

Hydrochemical characterization of various groundwater and seepage water resources located in the Bay of Puck, Southern Baltic Sea

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INTRODUCTION

Submarine groundwater discharge (SGD) has been recognized as a significant source of water and chemical substances such as trace metals, nutrients, organic and inorganic carbon to the coastal zone (Oberdorfer et al. 1990; Charette et al. 2001; Slomp et al. 2004; Burnett et al. 2006; Moore 2010). In some regions SGD has been responsible for a deterioration of the coastal environment affecting the local economy and management of the area (Valiela et al. 2002; Slomp et al. 2004; Andersen et al. 2007). Particularly sensitive to the SGD are enclosed or semi-enclosed reservoirs of a limited water exchange with the open sea (Cyberski 1993). The Bay of Puck, southern Baltic Sea, due to its morphological and hydrological features, is a good example of a basin partially separated from the open sea waters (Nowacki 1993; Nowacki 1993a). Moreover, the bay itself is divided into two parts by the Rybitwa Shallow (the average depths: 21m in the outer and 3m in the inner part, that additionally impedes highly the water renewal in the inner part) (Korzeniewski et al. 1994; Urbanski et al. 2007). The Bay of Puck borders with the continental land in the west and the thin Hel Peninsula in the north and north-east. Both, the continental part and the peninsula differ in terms of land use and management. Interestingly, the first studies on the SGD in the Baltic Sea region were also performed at the Hel Peninsula (Sadurski 1987). They were related to the seawater intrusion due to the intense exploitation of aquifers. As a consequence several groundwater wells were closed along the Hel Peninsula. Later a reverse phenomenon has started to be observed and scientists became interested in the identification and quantification of the groundwater seepage to the marine environment (Piekarek-Jankowska et al. 1992; Piekarek-Jankowska 1994; Piekarek-Jankowska et al. 1994). The anomalies in the chloride distribution due to the groundwater discharge were identified in the pore waters of the Bay of Puck sediments (Bołalek 1992). Recently, the fluxes of different chemical substances via SGD to the Bay of Puck have been estimated based on the experimental studies performed at the Hel Peninsula, off Hel (Szymczycha et al. 2012; Szymczycha et al. 2014; Szymczycha et al. 2016). In fact, the loads of P, Mn and DIC via SGD to the Bay of Puck reported by the authors are comparable to the loads supplied by the local rivers entering the basin. This suggests that the SGD can also be an important source of other chemical constituents and thus has a potential to shape the functioning of the unique ecosystem of the Bay of Puck (Szymczycha et al. 2012; Szymczycha et al. 2014; Szymczycha et al. 2016). Those estimations and conclusions were based on the assumption that the composition of the groundwater coming from the side of the Hel Peninsula and the continental part are similar. Our present research hypothesis assumes that the different aquifers exploitation, land use and management, diversified geological structure and differences in land-sea interactions along the Hel Peninsula and at the continental part differentiate the chemical composition of SGD coming from both these sides. The main aim of this study was to identify the provenance of the groundwater discharged to the bay and

processes influencing its composition. This was done based on the chemical composition of SGD.

