

Significance of groundwater discharge along the coast of Poland as a source of dissolved metals to the southern Baltic Sea

Beata Szymczycha^{1,2,*}, Kevin D. Kroeger², Janusz Pempkowiak¹

¹Institute of Oceanology, Polish Academy of Sciences, Powstańców Warszawy 55, 81-712, Sopot, Poland

²USGS Coastal and Marine Science Center, 384 Woods Hole Road, 10 Woods Hole, MA 02543, USA

*corresponding author

Keywords

Submarine groundwater discharge (SGD), speciation, trace metal fluxes, geochemistry, Bay of Puck

Abstract

Fluxes of dissolved trace metals (Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn) via groundwater discharge along the southern Baltic Sea have been assessed for the first time. Dissolved metal concentrations in groundwater samples were less variable than in seawater and were generally one or two orders of magnitude higher: Cd (2.1-2.8 nmolL⁻¹), Co (8.70-8.76 nmolL⁻¹), Cr (18.1-18.5 nmolL⁻¹), Mn (2.4-2.8 μmolL⁻¹), Pb (1.2-1.5 nmolL⁻¹), Zn (33.1-34.0 nmolL⁻¹). Concentrations of Cu (0.5-0.8 nmolL⁻¹) and Ni (4.9-5.8 nmolL⁻¹) were, respectively, 32 and 4 times lower, than in seawater. Groundwater-derived trace metal fluxes constitute 93% for Cd, 80% for Co, 91% for Cr, 6% for Cu, 66% for Mn, 4% for Ni, 70% for Pb and 93% for Zn of the total freshwater trace metal flux to the Bay of Puck. Groundwater-seawater mixing, redox conditions and Mn-cycling are the main processes responsible for trace metal distribution in groundwater discharge sites.

1. Introduction

Submarine groundwater discharge (SGD) is an important pathway for material transport to the nearshore ocean (Moore, 1996; Burnett et al., 2003; Burnett et al., 2006; Swarzenski, 2007; Kim et al., 2005; Beck et al., 2010; Jeong et al., 2012), and there is a substantial knowledge of nutrient concentrations and fluxes via SGD to the marine environment (i.e. Moore, 1996; Liu et al., 2012; Luo et al., 2014). In some settings the nutrient flux via SGD is equal or greater than that from surface runoff (Kroeger et al. 2007). Thus, in many locations it is impossible to balance coastal nutrient budgets without accounting for groundwater discharge (e.g. Kim et al., 2011; Waska et al., 2011; McAllister et al., 2014). In addition to providing macronutrients to coastal waters, groundwater discharge can also be a source of dissolved metals (Swarzenski et al., 2007; Knee and Paytan, 2011). Jeong et al. (2012) determined concentrations of selected trace elements (Al, Mn, Fe, Co, Ni and Cu) in groundwater and calculated their fluxes via SGD. The budget calculation showed that SGD was responsible for unusually enhanced concentrations of some trace elements in the summer in coastal seawater of the volcanic island Jeju. Charette et al. (2005) found elevated concentrations of dissolved iron and reduced concentrations of manganese in groundwater in comparison to seawater. Upon mixing anoxic groundwater with oxic seawater, a large fraction of dissolved iron and manganese were oxidized and precipitated within the sediments. The subterranean estuary is a zone of substantial changes in redox conditions impacting iron and manganese distribution and therefore other metals whose cycling is linked (Charette and Sholkovitz, 2002). Recent research has suggested that micronutrients, including B, Co, Cu, Fe, and Mo, may increase algal or cyanobacterial growth when concentrations of macronutrients (i.e., nitrogen and phosphorus) are already high and the system is already characterized as eutrophic (Zhang, 2000; Downs et al., 2008). As eutrophic conditions in coastal waters are expected to become more prevalent in the future (Rabalais et al., 2009; Dalsgaard et al., 2013), the role of micronutrients, including those associated with coastal groundwater, will likely become more important.

The Baltic Sea (Figure 1) is one of the largest, semi-enclosed, brackish, non-tidal seas in the world. The Baltic Sea catchment area is three times larger than the sea itself, and thus its contamination by macro-nutrients and trace metals have attracted the attention of marine scientists (HELCOM, 1998; Pohl and Henings, 1999; Pemkowiak et al., 2000; Pohl et al., 2002). The increasing concentrations of heavy metals in the coastal environment signify a serious threat to human health, living resources and ecological systems. Mobile and soluble heavy metal species are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. Heavy metals that pose a potential risk to the Baltic Sea environment, such as Cd, Cu, Hg, Pb, and Zn, have been included in the international Baltic Sea Monitoring Program (BMP) (HELCOM, 1998) which concluded that the main metals loads entering the Baltic Sea region come from river discharge, municipalities run-off and industrial plants (HELCOM, 1998; Pohl et al., 2002). However, metals fluxes via groundwater discharge have not been investigated so far.

Therefore, the purpose of the study is twofold. First, to conduct the first analysis of dissolved trace metals concentrations in areas with significant groundwater discharge in the southern Baltic Sea, off Poland, and to examine the processes influencing the cycling of metals in that system; and second, to quantify the significance, relative to other sources, of metals fluxes via groundwater into the Bay of Puck and to the southern Baltic Sea.

2. Methods

2.1 Study area: Polish coastline

The sampling sites were situated along the coast of the southern Baltic Sea (Figure 1): in the Bay of Puck (P) and off the Polish coast at Międzyzdroje (M), Kołobrzeg (K), and Łeba (L). These study sites are the primary tourist resorts off Poland in the Baltic Sea. The population in the area is concentrated along the coast and peaks in the summer. Thus, contamination of coastal groundwater is a major concern.

The Bay of Puck

The main study area (9,200 m²) was located off the Hel Peninsula (Szymczycha et al., 2012). The narrow, sandy peninsula is mostly recent alluvial deposits and the littoral zone consists of Holocene sediments 10 to 100 m thick (Korzeniewski, 1993). The Bay of Puck is divided into two parts: the Outer Puck Bay with an average depth of 20.5 m, and a markedly shallower part, called the Puck Lagoon, with an average depth of 3.1 m. A passage is situated at each end of the Rybitwia Shallow: Głębinka Narrows at the southwestern end and Kuźnica Passage at the northeastern end. Water exchange between these two sections of Puck Bay mainly occurs through these passages, especially through Głębinka Narrows (Nowacki 1993). The basin is characterized by considerably larger depths and a depth gradient in the direction of the open part of the Gulf of Gdańsk, reaching the depth of 54 m near the tip of the Hel Peninsula (Cyberski and Szeffler, 1993). Bottom sediments in the Bay of Puck are very diverse; including sands of various particle size and organic matter-rich silts (Bolałek and Graca, 1996). Their distribution at the surface is distinctly related to their morphology. Average salinity in the Bay of Puck ranges from 7.00 to 7.65 (Nowacki, 1993). The surface water (0 – 4 m) in Outer Puck Bay is characterized by relatively low salinity, from about 6.4 to 7, and poor transparency. The Secchi disk depth ranged from 2 to 2.5 m. In deeper layers the salinity is higher and the water transparency is considerably greater (Nowacki, 1993). Maximal concentrations of Cl⁻ ions only infrequently exceed 5g dm⁻³, with average being 3.5 - 4.0 g dm⁻³ (Piekarek-Jankowska, 1996).

The geomorphology of the Bay of Puck is quite complex. The Quaternary sediment located in the Bay of Puck are ~25 m thick. The Cretaceous formations lie at 108 – 125m (Piekarek-Jankowska, 1994). 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, 1994). The aquifers formed in the Tertiary unit are composed of Oligocene and Miocene sandy sediment. The Hel Peninsula developed during the Pleistocene and Holocene epochs (Piekarek-Jankowska, 1994). 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 sediment erosion, transport, accumulation and sediments redeposition in the coastal zone (Piekarek-Jankowska, 1994).

Polish coastline: Międzyzdroje (M), Kołobrzeg (K) and Łeba (L).

The geological structure of the Polish coastal zone is directly influenced by lower order tectonic units: the Kujawy-Pomorze Anticlinorium and the Peribaltic Syncline, which divide the coast into eastern and western parts and have different lithological formations. Subsequent development and decay of the Pleistocene ice sheets influences sediment erosive processes. On the seashore, sand bars are formed as a result of seawater movement. Southeast of the coast lies a belt of lake lands with terrestrial moraines (elevation reaching 300 m). The coast of Wolin Island consists of alternating sections of cliffs and barrier ridges overtopped by dunes. The cliffs are mainly built up of Pleistocene deposits. The maximum height above mean sea level of the Polish cliffs is 115 m.

2.2 Sample collection

Pore water (n=550) and seawater (n=100) samples were collected in the following periods: summer and fall 2009 and winter and spring 2010 in the Bay of Puck; summer 2013 and 2014 in all study sites. In 2009 and 2010, samples of river water (n=24) were collected from rivers close to the mouth: the Reda (0.6 km from mouth), the Zagórska Struga (0.1 km from mouth), the Płutnica (0.2 km from mouth), and the Gizdepka (0.2 km from mouth).

Salinity was used as a groundwater tracer. Samples were collected by means of drive-point piezometers with internal Teflon tubing. A detailed survey focused on nearshore waters of the Bay of Puck was carried out in August 2009 to identify groundwater discharge sites (Szymczycha et al., 2012). Two detailed transects running perpendicular to the shoreline were sampled in other sites in July 2013 and June 2014.

