baltic Sea is an example of the sea, which has a low buffer capacity due to low salinity (S) and is believed to be especially vulnerable to CO_2 - induced acidification. Recent studies in the Baltic show that surface water A_T has increased since the early twentieth century due to potential changes in precipitation patterns, continental weathering, agricultural liming, and internal A_T sources (Müller et al., 2016). The composition of Baltic Sea water is strongly affected by the freshwater component, which is well reflected in the brackish character of the basin. This results in a high number of ion anomalies observed here, including those directly influencing the structure of the marine CO_2 system and the distribution of A_T and DIC (Bełdowski et al., 2010; Kuliński et al., 2018; Kuliński et al., 2022). The regional impact depends on the lithology of the catchment area and the degree of management of the estuaries (e.g., Humborg et al., 2002; Ehlert von Ahn et al., 2023). Gustafsson et al. (2019) indicated assumed that known A_T sources do not explain A_T concentration in the Baltic Sea. Some of this missing A_T input can be attributed to the release from hypoxic and anoxic sediments, or coastal erosion of carbonate-bearing rocks. For example, Łukawska-Matuszewska (2016) calculated that the average diffusive flux of A_T from the fine-grained sediments in the southern Baltic Sea was 1397 ± 511µmol $m^{-2}d^{-1}$. Silberberger et al. (2022) indicated that benthic DIC fluxes in the Bay of Puck (ranged from −2.1 to 110.6mmol C $m^{-2}d^{-1}$) were partially decoupled from oxygen fluxes and could be a consequence of carbonate dissolution, anaerobic respiration and SGD. The potential influence of SGD on the marine CO_2 system in the Baltic Sea and marine benthic calcifying organisms has not been evaluated to date.

Here, we provide data showing that SGD is a significant source of A_T and DIC in the Bay of Puck, southern Baltic Sea. We prove that anaerobic OM mineralization causes the production of A_T and DIC in STE. We show that groundwater and SGD are enriched in CO_2 and hypothesise that SGD-derived CO_2 flux results in CO_2 release into the atmosphere. Furthermore, we present that SGD has a low pH and is undersaturated with respect to the forms of aragonite and calcite minerals of $CaCO_3$ that can affect the maintenance of the calcifying invertebrates.

2 Materials and methods

2.1 Study area

The Bay of Puck is located in the western part of the Gulf of Gdańsk, the southern Baltic Sea (Figure 1), and is separated from the open Baltic Sea by the Hel Peninsula. It consists of two parts: the Inner and Outer Bay of Puck. The natural sand barrier called Rybitwia Mielizna separates both parts, which differ in terms of depth and morphology. The westernmost end is only about 2 m deep (Inner Bay of Puck), while the entrance to the bay (Outer Bay of Puck) reaches 50 m depth (Nowacki, 1993). The hydrology of the outer part is mainly influenced by the inflow of water from the Gulf of Gdańsk (Nowacki, 1993). The water circulation in the inner part depends on the direction of the wind and the limited exchange of water with the eastern outer part (Nowacki, 1993). Additionally, the inner part receives input from numerous freshwater sources, such as rivers and springs, including the Reda, Płutnica, Gizdepka, and Zagórska Struga rivers, of which the Reda River has the highest runoff (the average runoff equals approximately $5m^3\ s^{-1}$; Szymczak and Piekarek-Jankowska, 2007). Fine-grained sands dominate the sediments of the inner part while in the outer part of the bay; coarse-grained sands to a depth of about 20m predominate, while fine-aurantite sands are the majority in the deepest parts (Piekarek-Jankowska and Łęczyński, 1993).

The Bay of Puck is surrounded by a young glacial landscape and consists of isolated fragments of a moraine plateau separated from each other with deeply cut ice marginal valleys (Kramarska et al., 1995; Szymkiewicz et al., 2020). The Bay of Puck region is covered with Quaternary deposits consisting of glacial moraine with layers of sand and gravel and glacial fluvial or river sand and silty sand in the valleys. The dominant soil types are sandy loam (glacial till), sandy loam covered with loamy sand (weathered glacial till), sand (of glacifluvial origin), and peat (in larger river valleys) (Kramarska et al., 1995; Szymkiewicz et al., 2020).

The bay has a complex hydrogeological system that consists of Cretaceous, Tertiary, and Quaternary aquifers (Piekarek-Jankowska, 1994; Piekarek-Jankowska, 1996; Szymkiewicz et al., 2020). Shallow groundwater up to 10 m below the ground level occurs in the form of small-perched aquifers and sand lenses enclosed in moraine deposits. The deeper Quaternary aquifers were shaped in glacial deposits (sand and gravel) separated with a coat of moraine till. Some of the aquifers are hydraulically connected; however, the majority are confined (piezometric head reaches 45m above mean sea level, Szymkiewicz et al., 2020), except

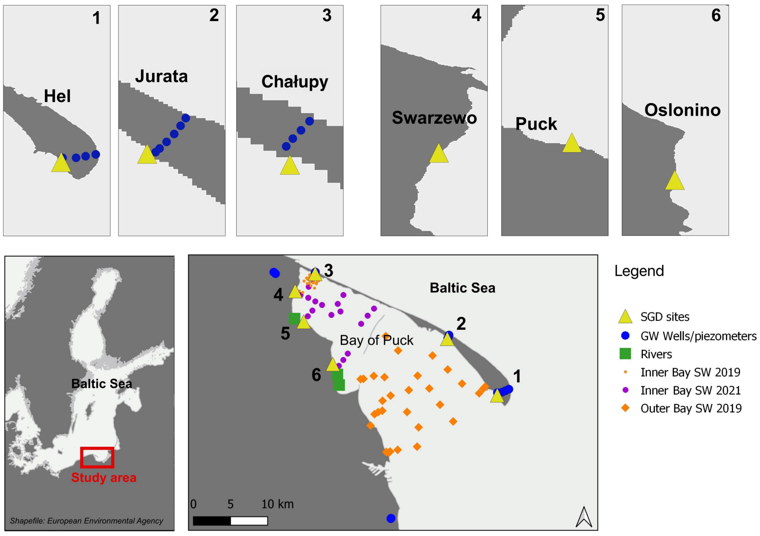

FIGURE 1
Diagram illustrating the study area. Yellow triangles correspond to sites where SGD has been identified such as Hel, Jurata, Chałupy, Swarzewo, Osłonino and Puck. The investigated area at each site was approximately $50m^2$. Green squares represent the sites where the rivers were sampled and blue dots represent the sites where groundwater was collected from piezometers and groundwater wells. Purple dots and orange dots correspond to the Inner Bay of Puck stations, while orange rhombus resembles to the Outer Bay of Puck stations, respectively, where surface seawater was collected.

for areas in the valleys where the till cover was eroded and the upper aquifer is exposed, unconfined, and indirectly connected with surface waters. Shallow groundwater is recharged by the infiltration of rainwater. Deeper aquifers receive seepage water from the layers above (Piekarek-Jankowska, 1994; Szymkiewicz et al., 2020).