METHODS

The research was carried out in years 2016-2017. In order to identify SGD sites salinity was used as a groundwater tracer (Szymczycha et al. 2012). Three active areas of SGD off Hel Peninsula (Hel, Jurata, Chałupy), and three off continental part of the bay (Puck, Swarzewo and Osłonino) were identified based on salinity and chloride measurements (Figure 1). Water samples were collected along the salinity transition zone: groundwater from piezometers located in the coastal zone, groundwater and seepage water from the subterranean estuary (groundwater – seawater mixing zone) and seawater. From each point, 10 mL sample for ions content analysis (Mg^{2+} , Ca^{2+} , K^+ , Na^+) were collected and filtered using syringe filters (0.45 μm pore size) to the PTE vials, which were previously digested for 24 h in nitric acid. The sample for metals analysis were conserved with 3M HNO_3 . 180 ml of water were collected for HCO_3^- , SO_4^{2-} and Cl^- analysis. Samples for HCO_3^- were conserved with $HgCl_2$. Samples for SO_4^{2-} and Cl^- were kept in refrigerator till the time of the analysis. The major ions (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , HCO_3^-) content was analyzed in 198 samples. The measurements of Ca^{2+} , Mg^{2+} , Na^+ , K^+ were conducted by means of AAS (SHIMADZU 6800). Concentrations of HCO_3^- and Cl^- were determined by potentiometric titration using ion-selective electrodes (ISE) Cerko Lab System Potentiometry for precise titration. Chloride ions were titrated with silver nitrate (0.1 M $AgNO_3$) and the bicarbonate ions were titrated with 0.1 molar hydrochloric acid (0.1 M HCl). The titration equivalent was determined by the first derivative (Dojlido 1987, Gajkowska-Stefańska et al. 2007). SO_4^{2-} was quantified by the precipitation of a sparingly soluble $BaSO_4$ in an acidic medium (Szczepaniak 2011). In addition, in the samples were measured parameters: the ORP, pH and oxygen content, with a multiparametric meter. Separation of individual types of water was made based on Cl^- content (Bolałek 1992). The seepage samples with chloride ions content smaller than $1 gCl^- \cdot dm^{-3}$ were identified as groundwater samples.

RESULTS

The major ions ratios in all groundwater samples fluctuated in the range: from 0.11 to 0.94 for Ca^{2+}/Cl^- , from 0.08 to 1.23 for Mg^{2+}/Cl^- , from 2.23 to 93.50 for Na^+/Cl^- , from 0.03 to 0.66 for K^+/Cl^- , from 0.01 to 0.32 for SO_4^{2-}/Cl^- , from 0.07 to 0.39 for HCO_3^-/Cl^- , from 0.57 to 3.42 for Mg^{2+}/Ca^{2+} , while for seawater samples were in the range from 0.01 to 0.02 for Ca^{2+}/Cl^- , from 0.01 to 0.06 for Mg^{2+}/Cl^- , from 0.58 to 0.75 for Na^+/Cl^- , from 0.01 to 0.02 for K^+/Cl^- , from 2.98 to 4.79 for Mg^{2+}/Ca^{2+} . The ionic ratios in water samples from piezometers ranged from 0.04 to 1.97 for Ca^{2+}/Cl^- , from 0.01 to 0.32 for Mg^{2+}/Cl^- , from 1.11 to 88.68 for Na^+/Cl^- , from 0.01 to 0.44 for K^+/Cl^- , from 0.01 to 0.06 for SO_4^{2-}/Cl^- , from 0.01 to 1.16 for HCO_3^-/Cl^- and from 0.20 to 2.20 for Mg^{2+}/Ca^{2+} . Water samples collected in the groundwater wells were characterized by the range: from 0.45 to 5.67 for Ca^{2+}/Cl^- , from 0.09 to 0.62 for Mg^{2+}/Cl^- , from 0.78 to 0.85 for Na^+/Cl^- , from 0.08 to 0.34 for K^+/Cl^- , from 0.03 to 4.49 for SO_4^{2-}/Cl^- , from 2.90 to 20.23 for HCO_3^-/Cl^- and from 0.18 to 0.35 for Mg^{2+}/Ca^{2+} . The maximum ratios in groundwater samples collected in the subterranean estuary were observed in Chałupy region and equal to 0.79 for Ca^{2+}/Cl^- , 1.23 for Mg^{2+}/Cl^- , 25.17 for Na^+/Cl^- and 0.66 for K^+/Cl^- , respectively. Comparable results were detected also in Swarzewo. In case of water samples coming from piezometers, the maximum ratios were observed in Hel and equal to 0.72 for Ca^{2+}/Cl^- , 0.27 for Mg^{2+}/Cl^- , 34.87 for Na^+/Cl^- , 0.08 for K^+/Cl^- , 0.06 for SO_4^{2-}/Cl^- , 0.46 for HCO_3^-/Cl^- , while the lowest ratios were recorded in Jurata and equal to 0.04, 0.01, 0.01, 0.0048 and 0.01, respectively. The ratios for groundwater samples collected