Once groundwater discharge areas were found, groundwater piezometers (Beck et al., 2007a) were installed (Szymczycha et al., 2014). Additionally, during every study campaign, we collected pore water in a nearby area without fresh groundwater discharge. Groundwater samples were collected from the depths of 0, 4, 8, 12, 16, 24 and 30 cm below the sediment–water interface. All components of the groundwater piezometers in contact with water samples were made from Teflon. Special care was taken to prevent contamination of samples collected for analysis of dissolved metals. All components of the groundwater lances used for collecting samples were soaked in a 3M HNO₃ bath for one day. After acid treatment, samplers were rinsed 5 times with MilliQ water, including ports and tubing. The entire equipment was wrapped in several layers of heavy plastic sheeting for transport. The groundwater lances were installed in the sediment and then allowed to equilibrate for ~24 hours. After the equilibration period, the sample tubes were each attached to dedicated, acid-washed, all-PE 50 ml syringes with short sections of acid-cleaned Teflon tubing. Each syringe, in turn, was detached and connected to an acid-washed, 25 mm diameter, 0.45 micron pore size, polypropylene (PP) syringe filter. A total of 35 ml of water was collected from each depth below the sediment-water interface. The collected samples were analyzed for dissolved metals (Co, Cd, Ni, Mn, Pb, Zn, and Cr) and dissolved organic carbon (DOC). For metals analyses a total of 10 ml of water were passed through a 0.45 µm syringe-

driven membrane filter, transferred into pre-washed, PTE vials and acidified to pH 2 by concentrated supra pure nitric acid. Initially, bottles were washed, rinsed with MilliQ water and soaked in a bath, filled with supra pure 3M HNO₃, for one day and then were rinsed with MilliQ water. Water samples for DOC analysis were passed through 0.45 µm pre-combusted glass-fibre filters. A total of 10 ml of the filtrate was acidified with 150 µl of concentrated HCl to remove carbonates and to prevent mineralization of dissolved organic matter, then stored in the dark at 4 °C until analysis. Seawater and river samples were similarly prepared according to the above-mentioned procedure. Samples were stored at 4 °C until analysis.

Water samples for salinity, pH and oxidation-reduction potential (ORP) measurements were collected to pre-washed PTE bottles and analyzed with a multimeter (WTW Multi 3400i Multi-Parameter Field Meters) immediately after sample collection.

Direct groundwater fluxes were measured using the seepage meter and the end-member calculation method. The end-member method is a method of hydrographic separation for quantifying discharge and chemical flux due to fresh (terrestrial) groundwater and brackish groundwater from circulation of marine water through sediments. It is based on mass balance (Burnett et al., 2006):

$$V_S = V_G + V_{SW}$$

$$S_S V_S = S_G V_G + S_{SW} V_{SW}$$

where *S* and *V* are the salinity and volume, respectively, and subscripts *S*, *G*, *SW* represent collected sample, groundwater and seawater, respectively. From those two equations, knowing *S_S*, *S_G*, *S_{SW}*, *V_S*, we solve for the two unknown values *V_G*, *V_{SW}*. The required variables are experimentally measured using a seepage meter

Seepage meters consisted of a polyethylene (PE) chamber (surface: 0.785 m²) with one end open, while the other end had a sample port with PTE collector (Burnett et al., 2006; Szymczycha et al., 2012). Groundwater seeping through the sediment passed up into a PTE collector. The change of water volume in the collector over a measured time interval provided the water flux. Salinity of the collected samples varied in the range from 2-4 indicating that it was a mixture of terrestrial groundwater and marine groundwater. The groundwater fraction in the collected sample was calculated using the end-member mass balance described above (Burnett et al., 2006), and finally groundwater flux was calculated as ratio of the collected groundwater volume and the collector surface area multiplied by time. In the remainder of this manuscript, the term “groundwater” indicates terrestrial-source, fresh groundwater.

2.3 Analytical methods

Concentrations of dissolved metals (Cu, Co, Cd, Ni, Mn, Pb, Zn, and Cr) were measured by ICP-MS (Elan 9000, Perkin Elmer). Analysis of standard reference material (SLEW 3, ERM) and water samples spiked with standard solution (2.5 and 5 µg L⁻¹-final volume) served as a quality check. Average recoveries of metals were in the range 95-103% (depending on the metal), while the precision given as relative standard deviation (RSD, n=5) was smaller than 3.5 %. The obtained metals concentrations of the procedural blank samples never exceeded 5 % of concentrations measured in the actual samples.

DOC analyses were carried out by means of a ‘HiPerTOC’ analyzer (Thermo Electron Corp., The Netherlands), using the UV/persulphate oxidation method and non-dispersive infrared (NDIR) detection (Kuliński and Pempkowiak, 2008). DOC concentrations in the analyzed 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 seawater CRMs (supplied by the Hansell Laboratory, University of Miami); average recovery was equal to 96 ± 3

% . The precision, described as the Relative Standard Deviation (RSD) of triplicate analyses, was no larger than 3%.

3. Results

3.1 Salinity, ORP, pH and DOC concentrations.

Salinity of surface seawater in the study areas was in the range of 6.8 to 7.0- typical for coastal water of the southern Baltic Sea, off Poland. Bottom salinity in the groundwater-impacted areas (GI) was slightly less at 6.6 to 7.1. Pore water salinity ranged 0.2 to 7.2 in the groundwater impacted area (GI) and groundwater not-impacted area (GNI). Individual salinity profiles in the groundwater discharge impacted sites are presented at Figure 2a. Salinity versus depths dependences present curvatures in the pore water profiles indicating active flow of groundwater (Schlüter et al., 2004). Figure 2b presents profiles of salinity, ORP, pH and DOC averaged by depths. Thus the obtained profiles indicate the averaged change by depth while errors bars represent the differences in the course of time at different study sites. Figure 2b denotes the difference in salinity profiles in GI and GNI. In GI pore water salinity decreases with depth, while in GNI pore water is characterized by constant salinity over entire 30 cm depth below the water/sediment interface. Generally, the pore water salinity of surface sediment shows salinity similar to the bottom seawater (Schultz, 2006). In groundwater discharge areas, due to groundwater seepage, a mixing zone of groundwater and seawater is formed. The depth of the sediment pore water layer where the mixing zone occurs can vary and depends on several factors such as seepage intensity, the granulometric properties of sediments, water depth, sea bottom relief and wave action. In our study, depths of the mixing zones occurred in the range of 10 cm to 15 cm below sediment-water interface (Szymczycha et al., 2012). The pore water salinity was used to identify the origin of pore water. Therefore, samples collected in GI with salinity higher or equal to 6.8 were called seawater, samples with salinity in the range from 0.5 to 6.8 were called seepage water samples (a mixture of groundwater and seawater) while samples with salinity lower or equal to 0.5 were called groundwater samples.

Seawater samples had oxidation-reduction potential (ORP) higher than 50 mV while pore water ORPs in the study areas, in GI and GNI, were in the range from -300 mV to 200 mV. Vertical distribution of ORP decreased with sediment depths both in GI and GNI (Figure 2b). Generally, first 5 cm of sediment pore water was relatively oxidized (ORP > 0mV). Below this depth pore water ORP significantly declined down to -300mV in groundwater impacted areas. In groundwater not impacted areas pore water ORP was mostly positive and decreased with sediment depths to -50 mV.

The pH of seawater samples (Figure 2b) were around 8.0, while the pore water pH ranged 6.9 to 8.2. The pore water pH profiles showed differences between GI and GNI. In GNI the pore water pH profile was constant with depth. In groundwater impacted areas pH decreased with sediment depths down to 6.9.

DOC in seawater was about 4.6 mg C L⁻¹. The pore water DOC ranged from 4.6 mg C L⁻¹ to 6.8 mg C L⁻¹. DOC in GI increased with pore water depths to 7.2 mg C L⁻¹, while in the area without apparent impact of groundwater seepage DOC declined from 4.6 mg C L⁻¹ to 3.5 mg C L⁻¹.

3.2 Trace metals concentrations in groundwater, seepage water and seawater samples

The trace metals concentrations in the collected seawater, seepage water and groundwater samples are presented in Table 1. Average concentrations were calculated for all collected samples while standard deviations represent temporal and spatial variabilities. Concentrations of dissolved metals in seawater samples Cd (0.02-0.9 nmol L⁻¹), Co (0.4-2.16 nmol L⁻¹), Cr (1.2-3.4 nmol L

⁻¹), Cu (17.6-19.9 nmol L⁻¹) Mn (10.0-140.0 nmol L⁻¹), Ni (20.4-22.4 nmol L⁻¹), Pb (0.03-0.05 nmol L⁻¹) and Zn (1.0-3.0 nmol L⁻¹) differ in course of time and study sites. Generally, the highest dissolved metals seawater concentrations occurred in the Bay of Puck in summer season. This is likely due to limited seawater exchange between the Bay of Puck and the Baltic Sea, and summer time heightened pollution caused from a growing population of tourists and additional activities like recreational cruises. The site located in the Bay of Puck is in close proximity with a small harbor. During summer season the intense tourist's cruises are organized. Similar results for the Bay of Puck were obtained by Boszke et al. (2003) and Boszke (2005) who also indicated higher dissolved trace elements concentrations on comparison with smaller metals concentrations in seawater off the open coast of the southern Baltic Sea (this study; Pempkowiak et al., 2000).

Dissolved metals concentrations in groundwater samples Cd (2.1-2.8 nmol L⁻¹), Co (8.70-8.76 nmol L⁻¹), Cr (18.1-18.5 nmol L⁻¹), Cu (0.5-0.8 nmol L⁻¹), Mn (2.4-2.8 μmol L⁻¹), Ni (4.9-5.8 nmol L⁻¹), Pb (1.2-1.5 nmol L⁻¹) and Zn (33.1-34.0 nmol L⁻¹) were less variable in comparison to seawater samples. Generally, concentrations of dissolved metals in groundwater were one (Cd, Co, Pb and Zn) or two (Mn) orders of magnitude higher than in seawater. No significant seasonal and spatial changes in trace metals concentrations in groundwater were detected in groundwater samples. This is in contrast to results obtained in other subterranean estuaries where some seasonal changes for selected trace elements (Al, Mn, Fe, Co, Ni, Cu) have been reported (Beck et al., 2010; Jeong et al., 2012). However, similar order of magnitude for selected trace metals concentrations in other groundwater impacted sites were also indicated such as copper and nickel in West Neck Bay, USA (Beck et al., 2007b) and lead in Great South Bay, USA (Beck et al., 2010) suggests occurrence similar groundwater chemistry.