The Bay of Puck was described in several studies as an active groundwater discharging area (Piekarek-Jankowska, 1994; Piekarek-Jankowska, 1996; Szymczycha et al., 2012; Kotwicki et al., 2014; Matciak et al., 2015; Donis et al., 2017; Kłostowska et al., 2020; Szymczycha et al., 2020a; Szymczycha et al., 2020b; Ehlert von Ahn et al., 2023). Groundwater models estimate that fresh groundwater discharge to the Bay of Puck from all aquifers is about 1.1 10^{-12} L cm^{-2} s^{-1} (Piekarek-Jankowska, 1994; Piekarek-Jankowska, 1996). Kłostowska et al. (2020) estimated that the total SGD (fresh and saline) in the Bay of Puck is significantly higher and ranges from 1.8 10^{-7} to 2.8 10^{-7}L cm^{-2} s^{-1}. High variability of SGD flux is due to short-time-scale factors (wind direction and monthly precipitation) and long-time-scale factors (total precipitation and large-scale sea-level variations).

Previous studies indicated that fresh anoxic groundwater seepage can influence the coastal marine environment of the Bay of Puck by the discharge of methane, nutrients, and dissolved organic and inorganic carbon, including pharmaceuticals and caffeine (Szymczycha et al., 2012; Kotwicki et al., 2014; Donis et al., 2017; Szymczycha et al., 2020a; Szymczycha et al., 2020b). It should be noted that the methane loads delivered by SGD to the Bay of Puck are believed to be only slightly oxidised within the sediments and have the potential to reach the atmosphere at a maximum rate of 3mmol CH_4 m^{-2} d^{-1} (Kotwicki et al., 2014; Donis et al., 2017).

2.2 Sampling strategy

Six coastal surveys were conducted seasonally from autumn 2017 to summer 2018 in the Bay of Puck, southern Baltic Sea (Hel, Jastarnia, Chałupy, Swarzewo, Puck and Osłonino (Figure 1). Three pore water salinity surveys were repeated in October 2019 (Hel, Chałupy and Swarzewo) and June 2021 (Hel, Chałupy, Swarzewo) (Figure 1). In all coastal surveys, salinity was used as a SGD tracer and the investigated area at each site equaled approximately $50m^2$. Additionally, two surface seawater surveys were also conducted: on r/v Oceania in the Outer Bay of Puck in October 2019 and with s/y Świrek in the Inner Bay of Puck in June 2021.

Surface seawater from the Outer Bay was collected with the pumping system installed on r/v Oceania and having the water inlet at the 2.5m depth, while in the Inner Bay of Puck, the water samples were taken using a Niskin bottle from a depth of about 0.5m.

Porewater samples were collected at several depths (5, 10 and 15cm) or at a depth of 10cm depending on the sediment type in transects every 1m up to 5m offshore using stainless steel lances and syringes (Szymczycha et al., 2012). The details regarding the sampling strategy including the spatial scale, coverage of groundwater endmember collection, and representativeness of the endmembers are given in Kłostowska et al. (2020).

Water samples from Reda, Zagórska Struga, and Płutnica rivers (R, n = 32) were also collected using the beaker during several campaigns (summer 2017-2019 and 2021).

Groundwater samples were collected from piezometers and coastal groundwater wells located in Chałupy, Jastarnia, and Hel on the Hel Peninsula and Władysławowo, Swarzewo and Gdynia on the mainland. Groundwater samples were collected during the standard method via a peristaltic pump using Teflon tubing connected to nylon tubing to prevent samples from degassing.

2.3 Chemical and statistical analyses

Salinity, pH, temperature, and oxidation-reduction potential (Eh) measurements of surface water from inner bay sediment pore water, groundwater and river water were performed with a WTW Multi 3400i Multi-Parameter Field Metre that yielded an accuracy of 0.02, 0.1, 0.1°C, respectively. Oxygen (O_2) and Eh were measured in coastal sampling campaigns from autumn 2017 to summer 2018 with an accuracy of 0.1mg L^{-1} and 0.1mV, respectively (e.g. Szymczycha et al., 2020a).

Unfiltered samples for DIC and A_T were collected in 250ml glass bottles, preserved with 100µL of a saturated $HgCl_2$ solution, tightly sealed and stored in the refrigerator until analysis. The DIC was measured in a TOC-L analyser (Shimadzu Corp., Japan). The measurement method is based on sample acidification and detection of evolving CO_2 in a nondispersive infrared (NDIR) detector. A_T was analysed using an automated open-cell potentiometric titration system developed by A. Dickson (California, San Diego; Dickson et al., 2007). The quality check for both parameters was ensured using certified reference materials (CRMs, Marine Physical Laboratory at the Scripps Institution of Oceanography, University of California, San Diego). The DIC and A_T measurement precisions, defined as the standard deviation, were equal to 7µmol L^{-1} and 4µmol kg^{-1}, respectively.

Analyses of DOC were carried out using a 'HyPerTOC' analyser (Thermo Electron Corp., The Netherlands), using the UV/persulfate oxidation method and non-dispersive infrared (NDIR) detection. The quality control of the DOC analysis was performed using seawater (supplied by the Hansell Laboratory, University of Miami) as the accuracy tracer for each series of samples (average recovery was equal to 96 ± 3%). The precision, described as the relative standard deviation of the analysis in triplicate, was not less than 3%. More details can be found in Szymczycha et al. (2014; 2020a).

During the cruises, a Seabird 9/11 + CTD sensor was used to measure conductivity, temperature, and density in the surface water of Outer Puck Bay. The accuracies of the CTD were: C=0.0003S cm^{-1}, T=0.001°C, and D=0.015%. Statistical analyses were performed using Statistica software (Statsoft). The partial pressure of carbon dioxide (pCO_2) was calculated based on T, S, pH, and DIC using the CO_2SYS programme (Pierrot et al., 2006). Knowing that the Baltic Sea characterizes is characterized by ion anomalies e.g. calcium (Millero, 1978; Anderson and Dyrssen, 1980); the saturation states of aragonite (Ω_{Ar}) and calcite (Ω_{Ca}) were calculated using two approaches: (A) based on T, S, pH, and DIC using the CO_2SYS programme (Pierrot et al., 2006) and (B) following Mucci (1983) including calcium concentrations derived from salinity based on Anderson and Dyrssen (1980) and carbonate ion concentrations based on CO_2SYS programme. Figure S2 presents Ω_{Ar} and Ω_{Ca} calculated using both approaches. Including calcium and carbonate concentration anomaly in the calculations (B) of Ω_{Ar} and Ω_{Ca} mostly influenced results for river water (Ω_{Ar} and Ω_{Ca} increase higher than in A) and seawater (Ω_{Ar} and Ω_{Ca} decrease lower than in A). Therefore, in further discussion, we used Ω_{Ar} and Ω_{Ca} obtained within approach (A) only, which is further justified as calcium concentrations derived based on Anderson and Dyrssen (1980) do not relate reflect the groundwater calcium concentrations found by Kłostowska et al. (2020).