in wells were highest in Swarzewo and equal to 5.67 for $\text{Ca}^{2+}/\text{Cl}^-$, 0.62 for $\text{Mg}^{2+}/\text{Cl}^-$, 0.85 for Na^+/Cl^- , 0.34 for K^+/Cl^- , 4.49 for $\text{SO}_4^{2-}/\text{Cl}^-$, 20.24 for $\text{HCO}_3^-/\text{Cl}^-$, except $\text{Mg}^{2+}/\text{Ca}^{2+}$ (0.35) that was identified in the Jurata.

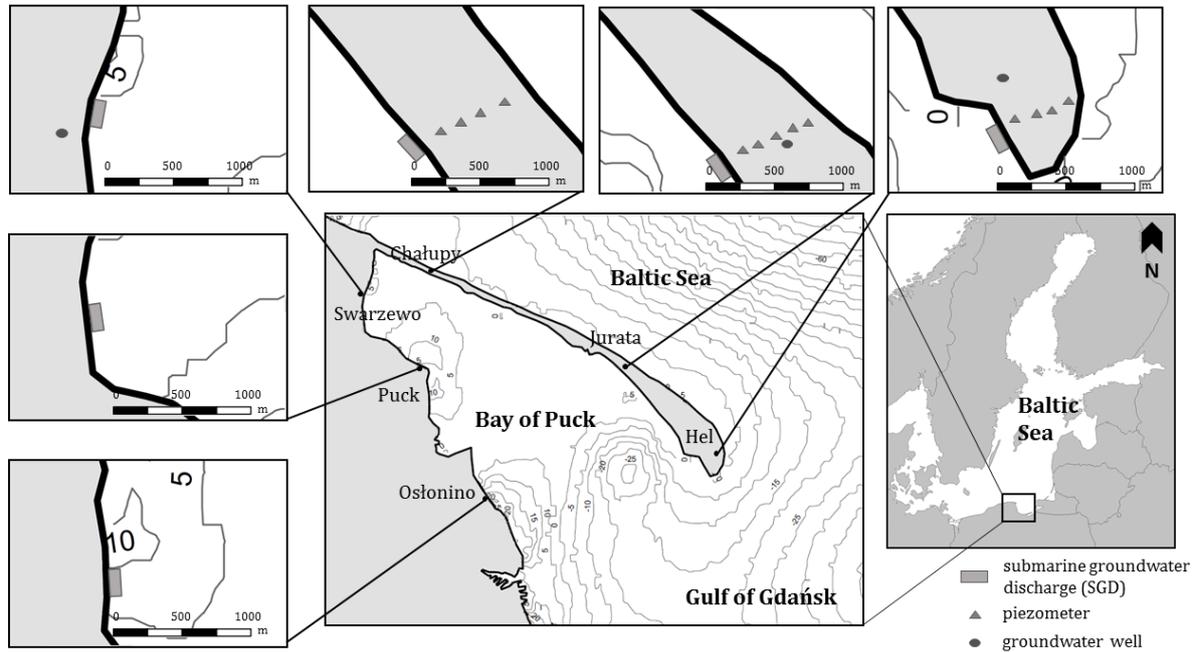


Figure 1. Map of the Bay of Puck showing the active areas of submarine groundwater discharge (SGD), locations of piezometers and groundwater well, along the Hel Peninsula (Hel, Jurata, Chalupy), and in the continental part of the bay (Puck, Swarzewo and Oslonino).