In Table 2 averaged trace metals concentrations in groundwater samples collected at southern Baltic (this study), Finnish coast (Peltonen, 2002), Lithuanian coast (Peltonen, 2002) and Swedish coast (Augustsson et al., 2009) are presented. Trace metals concentrations differ substantially between study areas. One reason for this can be different groundwater chemistry. Trace metals are reduced at different groundwater redox potential, which means that readily reduced species may occur in reduced form while others are still oxidized, and remain bound. Therefore their speciation between study sites will differ with respect to redox conditions. Another factor contributing to differences among sites in metals concentrations may be differences in DOC concentration. The positive correlation to DOC may indicate that the speciation of some metals is controlled by the formation of aqueous organo-metals complexes (Augustsson et al., 2009).

In seepage water samples trace metals concentrations were variable and usually spanned the range from the lowest to the highest concentrations characteristic of groundwater and seawater. Processes that influence dissolved metals concentrations in seepage water include dilution, redox-controlled solubility, adsorption onto Fe and Mn oxides or organic matter, release from oxides undergoing reductive dissolution, and desorption from sediments via ion-exchange reactions (Charette and Sholkovitz, 2006).

The trace metals concentrations in groundwater were comparable (Pb and Zn) or higher (Cd, Co, Cr, Mn) than those measured in samples collected in rivers entering the Bay of Puck (Table 3). Only concentrations of Cu and Ni were smaller in groundwater than in the investigated rivers. This indicates that groundwater can be an important source of trace metals to the Bay of Puck. The groundwater measured trace metals concentrations were two times lower than those observed in Vistula or Odra, the second (Sokolowski et al., 2001) and the fifth (Pohl et al., 2002) largest rivers discharging into the Baltic Sea. These rivers and their tributaries flow through some of the most industrialized (fertilizer plants, coal mines, steelworks, heat and power generating

plants) and urbanized regions of Poland, Germany and Belarus, and as a result they are highly contaminated (Pohl et al., 2002). Vistula and Odra discharge of trace metals have a significant influence of the total load and distribution of elements in the coastal waters of the Gulf of Gdańsk and the Pomeranian Bight of the Baltic Sea (Pempkowiak et al., 2000). Estimates of groundwater discharge to the Baltic Sea compared is around or above 1% of total run-off (Peltonen, 2002). However, locally, as in the Bay of Puck and other coastal areas, the contributions of chemical substances via groundwater are significant (Szymczycha et al., 2012; Szymczycha et al., 2014).

3.3 Trace metals pore water profiles in the Bay of Puck

The trace metal concentrations (Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn) in the sediment pore water for the GI (solid circles) and for the GNI (hollow circles) are presented as concentrations profiles (Figure 3). The results represent the metals profiles for the investigated study sites. The error bars represent the variation of the metals concentrations in the course of time. Generally, within all the sampling campaigns in the groundwater impacted areas two trends in trace metals pore water profiles can be distinguished such as concentration increase (Cd, Co, Cr, Mn and Zn) and concentration decrease with increasing depth in the sediment (Cu and Ni). The concentrations of most of the investigated metals (Cd, Co, Cr, Mn, Pb and Zn) increased with the sediment depths and were significantly higher than those in seawater (Table 1). The increase of concentration from the shallowest layer to the deepest layer were high and equal to 90% (Cd), 80% (Co), 85 % (Cr), 97 % (Mn), 95% (Pb) and 94 % (Zn). Concentrations of Cu decrease 6 times and concentration of Ni 2 times in comparison with the shallowest pore water layer.

In the groundwater not impacted area concentrations of dissolved metals were slightly higher than those in seawater (Table 1). The increase of concentrations were different for each dissolved element. The highest concentration increases were observed for Cd and Mn, equal to 93% and 88 %, respectively. The increase of concentration for other elements equal to 50% (Co), 58 % (Cr), 8% (Cu), 13% (Ni), 55% (Pb) and 67% (Zn).

Generally, the deepest pore water layer can be attributed to the pore water with the highest groundwater influence thus it can be assumed that groundwater is enriched in some investigated elements such as Cd, Cr, Cu, Mn, Pb, Zn and depleted in others such as Cu and Ni. During only one sampling campaign in the Bay of Puck, in November 2009, was wave action high enough that the seawater intrusion reached more than 30 cm in the sediment. Salinity at 30 cm was equal to 4.

Beck et al. (2010) observed similar concentration change of Pb for the SGD impacted site in Great South Bay, NY, at the end of Roe Avenue in the town of Patchogue, USA caused by enriched Pb concentrations in groundwater (Beck et al., 2009). Investigations on dissolved trace metals launched in Jamaica Bay, NY, USA indicated similar patterns for Zn and Co in the groundwater impacted site and provide evidence for trace metal input due to SGD (Beck et al., 2009).

The pore water profiles in groundwater impacted sites generally depend on the composition of seawater and groundwater, and therefore in each investigated environment the concentrations might be different (Knee and Paytan, 2011). Dissolved metal concentrations in aquifers can be as low as concentrations in the open ocean (Sañudo-Wilhelmy et al., 2002). Sometimes, due to the composition of the aquifer substrate, concentrations of metals in groundwater can be high. In West Bengal and Bangladesh, groundwater in the alluvial Ganges aquifer has natural levels of arsenic high enough to endanger the health of humans who drink it (Nickson et al., 1998). Concentrations of Ba are also often high in the subterranean estuaries because of this element's salinity-dependent desorption (Shaw et al., 1998). In some areas groundwater can become contaminated with trace metals. Usually, mean groundwater concentrations of Mn, V, Co, and Mo were 30, 10, 17, and 13

times, respectively, greater than in undeveloped areas immediately upslope. However, Zn, Cr, Cu, Cd, Pb, and Fe concentrations were not significantly different in developed areas. This was attributed to attenuation of these elements in the vadose zone, as other evidence indicated the presence of sewage, which contains all of them at high concentrations (Leung and Jiao, 2006). Elevated concentrations of Cu, Cr, Ni, Pb, Cd, and Zn in Sicilian springs were attributed to industrial activity (Povinec et al., 2006).

3.4 Groundwater discharges to the Bay of Puck

Salinity of water samples collected in three sites (S1, S2, and S3) located in the Bay of Puck were in the range from 3.2 to 6.3. In the course of each sampling campaign the measured values of seepage water fluxes were stable at each site. Variations of the obtained results did not exceed 5%. However, the differences in seepage water fluxes between the locations (S1, S2, and S3) during each sampling campaign were significant. In February 2010 the relative standard deviation (RSD) of the obtained average groundwater flux reached the value of 70% of the average. Moreover, the data indicate that fluxes in February 2010 and May 2010 were lower than fluxes measured in September 2009 and November 2009. The annual groundwater discharge was approximated at $12.1 \pm 10.3 \text{ L d}^{-1} \text{ m}^{-2}$. This, rather large, standard error for the annual average of the groundwater flux into the study area is caused by seasonal differences in groundwater discharge into the study area. The average groundwater discharge rates turned out to be well-correlated with the average monthly precipitation characteristic of the area (Cyberski and Szeffler, 1993). A close relation between groundwater discharge rates and precipitation was also reported in a study off the west coast of Ireland (Smith and Cave, 2012). Other studies indicate that groundwater discharge rates from shallow aquifers can also vary seasonally due to changes in precipitation (Cable et al, 1997; Capone and Slater, 1990). Thus, it can be assumed that groundwater discharge rate in the Bay of Puck depends strongly on precipitation.

The groundwater discharges calculated by means of the seepage meter method combined with the end-member method allow measuring seepage fluxes at the active seepage sites. It was established that the area of active seepage sites to the total surface area of the bay is equal to approximately 3% (Szymczycha and Pempkowiak, 2016). Thus literature groundwater discharge rate to the Bay was adopted.

Piekarek-Jankowska (1994) calculated the total groundwater discharge to the Bay of Puck. Briefly, Piekarek-Jankowska (1994) characterized hydrochemical changes in the aqueous environment of the near-bottom and pore water of the Bay of Puck, basing on oxygen and hydrogen stable isotopes- $\delta^{18}\text{O}$ and δD . She proved occurrence of submarine drainage of fresh groundwater through the Bay's floor and quantified yearly discharge at 0.03 km^3 . Thus to calculate trace metals fluxes via groundwater discharge to the Bay of Puck we used the flux calculated by Piekarek-Jankowska (1994).

4. Discussion

4.1 Dissolved metal fluxes via groundwater to the Bay of Puck and southern Baltic Sea

The accurate estimation of trace metals fluxes via groundwater discharge into the marine environment requires measurements of trace metals in the groundwater samples collected close to water-sediment interface. For conservative constituents, calculation of groundwater fluxes using hydrological balance flow estimates and concentrations determined at inland wells may provide an accurate representation of the total flux (Beck et al., 2007b) as their concentrations are independent of other factors than dilution. In case of the other measured metals, biogeochemical processes in the aquifer and in the seepage zone can profoundly alter the magnitude and chemical form of metals loads between time of export from the watershed and ultimate flux to sea.

In our study groundwater samples were collected at very close to water/sediment interface at 16-30 cm depth and the measured concentrations of trace metals in groundwater were stable in the course of time and space. Therefore, we assumed that the obtained concentrations are representative for groundwater discharging into the Bay of Puck and the southern Baltic Sea. Generally, trace metals elements were determined by multiplying the average concentrations of trace elements in the groundwater by the literature magnitude of groundwater flux.