3 Results

Groundwater samples (n=41) collected from wells and piezometers had low salinity (0.2 ± 0.2), and low pH (7.1 ± 0.5) (Figure 2, Table S1). The salinity of the rivers flowing into the Bay of Puck was comparable to groundwater (Figure 2, Table S2, $p>0.05$). However, the pH of river water was significantly higher (7.8 ± 0.3) than that of groundwater. The average salinity and pH of the SGD samples (n=84) equalled 3.3 ± 2.4 and 6.8 ± 0.5, respectively. The average salinity in the Inner Bay of Puck (6.6 ± 0.2) was slightly lower than in the Outer Bay of Puck (6.8 ± 0.3), while an average opposite trend was observed for pH (7.9 ± 0.2 and 7.8 ± 0.3, respectively). The concentrations of A_T and DIC in groundwater had a wide range, with mean concentrations equal to 4223 ± 1800µmol kg^{-1} and 4404 ± 1748µmol L^{-1}, respectively. The concentrations of A_T and DIC in the rivers were similar to those of groundwater; however, with a lower range (Figure 2, Table S2, $p>0.05$). In SGD A_T and DIC were similar to groundwater samples and characterised by a wide range of concentrations with mean values equal to 2954 ± 1263µmol kg^{-1} and 3217 ± 1434µmol L^{-1}, respectively. The surface waters of the Inner and Outer Bay of Puck showed A_T values of 1853 ± 61µmol kg^{-1} and 1779 ± 86µmol kg^{-1}, respectively, and DIC values of 1833 ± 68µmol L^{-1} and 1714 ± 84µmol L^{-1}, respectively (Figure 2). Although the salinity, A_T, and DIC of the rivers that flow into the Inner Bay of Puck were comparable to groundwater, they indicated a lower range of minimum and maximum concentrations (Figure 2, Table S2, $p>0.05$). Ar was the lowest in groundwater and SGD with averages equal to 0.3 and 0.1, respectively (Figure 2). At the same time in these samples, pCO_2 reached the highest level equal to 59881 and 67009µatm, respectively. Ω_{Ar} and pCO_2 in rivers ranged from 0.05 to 1.1 and from 622 to 12003µatm, respectively. In the Inner and Outer Bay of Puck, the mean pCO_2 was equal to 937 and 1578µatm while Ω_{Ar} was in the range of 0.2 to 0.7 and 0.0 to 0.9, respectively. Furthermore, we observed that SGD has a high average pCO_2 compared to the average of local surface seawater (Figure 2). Generally, Ω_{Ca} followed the Ω_{Ar} distribution in all sample types.

Eh, O_2, and DOC were not measured during all sampling campaigns, only from autumn 2017 to summer 2018. The results are published in Szymczycha et al. (2020a) and presented in Supplementary Figure 1. Within groundwater samples, Eh ranged from −225.5 to 94.2mV, and O_2 concentrations ranged from 0.08 to 9.0mg L^{-1} and DOC from 343.3 to 3318.3 µmol L^{-1}. Eh, O_2 and DOC had scattered concentrations in SGD that ranged from -246.0 to 142mV, from 0 to 7.6mg L^{-1} and from 278 to 2654µmol L^{-1}, respectively. In seawater Eh, O_2, and DOC were equal to 27mV, 9.0mg L^{-1} and 201µmol L^{-1}, respectively. Generally, fresh SGD was anoxic, had very low Eh and increased DOC compared to seawater.

4 Discussion

4.1 Carbonate system of SGD in the Bay of Puck

The A_T, DIC, pH, A_T: DIC, pCO_2, Ω_{Ar} and Ω_{Ca} in groundwater, rivers, SGD, and surface water of the Inner and Outer Bay of Puck have been plotted against salinity, additionally pCO_2, Ω_{Ar} and Ω_{Ca} also against pH (Figure 3). Distributions of DIC, A_T, and pCO_2 generally followed salinity, with higher concentrations of DIC, A_T and pCO_2 associating with lower salinities.

The average concentrations of A_T and DIC in groundwater, rivers and fresh SGD were 2.4 and 2.6, 1.7 and 1.9, 2.3 and 2.4 times higher than in surface waters, respectively, comprising a source of A_T and DIC to the bay. What is more the concentration of A_T in SGD was comparable to the Vistula River, the second-largest river entering the Baltic Sea (Hjalmarsson et al., 2008; Stokowski et al., 2021),

It should be noted that in the Inner Bay of Puck, both A_T and DIC were slightly higher than in the outer bay, which may suggest that the discharge of A_T and DIC through SGD and rivers has a more significant effect on this part of the Bay of Puck. The Outer Bay of Puck has direct contact with the open Baltic Sea waters; therefore, the impact of SGD - derived A_T and DIC can be smaller in comparison with the sheltered Inner Bay of Puck.

Both rivers and groundwater samples had a very variable pH ranging from 6.2 to about 8.5. In SGD, high pH variability also occurred, with an increase in pH along with a salinity up to values observed in surface water (Figure 3). The low pH of groundwater and SGD suggests a possible dissolution of $CaCO_3$ resulting in high values of values of DIC (Figure 3) (Deines et al., 1974; Winde et al., 2014; Wang et al., 2018; Liu et al., 2021). Freshwater end members that are enriched in A_T and DIC, are a common phenomenon observed in limestone-rich catchments such as the Puck Bay catchment (Giani et al., 2023). For example, samples collected in Moreton Bay (Australia) showed average groundwater concentrations of A_T and DIC 1.5 and 1.7 times higher than in the surface waters of Moreton Bay, respectively, which implies also that SGD may be a source of these solutes in surface waters (Stewart et al., 2015). Another example is from a limestone catchment in Taiwan where the average A_T and DIC were significantly higher than those found in local surface seawater in the coastal zone (Wang et al., 2018).

Although the A_T: DIC ratio oscillated around 1, relatively high variability of about ±0.5 have been observed for groundwater, rivers, and SGD. In this study, the A_T: DIC <<1 suggests the presence of high pCO_2 which is in good agreement with the generally low pH and Ω_{Ca} observed especially for groundwater and SGD (Figure 3).