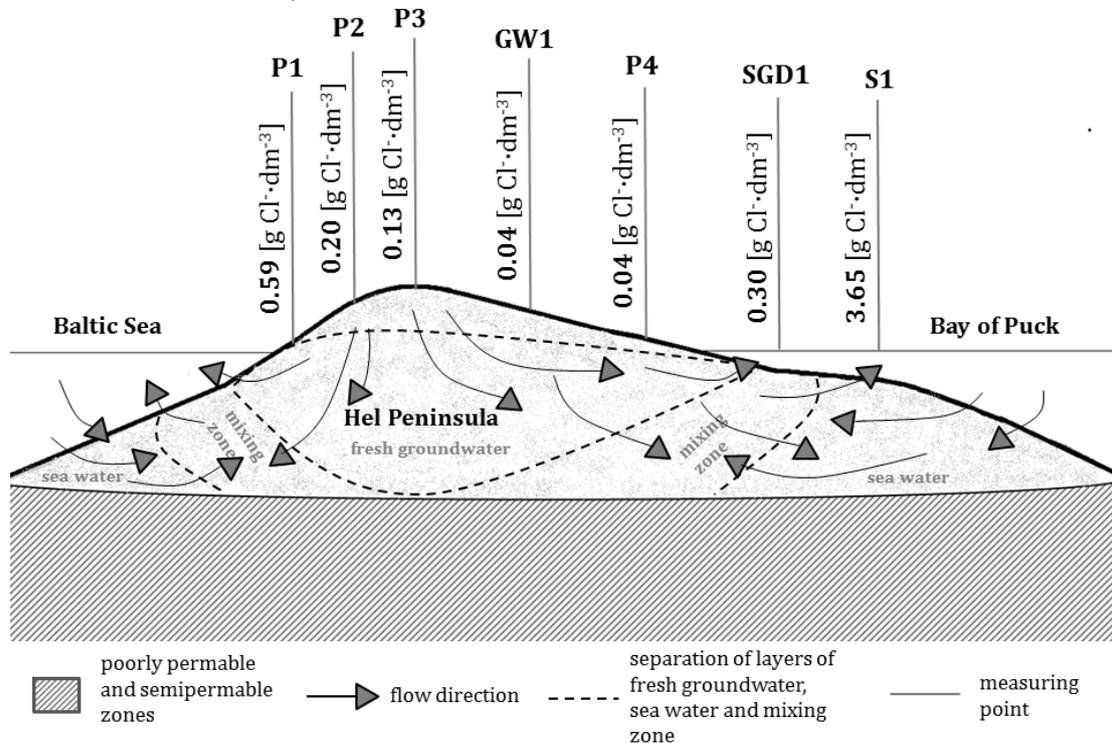


Figure 2. Schematic distribution of chloride concentration [gCl·dm⁻³] at submarine groundwater discharge (SGD), piezometers (P), groundwater well (GW) and sea water (S) in the Hel Peninsula, of Hel. Sampling points are marked schematically.

DISCUSSION AND CONCLUSIONS

The preliminary results indicate that SGD composition in Chałupy and Swarzewo are comparable. This suggests that groundwater discharged from both these sites located in the Inner Bay of Puck can have similar source. This hypothesis will be further verified by the analysis of the oxygen stable isotopes. For Hel and Jurata the ionic composition of the groundwater samples is mainly influenced by the land-sea interactions. Thus the increase of seawater level and atmospheric conditions such as storms will result in higher seawater intrusion (Sadurski, 1987). The vertical cross-section of groundwater composition located in Hel (Figure 2) is conditioned by the processes associated with the movement of seawater masses. This is observed at both sites of the peninsula. Osłonino and Swarzewo characterized with totally different ratios in comparison to other areas which can be explained by possible different source of groundwater relating to different land use and management. The results show that there is no clear separation between continental part and the peninsula in terms of groundwater composition. Further studies are necessary to understand the groundwater provenance and factors influencing SGD in the Bay of Puck.

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