The calculated groundwater flux to the Bay of Puck (Piekarek-Jankowska (1994 and 1996) allowed us to evaluate the role of groundwater discharge in the water balance of the entire Bay of Puck. The average yearly runoff of the studied rivers were derived from literature (Bełdowska et al., 2014) and the metals fluxes were calculated as the multiplication of average metals concentrations in rivers and annual runoff estimates from the literature. The loads of trace metals both delivered with river runoffs and via groundwater discharge to the Bay of Puck are presented in Table 4. The fluxes of metals via groundwater discharge were significantly higher than these delivered by river runoff. The groundwater-derived metals fluxes constitute to 70% for Pb, 93% for Cd, 80% for Co, 66% for Mn, 6 % for Cu, 4 % for Ni, 93% for Zn and 91% for Cr of the total annual sum of river and groundwater fluxes to the Bay of Puck.

Given the absence of previous groundwater discharge metals load estimates, we calculated the metals inputs to the entire southern Baltic Sea using groundwater discharge rates from the available publications (Kryza and Kryza, 2006; Peltonen, 2002) and groundwater metals concentrations measured during this study. Peltonen (2002) compiled the existing data regarding SGD to the Baltic Sea in the course of several workshops. He estimated the groundwater discharge for every country surrounding the Baltic Sea using a hydrogeological approach. Kryza and Kryza (2006) estimated groundwater discharge to the Baltic Sea from the territory of Poland based on the same hydrogeological approach. Four main aquifers (The Bay of Puck, and three regions located along the Polish coastline near Władysławowo, Łeba and Wolin) were assigned active status, indicating active seepage, and their parameters were characterized. Then, two numeric models for groundwater discharge to four representative areas were constructed. The results obtained by the two methods were comparable. Peltonen (2002) estimated the groundwater discharge to the southern Baltic Sea to be $1.4 \text{ km}^3 \text{ yr}^{-1}$, indicating that 40% of it comes from the coast of Poland while Kryza and Kryza (2006) estimated that the direct groundwater inflow to the Baltic Sea from the territory of Poland equals to $0.2 \text{ km}^3 \text{ yr}^{-1}$. The possible explanation of smaller groundwater discharge rate calculated by Kryza and Kryza (2006) as compared to the one made by Peltonen (2002) is that the former estimate assumed that groundwater discharges to the sea at the shoreline and not further seaward. The loads of metals via groundwater discharge to the southern Baltic Sea are presented in Table 5. Loads of dissolved metals are three (Mn) and two (Co, Cr, Zn) orders of magnitude higher than loads of dissolved Cd, Cu, Ni and Pb.

It is of interest how loads of metals delivered to the Baltic Sea with groundwater discharge compare to loads originating from other sources. For this purpose the groundwater discharge loads were approximated based on the available data on metal concentrations in several locations along the Baltic shoreline (Table 2). Based on averaged trace metals concentrations (Table 2) in shallow groundwater wells located at the coast of Lithuania, Finland and Sweden (Peltonen, 2002; Augustsson et al., 2009) and averaged trace metals groundwater concentrations obtained in the course of this study, total dissolved Cd, Cu and Pb fluxes via groundwater were calculated using rates from the literature for groundwater discharge to the entire Baltic Sea (Peltonen, 2002). The obtained results for Cd, Cu and Pb were compared with metals fluxes from other sources (Table 6). The calculations indicate that metals fluxes via groundwater discharge to the Baltic Sea surface

sediment equals to 0.4% Cd, 0.1% for Cu and 0.3% for Pb of the annual metals load going to the Baltic Sea via rivers, municipalities and industrial plants. However, it must be kept in mind that the calculated loads represent the order of magnitude of the groundwater metal loads and thus are to be approached with caution.

The approach applied here to calculate the groundwater-derived trace metal loads did not include the processes impacting the trace metals concentrations in the uppermost layer of sediments (0-15cm). It is assumed that groundwater advecting upwards delivers the comprised chemical substances to sea water overlying the sediments. Using the concentration of metals in the uppermost 0-1cm sediment pore water (seepage water) and the groundwater discharge flux would provide incorrect results. In this study total loads of metals delivered to seawater via groundwater discharge are presented independently of speciation and using the groundwater discharge rates. Therefore, we state that groundwater is a source of metals to the pore water in the surface sediment first, then to seawater and that the calculated trace metals loads delivered to the Bay of Puck, and further to the southern Baltic Sea represent upper bound load estimations.

Based on the obtained data (Table 4 and 5) we can assume that metals fluxes via groundwater discharge to the southern Baltic can be a significant source of metals only at the local scale e.g. in the Bay of Puck. Other studies indicated that groundwater discharge can be a potentially important pathway for metals to enter the coastal ocean and influence the chemical cycling in the coastal zones (Long Island, New York, USA; Montluçon and Sañudo-Wilhelmy, 2001). Calculated fluxes of Co via groundwater discharge into West Neck Bay (Long Island, New York, USA) ranged from $3.4 \times 10^2 \mu\text{mol day}^{-1}$ to $8.2 \times 10^3 \mu\text{mol day}^{-1}$, depending on sampling location and season. Other research has suggested that micronutrients, including B, Co, Cu, Fe, and Mo, can increase algal or cyanobacterial growth when concentrations of macronutrients (i.e., nitrogen and phosphorus) are already high and the system is already characterized as eutrophic (Zhang, 2000; Downs et al., 2008). As eutrophic conditions in coastal waters are expected to become more prevalent in the future (Rabalais et al., 2009), the role of metal micronutrients, including those associated with groundwater discharge, may become more important. In addition to supporting the growth of both desirable and undesirable primary producers, some metals can also be toxic to plants, animals, and humans.

4.2 Processes influencing trace metals distribution in groundwater discharge sites

In groundwater impacted sites, metals can occur in various forms. They may be dissolved in groundwater, suspended as colloids, or bound to particle surfaces and can form several chemical compounds depending on the groundwater chemistry and redox state. The form in which a metal occurs can affect its mobility, reactivity, and toxicity. Metals carried by groundwater seaward from inland aquifer areas through the groundwater/marine porewater mixing area (subterranean estuary), often undergo chemical transformations affecting the coastal waters metals concentrations. In order to test for non-conservative behavior within the subterranean estuary, we examined plots of the dissolved metal concentration versus salinity, as a conservative groundwater tracer. Relationships between concentrations of each dissolved metal versus salinity are presented in Figure 4. As the endmembers of the system mix a salinity gradient is formed. Both groundwater and seawater are characterized by different concentrations of studied metals (Table 1). Thus a gradient of a given metal concentration is created. The linear regression marked on each of the graphs (Figure 4) represents concentration changes upon diluting groundwater (0.2) and seawater (7.0) relative to conservative mixing (Beck et al., 2007).

Dissolved Co, Cd, Pb and Zn present decrease with increase of salinity. Some of the samples are located below (Pb and Zn) or above (Co and Cd) the line presenting the trace metals

concentrations due to conservative mixing. However, the concentration change is caused most likely by dilution. Dissolved Cr, Mn, Cu and Ni concentrations differ substantially from those expected in the course of conservative mixing and show non-conservative behavior upon mixing of the endmembers. Dissolved Cr shows lower concentrations than expected from conservative mixing of pore water. The chemistry of Cr is highly sensitive to changes in pH and redox conditions. At lower redox potentials, the reduced forms (Cr (III)) precipitate as insoluble oxides such as Cr (OH)₃ or Cr₂O₃. As would be expected from this redox dependence, the concentrations of Cr are lower than conservative mixing concentrations (Shultz, 2006). Dissolved Mn concentrations in the 0-6 salinity range displayed nearly linear dependence with increasing salinity. However, at salinity 6 there is a rapid drop of dissolved Mn concentrations, caused most likely by change of conditions from anaerobic to aerobic. Dissolved Cu and Ni rise with increase of salinity, although Cu shows lower and Ni higher concentrations than expected from conservative mixing.

Metals that do not exhibit conservative behavior upon groundwater and seawater mixing are likely influenced not only by dilution but also other processes such as redox-controlled solubility, adsorption onto Fe and Mn oxides or organic matter, release from oxides undergoing reductive dissolution, and desorption from sediments via ion-exchange reactions (Charette and Sholkovitz, 2006). The influence of some processes can be presented in Figure 5, 6 and 7. Changes in ORP clearly impact the speciation of the metals (Schultz, 2006). The dependences between the measured trace metals and ORP are presented in Figure 5. Some metals such as Cu and Ni become more soluble with increasing ORP, while the opposite trend is true for Pb, Cd, Co, Mn and Cr. These metals change into solid phase when the ORP increases. Thus, concentrations of dissolved Pb, Mn and Cr exhibit concentrations of zero or close to zero in oxidizing conditions. Usually, Co, Pb, and Zn are found to be more soluble at low ORP because this condition is less favorable for adsorption onto Fe and Mn oxides (Reddy and Patrick, 1977; Iu et al., 1982). Therefore, redox conditions play an important role in the cycling of elements in groundwater discharge zones.

Coprecipitation with manganese oxides upon entering the truly oxic layer is presented in Figure 6. Cycling of Cd, Cr, Cu, Ni, Pb strongly depends on Mn distribution in the groundwater impacted area along the southern Baltic Sea. Charette et al. (2005) indicated similar observations and suggested that the distribution of Mn within the GI-area provides strong evidence that there is a plume of Mn-rich groundwater moving to the study area (Waquit Bay) that affects metals mobility.