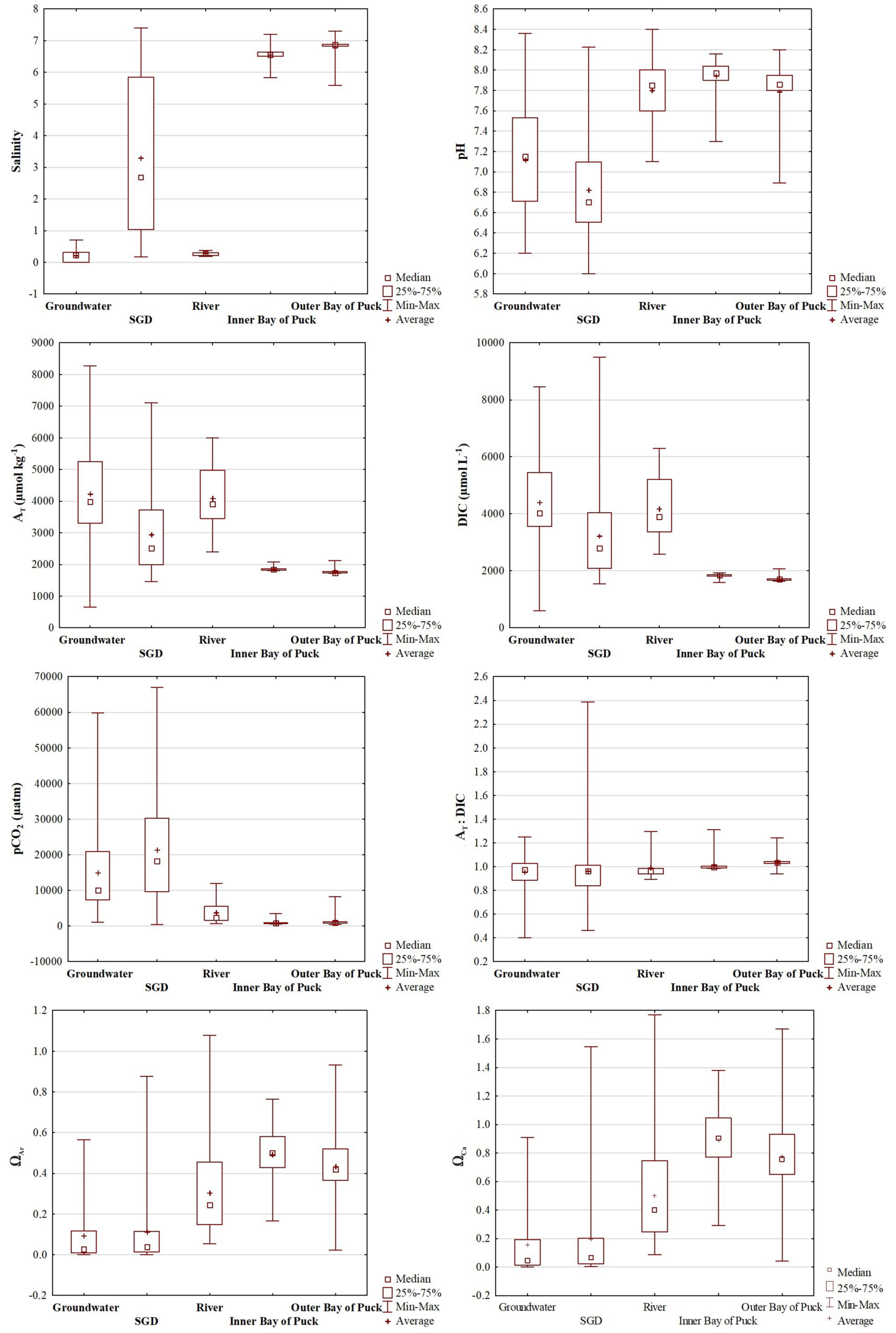

FIGURE 2

Box plot of salinity, pH, A_T, DIC, pCO_2, AT: DIC, Ω_{Ar} and Ω_{Ca} in different types of collected water samples.

On the other hand, A_T: DIC >> 1 may indicate a high share of noncarbonate components in alkalinity and/or low pCO_2, however, the latter was probably not the case considering the cooccurrence of a relatively low pH (Figure 3).

Groundwater generally has a long residual time and, consequently, accumulates more products of OM decomposition, chemical weathering, and human activities, such as potential contamination by sewage or fertilisers (Knee and Paytan, 2011; Wang et al., 2018; Chen et al., 2019; Liu et al., 2021; Santos et al., 2021). In addition, it can flow through coastal aquifers that are organized in a complex matrix of confined, semi-confined and unconfined systems, influencing its composition (Moosdorf et al., 2021). Moreover, both A_T and DIC concentrations can be modified in different ways by various diagenetic reactions within the STE due to the different importance of electron acceptors and donors (e.g., Froelich et al., 1979; Moosdorf et al., 2021).

To determine the behaviour of A_T and DIC in the STE, a two-endmember mixing model was created using salinity as a