The dependences between measured trace metals and DOC are presented in Figure 7. The concentrations of dissolved Mn, Co, Cd, Cr, and Zn generally increased with increasing DOC while concentrations of Cu and Ni decreased with increasing DOC. The mineralization of organic matter (POC) can be responsible for releasing bound trace elements to dissolved phase. The dependences between metals and DOC are irregular, and can be caused by weakly-bound organic ligands or partitioning of metals between dissolved and colloidal phases (e.g. metals affinity for humic substances in the sediments) (Sañudo-Wilhelmy, 2002).

5. Conclusions

Groundwater discharge is an important source of Cd, Co, Cr, Mn and Zn for the southern Baltic Sea. Locally, as in the Bay of Puck, groundwater discharge can be a significant source of metals in comparison with rivers. The trace elements concentrations in the groundwater are one (Cd, Co, Cr, Pb and Zn) to two (Mn) orders of magnitude higher than in seawater. Cu and Ni concentrations were smaller in groundwater, similar to the pattern seen for Hg concentrations (Szymczycha et al., 2013). Dissolved Co, Cd, Pb and Zn decrease with increase of salinity. Some

of the samples are located below (Pb and Zn) or above (Co and Cd) the line representing conservative mixing. However, variations in concentration are primarily controlled by dilution. Dissolved Cr, Mn, Cu and Ni concentrations differ substantially from those expected in the course of conservative mixing and show non-conservative behavior upon the end-members mixing. Dissolved Cr concentrations were lower than expected from conservative mixing concentrations on increasing salinity of pore water. Redox conditions and co-precipitation with manganese oxides play an important role in the cycling of elements in groundwater discharge sites.

Metals contributed to the Baltic Sea coastal waters by sustained groundwater discharge can provide essential micronutrients but can also have toxic effects. As eutrophic conditions in coastal waters are expected to become more prevalent in the future (Rabalais et al., 2009, Dalsgaard et al., 2013), the role of metal micronutrients, including those associated with groundwater, may become more important. Thus, more accurate groundwater discharge estimation to the Baltic Sea including the non-conservative transport of some trace elements into the sea are critical in order to establish the most reliable chemical budgets for the coastal zones and the entire Baltic Sea.

Acknowledgements

The study reports the results obtained within the framework of the following projects: the statutory activities of the Institute of Oceanology Polish Academy of Sciences theme 2.2, research project No. 2012/05/N/ST10/02761 sponsored by the National Science Centre, and AMBER, the BONUS+ EU FP6 Project. We would like to thank Polish-U.S. Fulbright Commission for funding Szymczycha B. post-doctoral studies at USGS. Use of tradenames does not indicate endorsement by the U.S. government.

Literature:

- Augustsson A, Bergbäck B, Åström M, 2009. Trace metals in recharge and discharge ground waters at two sites at the Baltic coast of Sweden *Applied Geochemistry* 24, 1640–1652.
- Beck, M., Dellwig, O., Kolditz, K., Freund, H., Liebezeit, G., Schnetger, B., Brumsack, H.J., 2007a. In situ pore water sampling in deep intertidal flat sediments. *Limnology and Oceanography*, 5: 136-144.
- Beck A.J., Rapaglia JP, Cochran J.K., Bokuniewicz H.J., 2007b. Radium mass-balance in Jamaica Bay, NY: Evidence for substantial flux of submarine groundwater. *Marine Chemistry* 106, 419-441.
- Beck A.J, Cochran J.K, Sañudo-Wilhelmy S.A., 2009. Temporal trends of dissolved trace elements in Jamaica Bay, NY: importance of wastewater input and submarine groundwater discharge in an urban estuary. *Estuaries and Coasts* 32, 535-550.
- Beck, A.J., Cochran, K.J., Sañudo-Wilhelmy, S.A., 2010. The distribution and speciation of dissolved trace metals in a shallow subterranean estuary. *Marine Chemistry* 121, 145-156.
- Bełdowska, M., Saniewska, D., Falkowska, L., 2014. Factors influencing variability of mercury input to the southern Baltic Sea. *Marine Pollution Bulletin* 86, 283-290.
- Bolalek, J., Graca, B., 1996. Ammonia nitrogen at the water-sediment interface in the Puck Bay (Baltic Sea), *Estuarine, Coastal and Shelf Science*, 43, 776-779.
- Boszke, L., Siepak, J., Falandysz, J., 2003. Total Mercury contamination of selected organisms in Puck Bay, Baltic Sea, Poland. *Polish Journal of Environmental Studies*, 12:275-285
- Boszke, L., 2005. Fluxes and balance of mercury in the inner Bay of Puck, southern Baltic, Poland: an overview. *Oceanology*, 47: 325–350
- Burdige, D. J., 1993. The biogeochemistry of manganese and iron reduction in marine sediments. *Earth Science Review*. 35, 249–284.

- Burnett, W.C., Bokuniewicz, H.J., Huettel, M., Moore, W.S., Taniguchi, M., 2003. Groundwater and pore water inputs to the coastal zone. *Biogeochemistry* 66, 3–33.
- Burnett, W.C., Aggarwal, P.K., Aureli, A., Bokuniewicz, H.J., Cable, J.E., Charette, M.A., Kontar, E., Krupa, S., Kulkarni, K.M., Loveless, A., Moore, W.S., Oberdorfer, J.A., Oliveira, J., Ozyurt, N., Povinec, P., Privitera, A.M.G., Rajar, R., Ramessur, R.T., Scholten, J., Stieglitz, T., Taniguchi, M., Turner, J.V., 2006. Quantifying submarine groundwater discharge in the coastal zone via multiple methods. *Science of the Total Environment* 367, 498-543.
- Charette, M.A., Sholkovitz, E.R., 2002. Oxidative precipitation of groundwater derived ferrous iron in the subterranean estuary of a coastal bay. *Geophysical Research Letters* 29 (10). doi:10.1029/2001GL014512.
- Charette, M.A., Sholkovitz, E.R., Hansel, C.M., 2005. Trace element cycling in a subterranean estuary Part 1. Geochemistry of the permeable sediments. *Geochimica et Cosmochimica Acta* 66, 2095-2109.
- Charette, M.A., Sholkovitz, E.R., 2006. Trace element cycling in a subterranean estuary: Part 2. Geochemistry of the pore water. *Geochimica et Cosmochimica Acta* 70 (4), 811–826.
- Cyberski J, Szeffler K, 1993. *Klimat Zatoki i jej zlewiska: Zatoka Pucka*. Edited by Korzeniewski K. Fundacja Rozwoju Uniwersytetu Gdańskiego, Gdańsk, Poland, 14-39.
- Dalgaard T, De Brander L, Hall POJ, 2013. Denitrification in the water column of the central Baltic Sea, *Geochim. Cosmochim. Acta*, 106, 247-260.
- Downs, T.M., Schallenberg, M., Burns, C.W., 2008. Responses of lake phytoplankton to micronutrient enrichment: a study in two New Zealand lakes and an analysis of published data. *Aquatic Sciences – Research across Boundaries* 70, 347–360.
- Emelyanov, E.M., 2014. Biogenic components of the Baltic Sea Sediments. *Russian Geology and Geophysics* 55, 1404-1417.
- Guéguen, C., Gilbin, R., Pardos, M., Dominik, J., 2004. Water toxicity and metal contamination assessment of a polluted river: the Upper Vistula River (Poland). *Applied Geochemistry* 19, 153-162.
- HELCOM, 1998. HELCOM Scientific Workshop: The Effects of 1997 Flood of the Odra and Vistula Rivers. 13. Berlin. ISSN 0946-6010.
- Jeong, J., Kim, G., Han, S., 2012. Influence of trace element fluxes from submarine groundwater discharge (SGD) on their inventories in coastal waters off volcanic island, Jeju, Korea. *Applied Geochemistry* 27, 37-43.
- Kim, G., Ryu, J., Yang, H., Yun, S., 2005. Submarine groundwater discharge (SGD) into the Yellow Sea revealed by Ra and Ra isotopes: implications for global silicate fluxes. *Earth Planet. Science Letters* 237, 156–166.
- Kim, G., Kim, J.S., Hwang, D.W., 2011. Submarine groundwater discharge from oceanic islands standing in oligotrophic oceans: implications for global biological production and organic carbon fluxes. *Limnology and Oceanography* 56, 673– 682.
- Knee, K.I, Paytan ,A., 2011. Submarine Groundwater Discharge: A Source of Nutrients, Metal and Pollutants to the Coastal Ocean. In Wolanski E and McLucky DS (eds) *Treatise on Estuarine and Coastal Science*, 4, 205-233pp. Waltham:Academic Press.
- Kotwicki, L., Grzelak, K., Czub, M., Dellwig, O., Gentz, T., Szymczycha, B., Brotcher, M., 2014. Submarine groundwater discharge to the Baltic coastal zone – impact on the meiofaunal community, *Journal of Marine Systems*, 129, 118-126.
- Korzeniewski, K., 1993. *Zatoka Pucka*. Gdynia: Instytut Oceanografii Uniwersytetu Gdańskiego.

- Kroeger, K.D., Swarzenski, P.W., Greenwood, W.J., Reich, C., 2007. Submarine groundwater discharge to Tampa Bay: Nutrient fluxes and biogeochemistry of coastal aquifer. *Marine Chemistry* 104, 85-97.
- Kryza, J., Kryza, H., 2006. The analytic and model estimation of the direct groundwater flow to Baltic Sea on the territory of Poland. *Geologos* 10, 154-165.
- Kuliński, K., Pempkowiak, J. 2008. Dissolved organic carbon in the southern Baltic Sea: quantification of factors affecting its distribution, *Estuarine Coastal and Shelf Science*, 78, 38–44, 2008.
- Leung, C.M., Jiao, J.J., 2006. Heavy metal and trace element distributions in groundwater in natural slopes and highly urbanized spaces in Mid-Levels area, Hong Kong. *Water Research* 40, 753–767.
- Liu, Q., Dai, M., Chen, W., Huh, C. A., Wang, G., Li, Q., and Charette, M.A., 2012. How significant is submarine groundwater discharge and its associated dissolved inorganic carbon in a river-dominated shelf system?, *Biogeosciences* 9, 1777-1795.
- Luo, X., Jiao, J.J., Moore, W.S., Lee, C.M., 2014. Submarine groundwater discharge estimation in an urbanized embayment in Hong Kong via short-lived radium isotopes and its implication of nutrient loadings and primary production. *Marine Pollution Bulletin* 82, 144-154.
- Mateciak, M., Bielenik, S., Botur, A., Podgorski, M., Trzcinska, K., Daganska, K., Jasniewicz, D., Kurszewska, A., Wentka, M., 2015. Observations of presumable groundwater seepage occurrence in Puck Bay (the Baltic Sea). *Oceanological and Hydrobiological Studies* 44, 139-281.
- McAllister, S.M., Barnett, J.M., Heiss, J.W., Findlay, A.J., MacDonald, D.J., Dow, C.J. Luther III, G.W., Michael, H.A., Chan, C.S, 2014. Dynamic hydrologic and biogeochemical processes drive microbially enhanced iron and sulfur cycling within the intertidal mixing zone of a beach aquifer. *Limnology and Oceanography* 60, 329-345.
- Miao, A.J., Wang, W.X., 2006. Cadmium toxicity to two marine phytoplankton under different nutrient conditions. *Aquatic Toxicology* 78, 114–126.
- Moore, W.S., 1996. Large groundwater inputs to coastal waters revealed by ²²⁶Ra enrichments. *Nature* 380, 612–614.
- Montluçon, D., Sañudo-Wilhelmy, S.A., 2001. Influence of groundwater seepage on nutrient and metal concentrations in a coastal environment: Flanders Bay, Long Island, NY. *Environmental Science and Technology* 35, 480–486.
- Nickson, R., McArthur, J., Burgess, W., Ahmed, K.M., Ravenscroft, P., Rahman, M., 1998. Arsenic poisoning of Bangladesh groundwater. *Nature* 395, 338.
- Nowacki, J., 1993. Termika, zasolenie i gęstość wody, In: *Zatoka Pucka*. Edited by Korzeniewski K., 1993. Fundacja Rozwoju Uniwersytetu Gdańskiego, Gdańsk, Poland, 79-112.
- Peltonen, K., 2002. Direct Groundwater Flow to the Baltic Sea, Nordic Council of Ministers, Temanord, Copenhagen, 78pp.
- Pempkowiak J, Chiffolleau J-F, Staniszewski A, 2000. The Vertical and Horizontal Distribution of Selected Trace Metals in the Baltic Sea off Poland. *Estuarine, Coastal and Shelf Science* 51, 115-125.
- Piekarek- Jankowska H, 1996. Hydrochemical effects of submarine groundwater discharge to the Puck Bay (Southern Baltic Sea, Poland). *Geographia Polonica* 67, 103-119.
- Piekarek-Jankowska, H., 1994. *Zatoka Pucka jako obszar drenażu wód podziemnych*. Wydawnictwo Uniwersytetu Gdańskiego. Gdańsk, Poland.

- Pohl, C., Hennings U., 1999. The effect of redox processes on the partitioning of Cd, Pb, Cu and Mn between dissolved and particulate phases in the Baltic Sea. *Marine Chemistry* 65, 41-53.
- Pohl, C., Hennings, U., Siegel, H., Bachor, A., 2002. Trace metal impact into the Baltic Sea during the exceptional Oder flood in summer 1997. *Marine Chemistry* 79, 101-11.
- Povinec, P.P., Aggarwal, P.K., Aureli, A., Burnett, W.C., Kontar, E.A., Kulkarni, K.M., Moore, W.S., Rajar, R., Taniguchi, M., Comanducci, J.F., 2006. Characterisation of submarine groundwater discharge offshore south-eastern Sicily. *Journal of Environmental Radioactivity* 89, 81–101.
- Rabalais, N.N., Turner, R.E., Diaz, R.J., Justic, D., 2009. Global change and eutrophication of coastal waters. *ICES Journal of Marine Science* 66, 1528–1537.
- Rosko, J.J., Rachlin, J.W., 1975. The effect of copper, zinc, cobalt and manganese on the growth of the marine diatom *Nitzschia closterium*. *Bulletin of the Torrey Botanical Club* 102, 100–106.
- Rybicka, E.H., Adamiec, E., Aleksander-Kwaterczak U., 2005. Distribution of trace metals In the Odra River system: Water-suspended matter-sediments. *Limnologia* 35, 185-198.
- Sañudo-Wilhelmy, S.A., Rossi, F.K., Bokuniewicz, H., Paulsen, R.J., 2002. Trace metal levels in uncontaminated groundwater of a coastal watershed: importance of colloidal forms. *Environmental Science and Technology* 36, 1435-1441.
- Shaw, T.J., Moore, W.S., Klopfer, J., Sochaski, M.A., 1998. The flux of barium to the coastal waters of the southeastern USA: the importance of submarine groundwater discharge. *Geochimica et Cosmochimica Acta* 62, 3047–3054.
- Schlüter M., Sauter E.J., Andersen C.A., Dahlgaard H, Dando P.R., 2004. Spatial distribution and budget for submarine groundwater discharge in Eckernförde Bay (Western Baltic Sea). *Limnology and Oceanography* 49, 157-167.
- Schultz, H.D., 2006. Quantification of Early Diagenesis: Dissolved Constituents in Marine Pore Water, in: Schulz, H. D., and Zabel, M. eds.: *Marine Geochemistry*, Springer-Verlag, Berlin, Heidelberg.
- Sokolowski, A., Wolowicz, M., Hummel, H., 2001. Distribution of dissolved and labile particulate trace metals in the Vistula overlying bottom water in the Vistula river plume (Southern Baltic Sea). *Marine Pollution Bulletin* 42, 967-980.
- Swarzenski, P.W., 2007. U/Th series radionuclides as tracers of coastal groundwater. *Chemical Reviews* 107, 663-674, DOI: 10.1021/cr0503761.
- Swarzenski, P.W., Simonds, F.W., Paulson, T., Kruse, S., Reich, C.D., 2007. A Geochemical and Geophysical Examination of Submarine Groundwater Discharge and Associated Nutrient Loading Estimates into Lynch Cove, Hood Canal, WA. *Environmental Science and Technology* 41, 7022-7029.
- Szymczycha, B., Vogler, S., Pempkowiak, J. 2012 Nutrients fluxes via Submarine Groundwater Discharge to the Bay of Puck, Southern Baltic. *Science of the Total Environment*, 438: 86–93.
- Szymczycha, B., Miotk, M., Pempkowiak, J., 2013. Submarine Groundwater Discharge as a source of mercury in the Bay of Puck. *Water, Soil and Air Pollution* 224, DOI 10.1007/s11270-013-1542-0.
- Szymczycha, B., Maciejewska, A., Winogradow, A., Pempkowiak, J., Could submarine groundwater discharge be a significant carbon source to the southern Baltic Sea? *Oceanologia*, 2014, 56 (2), 327–347.

- Szymczycha, B; Pempkowiak J., 2016. The Role of Submarine groundwater Discharge as a material Source to the Baltic Sea, Springer, GeoPlanet: Earth and Planetary Sciences, ISSN: 2190-5193.
- Waska H, Kim G, 2011. Submarine groundwater discharge (SGD) as a main nutrient source for benthic and water-column primary production in a large intertidal environment of the Yellow Sea. *Journal of Sea Research* 65, 103-113.
- Zhang, J., 2000. Evidence of trace metal limited photosynthesis in eutrophic estuarine and coastal waters. *Limnology and Oceanography* 45, 1871–1878.

List of Tables:

Table 1. Average trace metals concentrations in seawater samples collected at the study areas (the Bay of Puck, Łeba, Kołobrzeg, Międzyzdroje) and in the groundwater discharged to the southern Baltic Sea.

Metal	Concentrations					
	Seawater Average±SD		Seepage water Average±SD		Groundwater Average±SD	
	nmol* L ⁻¹	µg* L ⁻¹	nmol* L ⁻¹	µg* L ⁻¹	nmol* L ⁻¹	µg* L ⁻¹
Pb	0.04±0.01	0.009±0.002	0.4±0.3	0.1±0.1	1.2±0.4	0.2±0.1
Cd	0.2±0.2	0.03±0.02	1.1±0.8	0.3±0.1	2.5±0.4	0.30±0.04
Co	1.3±0.5	0.07±0.03	4.2±2.4	0.3±0.1	8.70±0.02	0.50±0.01
Mn	(0.05±0.05)*10 ³	3.0±2.6	(1.2±0.9)*10 ³	68±51	(2.7±0.2)*10 ³	146±11
Cu	19.4±2.8	1.2±0.2	10.1±7.1	0.6±0.5	0.6±0.1	0.04±0.01
Ni	21.5±1.5	1.3±0.1	17.5±4.7	1.0±0.3	5.3±0.5	0.3±0.03
Zn	1.7±0.7	0.1±0.05	12.5±11.4	0.8±0.6	33.6±0.3	2.2±0.02
Cr	2.1±1.7	0.1±0.1	6.3±4.8	0.3±0.3	18.3±0.2	1.0±0.01

Table 2. Trace metals concentrations in shallow groundwater collected at Polish coastline: the Bay of Puck, Łeba, Kołobrzeg, Międzyzdroje (this study), Finland and Lithuania (Peltonen, 2002) and Sweden (Augustsson et al., 2009).