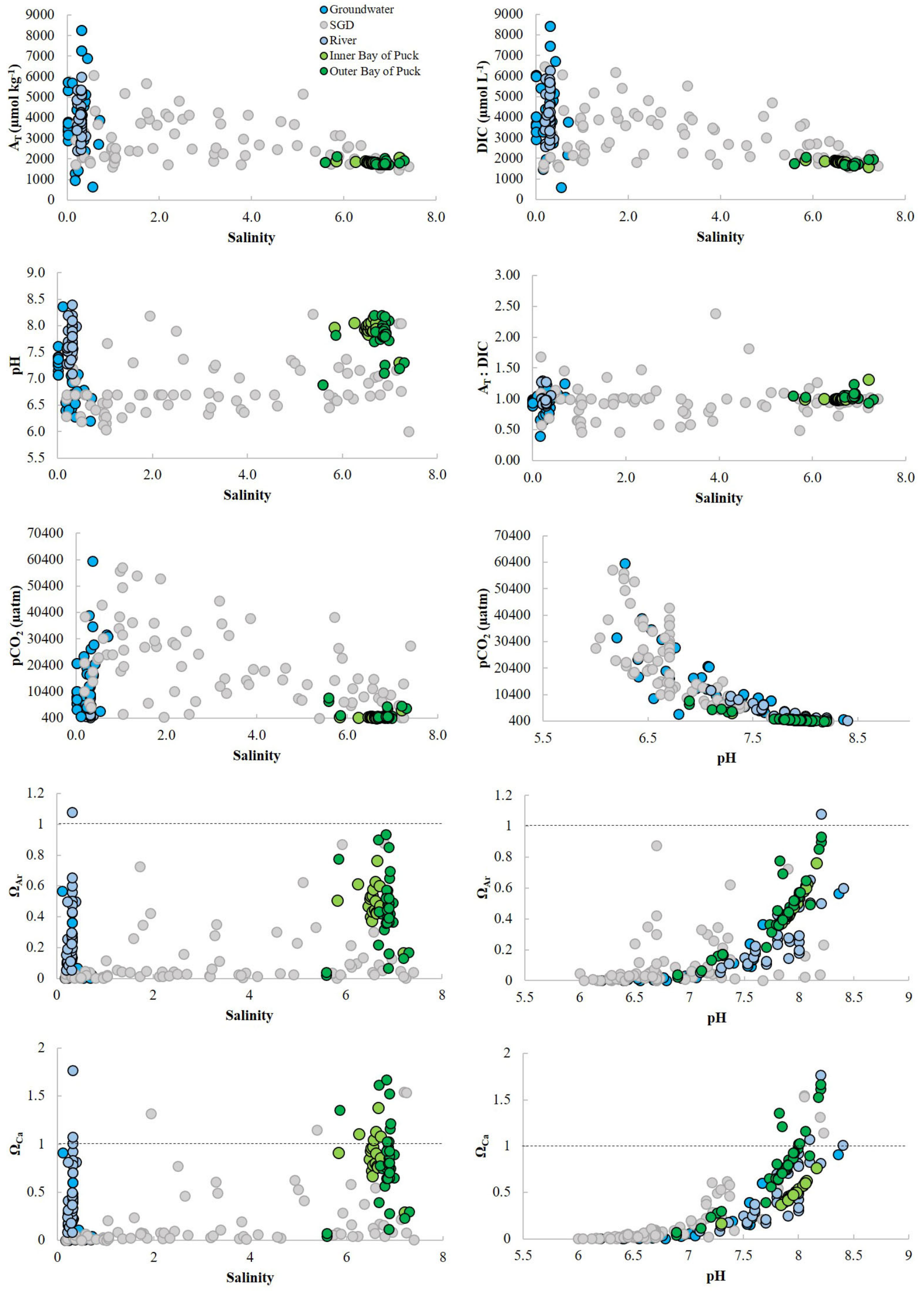

FIGURE 3
Relationship between A_T, DIC, pH, A_T: DIC, pCO_2, Ω_{Ar}, Ω_{Ca} with salinity and pCO_2, Ω_{Ar} and Ω_{Ca} with pH in collected samples.

conservative parameter to qualitatively depict sources and sinks of A_T and DIC in the STE following Liu et al. (2021). The distribution of the average concentrations of A_T and DIC (1 PSU step) in all SGD samples shows great variability (Figure 4). It must be noted that fresh SGD end members were already enriched in A_T and DIC most likely coming from $CaCO_3$ dissolution, and diagenetic processes occurring already in the aquifers, therefore the calculated production of A_T and DIC in SGD (the anomaly from the conservative mixing) already included the A_T and DIC signal derived from groundwater. The substantial increase in the mean values of A_T and DIC identified in the mixing zone indicates the potential importance of the processes that occur in STE that release both A_T and DIC. The conservative behaviour of A_T was also observed when the results of different study sites were evaluated separately, e.g. in Jurata (Figure 4). However, in most sites, the A_T concentration was higher than the conservative mixing line, indicating the production of A_T. It must be underlined that the decomposition of OM generally lowers pH in the aerobic environment. In this study, the average pH of the SGD was significantly lower than that of the local surface seawater (Figures 2, 3). For A_T and DIC, their concentration rises with the decomposition of organic matter (Liu et al., 2021). The calculated production of A_T and DIC was in the range of 31 to 4505µmol kg^{-1} and to 6274µmol L^{-1}, respectively. Modulations of A_T and DIC in

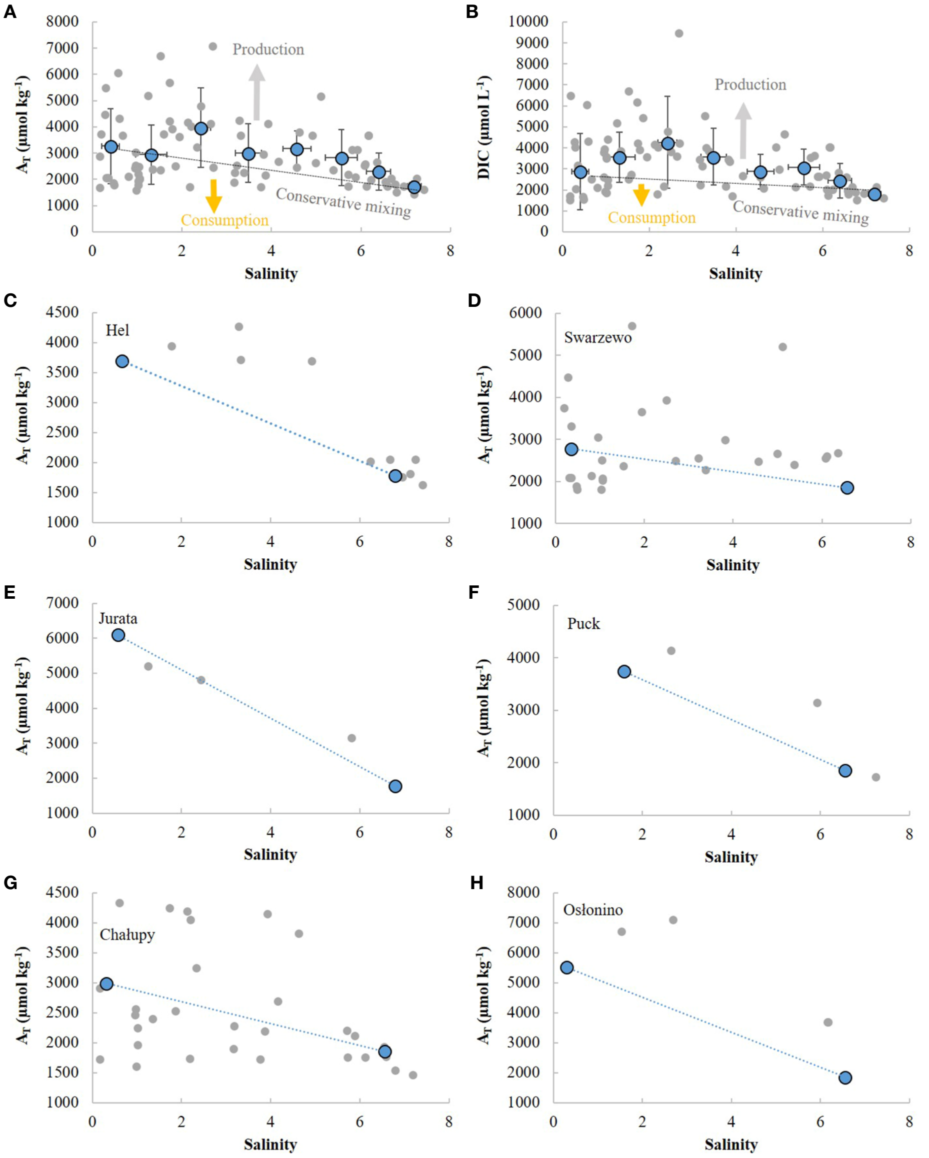

FIGURE 4
Relationship between **(A)** A_T and **(B)** DIC with salinity in the freshwater-seawater mixing zone where the blue dots represent the averaged A_T and DIC concentrations for every 1PSU with standard deviations denoted as error bars. **(C-H)** presents the relationship between A_T and salinity in SGD (grey dots) divided into locations from where the samples were collected. The conservative mixing line shows the mixing between the fresh SGD endmember and saline endmember (seawater) (blue dots). The saline endmembers were calculated separately for Hel and Jurata (Outer Bay of Puck) and Chałupy, Puck, Swarzewo, and Osłonino (Inner Bay of Puck).

the mixing zone are usually the result of the dissolution or precipitation of carbonates, sulphur minerals and different biogeochemical pathways such as aerobic respiration and the spectrum of anaerobic redox reactions as previously described by Cai et al. (2003); Santos et al. (2015), and Liu et al. (2021).

To illustrate the importance of different biogeochemical pathways the ΔA_T has been plotted against ΔDIC with division into the study area and type of SGD (Figure 5). ΔA_T and ΔDIC were calculated according to the offset between the measured data and the conservative mixing (Figure 4). The presented method provides information only on the cumulative effect of processes generating or consuming A_T and DIC, therefore the influence of different processes can be masked in such a diagram. However, the possible production and depletion pathways have been added to Figure 5. The stoichiometric ratios were taken from Liu et al. (2021). The positive ΔA_T and ΔDIC in most of the SGD collected in Swarzewo, Puck and Osłonino were located close to the denitrification and sulfate reduction pathway (ΔA_T: ΔDIC=0.9 and 1, respectively) Samples collected in Hel were located a bit below the denitrification and sulfate reduction pathway. Part of the samples from Swarzewo and Chałupy followed the aerobic respiration pathway (ΔA_T:ΔDIC=-0.2). The negative ΔA_T and ΔDIC in Swarzewo and Chałupy were located close to the FeS precipitation pathway (ΔA_T: ΔDIC=-1). $CaCO_3$ precipitation pathway was not considered as all SGD samples were characterized with low Ω_{Ca}. In all SGD samples (saline, mixed

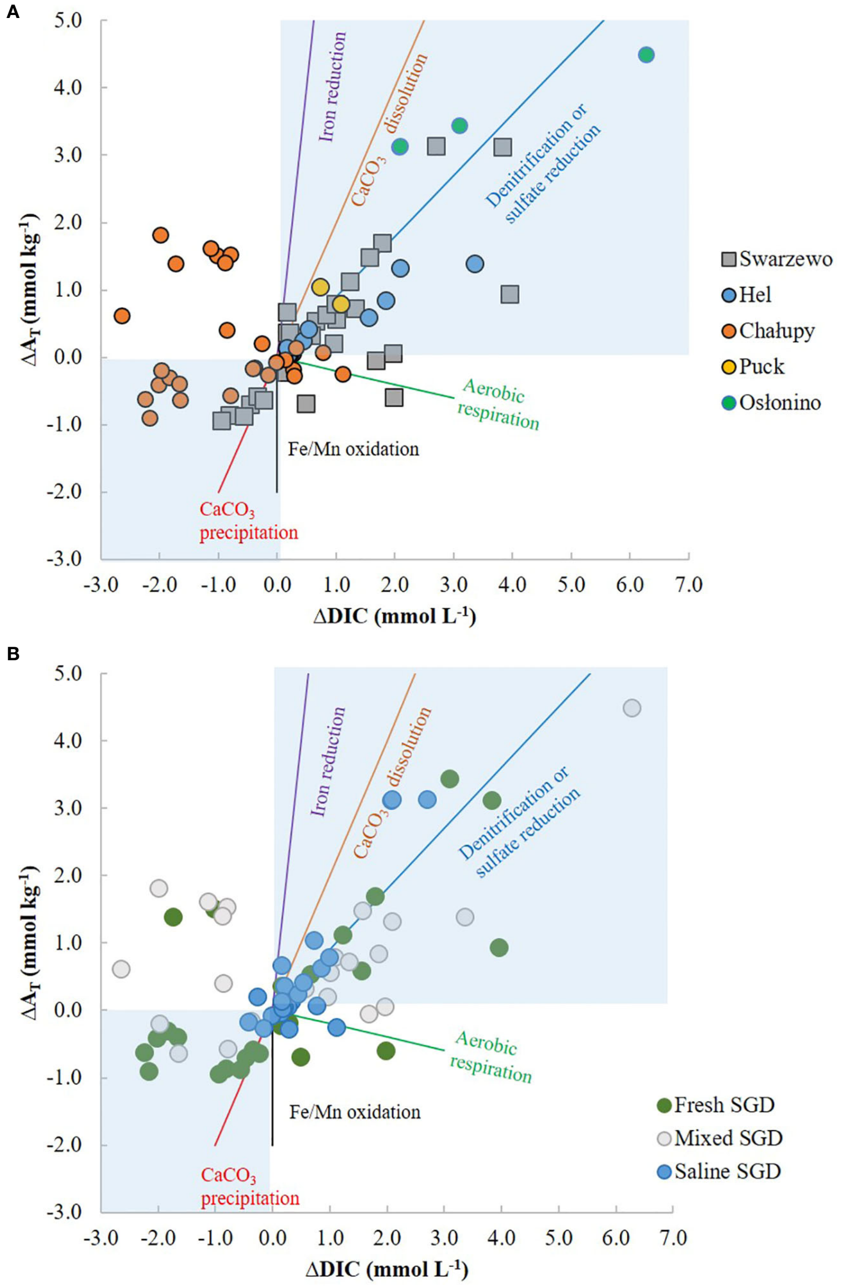

FIGURE 5
Relationship between ΔA_T and ΔDIC to identify the biogeochemical pathways of carbonates in the freshwater-seawater mixing zone **(A)** with division into the study site, **(B)** with division into SGD type.

and fresh) denitrification pathway and sulfate reduction pathway were responsible primarily for the production of A_T and DIC (Figure 5). The depletion of ΔA_T and ΔDIC was observed only in some fresh and mixed SGD samples and can be attributed to the FeS precipitation pathway. Our results suggest that the production of A_T and DIC in STE was mainly due to denitrification and sulphate reduction. This is consistent with previous studies showing depletion or absence of nitrate and nitrite (Szymczycha et al., 2012; Szymczycha et al., 2020b), absence of oxygen and occurrence of sulphides (Donis et al., 2017).