Metal	Groundwater µg* L ⁻¹					
	Polish coast	Sweden Forsmack	Sweden Simpevarp	Finland	Lithuania	Average±SD
Pb	0.2	0.09	1.3	2	1.1	0.9±0.8
Cd	0.3	0.006	0.02	0.2	0.2	0.1±0.1
Co	0.5	-	-	-	1.0	0.8±0.4
Mn	146.0	-	-	64.7	127.0	112.6±42.5
Cu	0.04	0.5	3.2	4.3	1.4	1.9±1.8
Ni	0.3	0.8	2.8	3.5	1.6	1.8±1.3
Zn	2.2	0.9	7.9	16.4	9.5	7.4±6.2
Cr	1	0.2	2.1	-	1.1	1.1±0.8

Table 3. Trace metals concentrations in: surface sandy sediments located along the polish coastline and several rivers: Odra, Vistula, Gizdepka, Plutnica, Zagórska Struga and Reda.

Metal	Concentrations						
	Surface sandy sediments mg* kg ⁻¹	Odra µg* L ⁻¹	Vistula µg* L ⁻¹	Gizdepka µg* L ⁻¹	Plutnica µg* L ⁻¹	Zagórska Struga µg* L ⁻¹	Reda µg* L ⁻¹
Pb	1.3 ^a	up to 10.9 ^c	nd.	0.10±0.01	0.11±0.02	0.2±0.01	0.08±0.01
Cd	0.016 ^a	0.001-1.09 ^c	0.51-0.73 ^d	0.01±0.01	0.02±0.01	0.05±0.01	0.01±0.01
Co	2.0 ^a	nd.	0.25-3.03 ^d	0.16±0.02	0.17±0.02	0.16±0.01	0.12±0.01
Mn	40 ^a	0.82-334 ^c	5.4-603.5 ^d	0.16±0.01	262.5±0.5	52.18±0.02	34.6±0.2
Cu	1.4 ^a	0.10-23.5 ^c	0.9-90.0 ^d	0.6±0.02	0.16±0.01	1.58±0.02	0.81±0.01
Ni	3.2 ^a	0.067-27.2 ^c	nd.	0.09±0.01	13.9±0.1	14.94±0.05	11.82±0.01
Zn	3.9 ^a	1.26-202 ^c	nd.	1.27±0.02	1.4±0.1	3.28±0.03	1.53±0.05
Cr	3.7 ^a	up to 37.1 ^c	0.98-13.18 ^d	0.08±0.01	0.04±0.01	0.18±0.01	0.11±0.01

^aEmelyanov, 2014.

^bSokolowski et al., 2001

^cRybicka et al. 2005

^dGuéguen et al., 2003

Table 4. Loads of trace metals delivered to the Bay of Puck with river run-off and groundwater discharge.

Metal	Metals fluxes to the Bay of Puck kg*yr ⁻¹					
	Gizdepka	Plutnica	Zagórska Struga	Reda	Total river flux	Groundwater discharge
Pb	0.6	0.7	1.3	0.5	3.1	7.3±0.4
Cd	0.1	0.1	0.3	0.1	0.6	8.5±0.1
Co	1.0	1.1	1.0	0.8	3.9	15.4±0.1
Mn	1.0	1656.0	329.1	218.8	2204.9	4381.3±94.8
Cu	3.8	1.0	10.0	5.1	19.9	1.2±0.3
Ni	0.6	87.9	94.2	74.6	257.3	9.4±0.9
Zn	8.0	9.2	20.7	9.7	47.6	655.9±0.5
Cr	0.5	0.3	1.1	0.7	2.6	28.7±0.4

Table 5. Trace metals fluxes via groundwater discharge to the southern Baltic Sea.

Metal	Metals fluxes via groundwater discharge to the southern Baltic Sea			
	Based on groundwater discharge calculated by Kryza and Kryza, 2006		Based on groundwater discharge calculated by Peltonen, 2002	
	Average±SD mol*yr ⁻¹	Average±SD kg*yr ⁻¹	Average±SD mol*yr ⁻¹	Average±SD kg*yr ⁻¹
Pb	235±13	50±3	704±40	146±8
Cd	504±1	56.7±0.1	1512±2	170±0.2
Co	1746±4	102.9±0.3	5239±13	309±1
Mn	531,668±11501	29,209±632	1,595,004±34,504	8,7626±1896
Cu	121±27	8±2	363±81	23±5
Ni	1070±100	63±6	3210±300	188±18
Zn	6718±52	440±4	20154±155	1318±10
Cr	3675±45	190±2	11,025±135	573±7

Table 6. Total trace metal loads entering the Baltic Sea with river run-off, domestic and industrial wastewater in 1995. Modified after Pohl et al., 2002.

Metal	Metals fluxes via different sources to the Baltic Sea							
	Rivers		Municipalities		Industries		Total	
	kmol*yr ⁻¹	t*yr ⁻¹	kmol*yr ⁻¹	t*yr ⁻¹	kmol*yr ⁻¹	t*yr ⁻¹	kmol*yr ⁻¹	t*yr ⁻¹
Pb	1452	300.5	159	32.9	19.1	4.0	1628	337.4
Cd	146	16.4	58.6	6.6	5.4	0.6	210	23.6
Cu	23,122	1469	1194	75.9	781	49.6	25,098	1595
Hg	57.7	11.6	5.7	1.1	3.0	0.6	66.5	13.3

Figures captions:

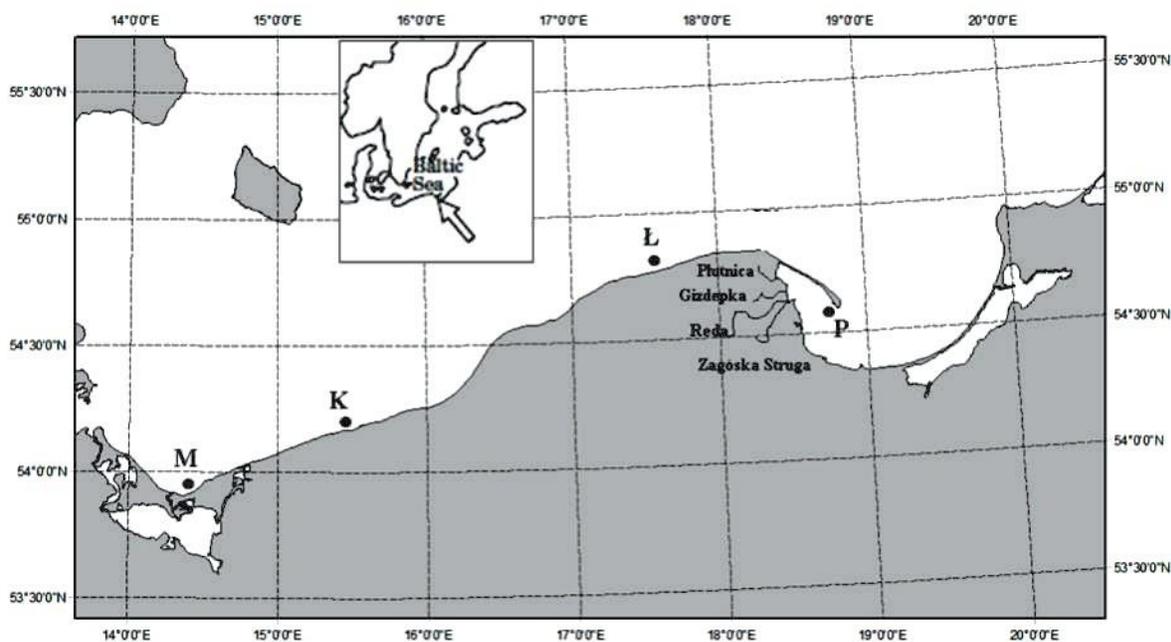


Figure 1. A map of the Baltic Sea showing the location of the study areas: the Bay of Puck (P), Międzyzdroje (M), Kołobrzeg (K) and Łeba (L) and sampled rivers: Reda, Zagórska Struga, Płutnica and Gizdepka.

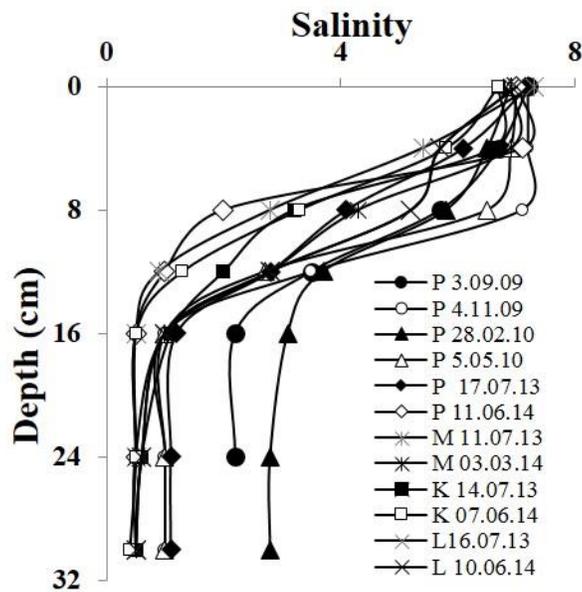


Figure 2a. Examples of pore water profiles of salinity. Samples were collected at the groundwater discharge impacted sites in the Bay of Puck (P) and off the Polish coast at Międzyzdroje (M), Kołobrzeg (K) and Łeba (L).