However, it should be noted that once hypoxic/anoxic SGD reaches oxic conditions (Figure 3) decrease in A_T and DIC can be observed. Part of the depletion can be attributed to the mixing of A_T and DIC enriched SGD with A_T and DIC decreased seawater. A_T depletion can also be attributed to nitrification, iron oxidation, and manganese oxidation. The decrease in A_T and DIC can be further explained by the precipitation of FeS and $CaCO_3$ while DIC can drop due to the CO_2 outgassing (Liu et al., 2021).

The concentration of nutrients in SGD at the same time of sampling and in the same area was lower (NO_3^-: 26.4 ± 38.9μmol L^{-1},

NH_4^+: 110.9 ± 25.6µmol L^{-1}, PO_4^{3-}: 10.8 ± 3.6µmol L^{-1}, Szymczycha et al., 2020b) than the average excess DIC supported by SGD (DIC: from 1354µmol L^{-1} to 6274µmol L^{-1}). Therefore, the primary production supported by the input of nutrients from SGD is insufficient to compensate for the high DIC and pCO_2 supplied by SGD. As a result, the SGD in the Puck of Bay leads to a CO_2 outgassing to the atmosphere. To calculate the loss of A_T and DIC in SGD, we used the regressions for A_T and DIC and calculated the differences for fresh ad saline end-members. The loss of A_T and DIC reached 32% and 37%, respectively. The uncertainty is considered to be less than 3% based on the standard deviations for A_T and DIC measurements.

4.2 A_T and DIC fluxes via SGD to the Bay of Puck

To estimate the A_T and DIC fluxes via SGD, the average A_T and DIC concentrations in SGD samples were multiplied by the minimal and maximal SGD fluxes calculated at the same study sites which were equal to 1.8 10^{-7}L cm^{-2} s^{-1} and 2.8 10^{-7} L cm^{-2} s^{-1}, respectively (Kłostowska et al., 2020). The obtained A_T fluxes ranged from 0.5 mol m^{-2} d^{-1} to 0.7 mol m^{-2} d^{-1} while the DIC fluxes ranged from 0.5 mol m^{-2} d^{-1} to 0.8mol m^{-2} d^{-1}. As the change from anoxic to oxic conditions led to a decrease in A_T and DIC by 32 and 37%, respectively, we included this loss in calculations of the SGD-A_T and SGD-DIC fluxes. The final A_T and DIC fluxes through SGD ranged from 0.1 to 0.2mol m^{-2} d^{-1} and from 0.2 to 0.3mol m^{-2} d^{-1}, respectively. The benthic flux of A_T in the Gdańsk Deep calculated as the sum of fluxes of particular A_T components and assuming complete oxidation of released sulfide, equalled 0.001263 ± 0.000518mol m^{-2} d^{-1} (Łukawska-Matuszewska and Graca, 2018). The DIC benthic fluxes characteristic for the coastal zone of the southern Baltic Sea ranged from −0.0021mol m^{-2} d^{-1} to 0.1106mol m^{-2} d^{-1} (Silberberger et al., 2022). A_T and DIC fluxes calculated in this study were significantly higher than the benthic fluxes characteristic of the southern Baltic Sea.

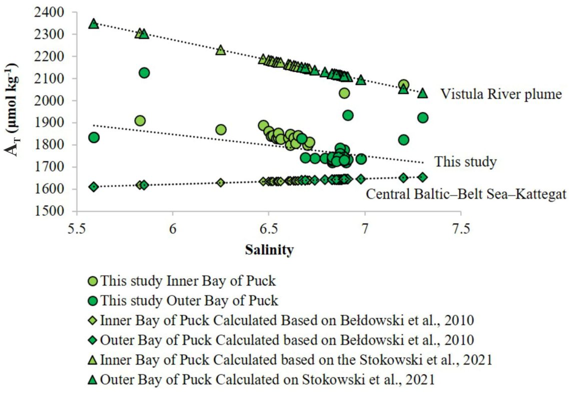

FIGURE 6
Measured salinity and A_T concentrations in seawater (this study), and the calculated A_T based on the A_T-S functions from Bełdowski et al. (2010) and Stokowski et al. (2021). The dotted lines represent the regression lines.

In the surface ocean, the distribution of A_T is often strongly interlinked with salinity, as it is mainly controlled by freshwater addition (such as a river, groundwater discharge, and ice melting) or removal (e.g. ice formation) (Millero et al., 1998). We compared A_T results found in the surface waters of the Bay of Puck (this study) with those calculated based on the dependences of A_T-S available for the Central Baltic–Belt Sea–Kattegat region: A_T=25.3*S +1470µmol kg^{-1} (Bełdowski et al., 2010) and for the Vistula River plume region (southern Gulf of Gdansk): A_T=-184*S + 3379µmol kg^{-1} (Stokowski et al., 2021) taking into account the typical salinity for surface waters in the Bay of Puck, of about 7 (Figure 6). The average A_T concentration in the Bay of Puck based on this study is equal to 1941 ± 126µmol kg^{-1} and was significantly higher than the estimated average A_T concentration(A_T=1653 ± 1.4µmol kg^{-1}) based on A_T-S dependence from Bełdowski et al. (2010) and slightly lower than that calculated based on A_T-S dependence from Stokowski et al. (2021) (S=7, A_T=2049 ± 10.6µmol kg^{-1}). Knowing that the Bay of Puck is under the limited influence of the Vistula River, as westerly winds are predominant in that region, and the river outflow is typically directed east along the coast and slowly entrained into the Baltic anticyclonic current (Matciak and Nowacki, 1995; Wielgat-Rychert et al., 2013) we propose that the increased surface seawater concentration of A_T in comparison to the Central Baltic–Belt Sea–Kattegat region may be mostly a result of SGD derived A_T fluxes.

What is worth underlining, Bay of Puck surface seawater concentrations of both A_T and DIC in the Bay of Puck are higher than those obtained in the reported for other areas of the Baltic Sea. A_T concentrations in the surface seawater of the Baltic Sea (including Baltic Proper, Gulf of Bothnia, Gulf of Riga and Gulf of Finland) were described in Bełdowski et al. (2010). Figure 7 presents the averaged A_T concentrations in the rivers, groundwater, SGD and seawater in the Bay of Puck in comparison to the surface waters of all areas of the Baltic Sea apart from the Gulf of Riga (Bełdowski et al., 2010). In addition, DIC concentrations in surface seawater obtained in this study (from 1714 ± 84µmol L^{-1} to 1833 ± 68µmol L^{-1}) were higher than those obtained reported for the Baltic Sea (surface water in the Arkona Deep) that ranged from 1506µmol L^{-1} to 1584µmol L^{-1} (Kuliński et al., 2011). Therefore, it seems that SGD is the most important factor contributing to the A_T pool in the

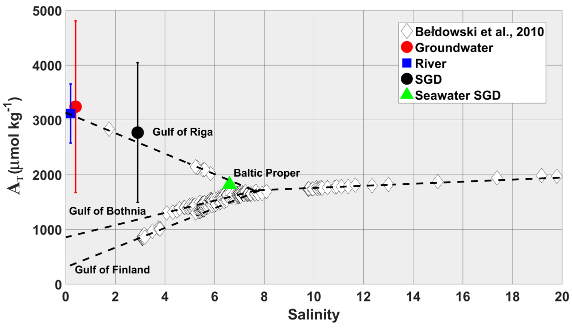

FIGURE 7
Surface A_T concentrations in the Baltic Sea (modified after Bełdowski et al., 2010).

Bay of Puck. Along the Polish coast, SGD has a similar DIC concentration (Szymczycha et al., 2014) therefore, it can be speculated that A_T concentrations are also comparable to those in the Bay of Puck. Consequently, the A_T input through SGD along the Polish coast can be an important mechanism explaining A_T concentration in the southern Baltic Sea. However, this assumption needs to be confirmed by further SGD studies along the Baltic Sea coast.

4.3 The influence of SGD on marine calcifying invertebrates

Marine calcifying organisms are threatened by global stressors, such as increasing sea surface temperatures and ocean acidification, and by local stressors such as land-based sources of pollution and/or SGD that can magnify the effects of OA (Ni et al., 2018; Prouty et al., 2022).

In shallow regions of the Gulf of Gdańsk (Figure 1), invertebrates that can form calcium carbonate skeletons are commonly found. In a study by Piwoni-Piórewicz et al. (2021) aragonitic bivalves *Cerastoderma glaucum*, *Limecola balthica*, and *Mya arenaria* were detected in the Bay of Puck; while at the border of the Puck Bay and Gulf of Gdańsk occur bimineralic bivalve *Mytilus trossulus* and calcite arthropod *Amphibalanus improvises* were detected. The Mg-calcite-forming *Spirorbis spirorbis* has been found in the Baltic Sea (Kiel Bight, Ni et al., 2018) attached to the brown macroalgae *Fucus*.

Generally, inorganic precipitation of calcium carbonate is likely to occur substantially above saturation degrees of 1 (e.g., Michaelis et al., 1985), whereas carbonate dissolution occurs with Ω decreasing further below 1. Tyrrell et al. (2008) in a seasonal study proved that the Gotland Sea, Gulf of Riga, and Bothnian Bay (Baltic Sea) become undersaturated in winter. They claimed that the absence of the coccolithophore *Emiliania huxleyi* could therefore potentially be explained by the dissolution of their coccoliths in winter, suggesting that minimum annual (wintertime) saturation states could be most important in determining future ocean acidification impacts. In a mesocosm study using coastal Baltic Sea water (Wahl et al., 2015), CO_2 enrichment led to the co-occurrence of *S. spirorbis* growth and corrosion (Ni et al., 2018). In addition, Stokowski et al. (2021) observed an undersaturation ($\Omega<1$) with aragonite in the mouth of the Vistula River (Gdańsk Gulf) in wintertime. In a study by Thomsen et al. (2010) *Mytilus edulis*, a dominant macrobenthic species in the Baltic Sea, was found to maintain shell and somatic growth rates at ca.1400 µatm CO_2 (pH around 7.6). Their unusual ability to maintain physiological function despite substantial levels of acidification was due in part to an abundance of food, which provided the energy needed to offset the physiological costs of maintenance and growth at such low ambient pH (Melzner et al., 2011). However, more sensitive early stages of the Skagerrak *Mytilus edulis* life history have been shown to respond differently to OA: fertilisation success increased at reduced pH (induced by high pCO_2) whereas subsequent larval shell growth was negatively affected.

In our study, low Ω_{Ar} and Ω_{Ca} together with low pH were found in SGD. In addition, low Ω_{Ar} and Ω_{Ca} were also found in surface seawater. The average Ω_{Ar} and Ω_{Ca} in the surface seawater of the Inner Bay of Puck (summer) was equal to 0.5 ± 0.1 and 0.9 ± 0.2, respectively (Figure 2), while in the Outer Bay of Puck (beginning of autumn) the average Ω_{Ar} and Ω_{Ca} equalled 0.4 ± 0.2 and 0.7 ± 0.4, respectively. The conditions in SGD-impacted sediments and, generally, seawater of the Bay of Puck (undersaturation with respect to the forms of the aragonite and calcite minerals of $CaCO_3$ and low pH) are, most probably, negatively influencing the growth and functioning of calcifying invertebrates. We think further studies are needed to understand how SGD affects the Bay of Puck ecosystem.

5 Conclusions

The concentrations of A_T, DIC, and pCO_2 and pH for groundwater, rivers, SGD, and surface water in the Bay of Puck have been presented. A_T and DIC production in the STE has been observed. The nutrients supplied by SGD are, most probably, insufficient to maintain production high enough to compensate for the high DIC release, and therefore SGD in the Bay of Puck can be a source of CO_2 for the atmosphere. Although SGD and accompanying A_T fluxes enhance the buffer capacity of the Bay of Puck against ocean acidification, still low pH caused by high CO_2 release, and thus low Ω_{Ar} and Ω_{Ca} can negatively influence the marine benthic calcifying organisms.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material. Further inquiries can be directed to the corresponding author.

Author contributions

BS was responsible for the preparation of the concept of research, sampling, participation in the analysis of environmental samples, preparation of figures and tables, interpretation of results, and writing and editing of the manuscript. CA participated in the sampling campaigns and the conventionalization of the study. MB, MD, KK-M, KK, and CA contributed to data discussion in the writing and editing of the manuscript. MD and AW were responsible for AT and DIC analyses. The PM was involved in sampling, figures preparation and manuscript editing. The authors declare that they did not use artificial intelligence-based software to produce any parts of the text in this study. All authors contributed to the article and approved the submitted version.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher's note

Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fmars.2023.1218245/full#supplementary-material

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