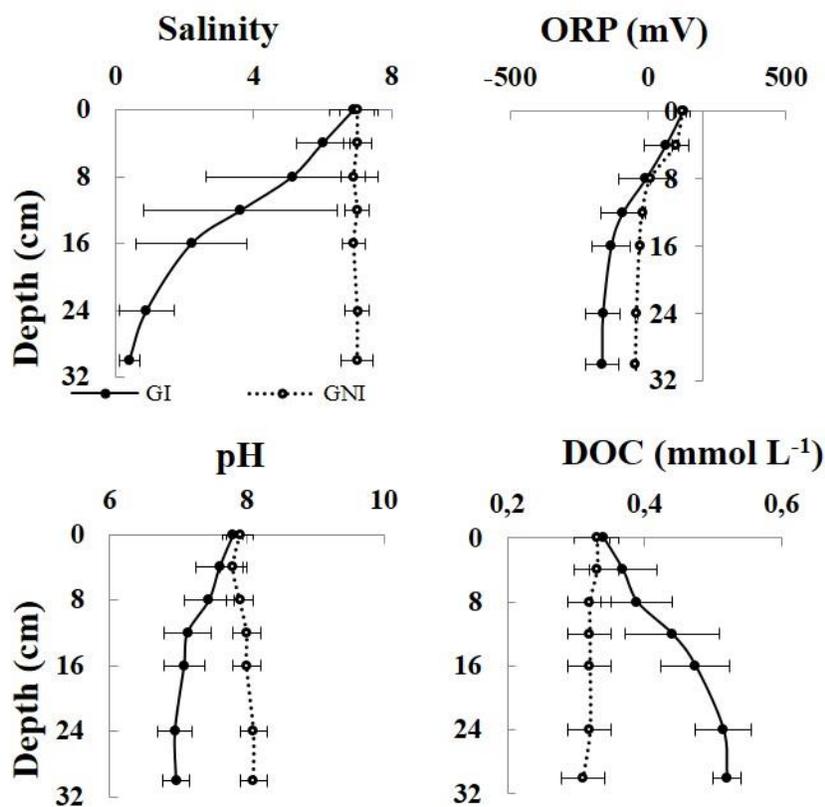


Figure 2b. The average salinity, DOC, pH and ORP profiles in the sediments pore water obtained of groundwater impacted (GI)- solid circles and groundwater not-impacted (GNI)- hollow symbols.

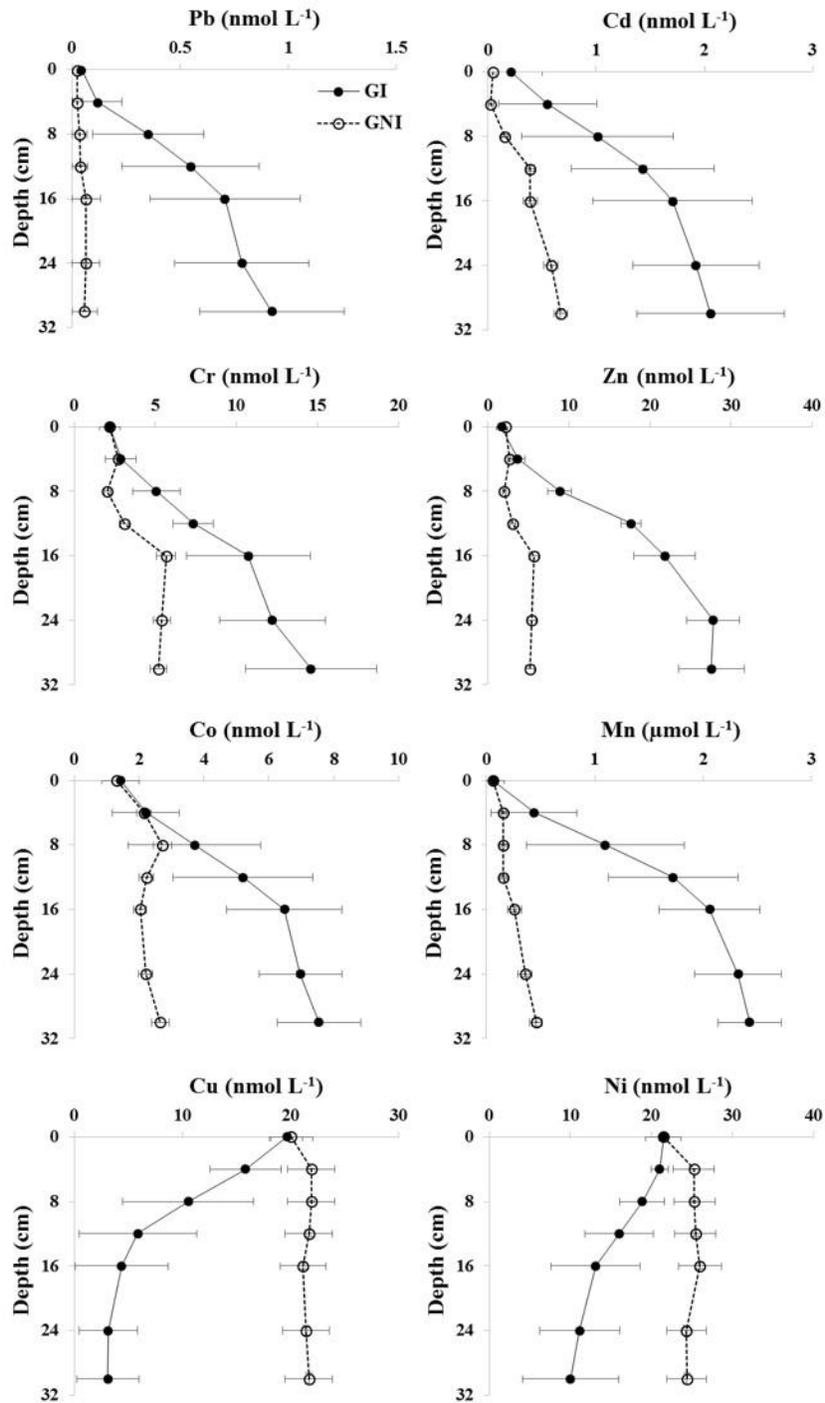


Figure 3. The average trace metals profiles in the sediments pore water obtained of groundwater impacted areas (GI)- solid circles and groundwater not-impacted (GNI)- hollow symbols.

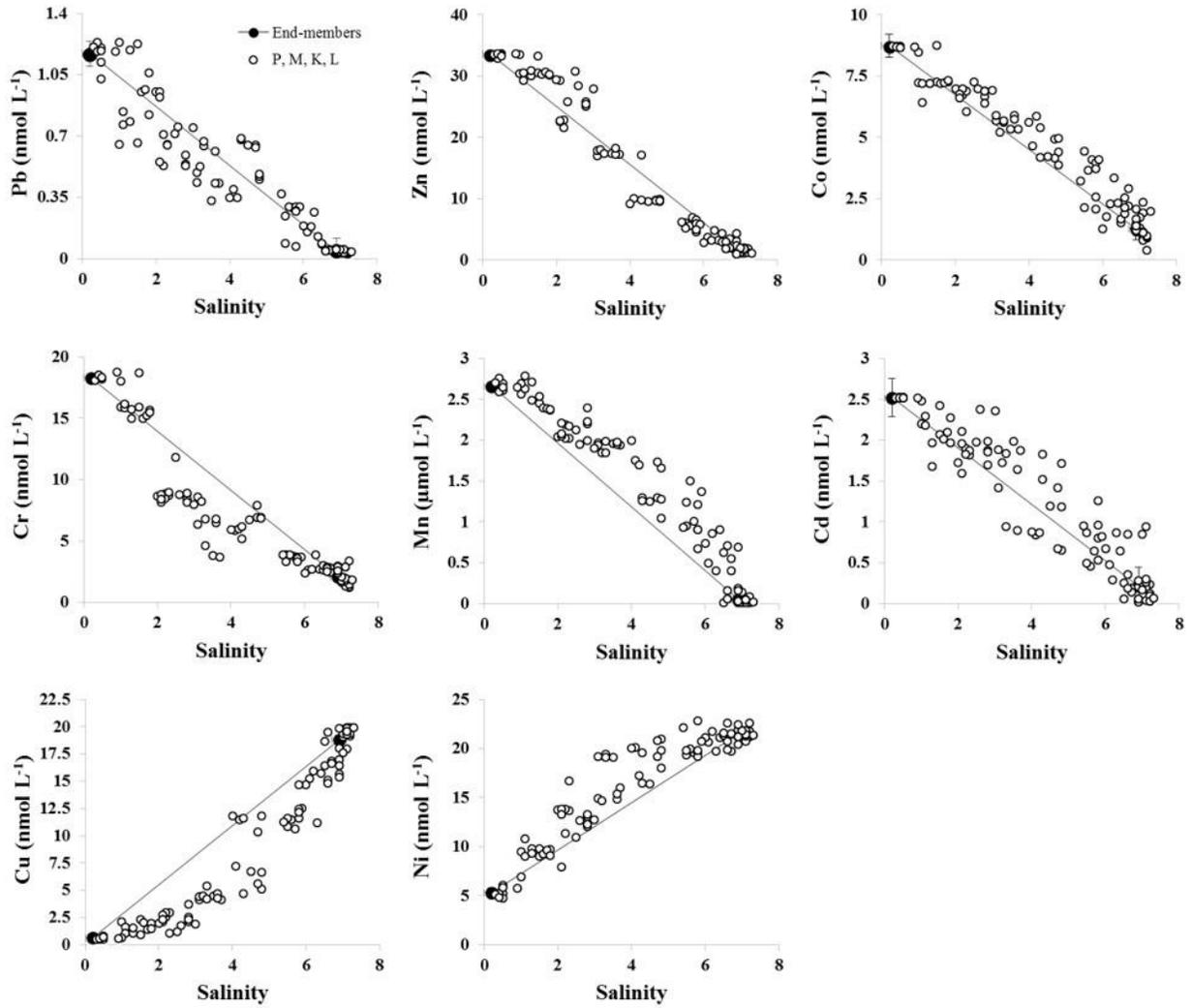


Figure 4. The dependences between trace dissolved metals pore water concentrations (Cu, Co, Cd, Ni, Mn, Pb, Zn, and Cr) and salinity in the groundwater impacted areas.

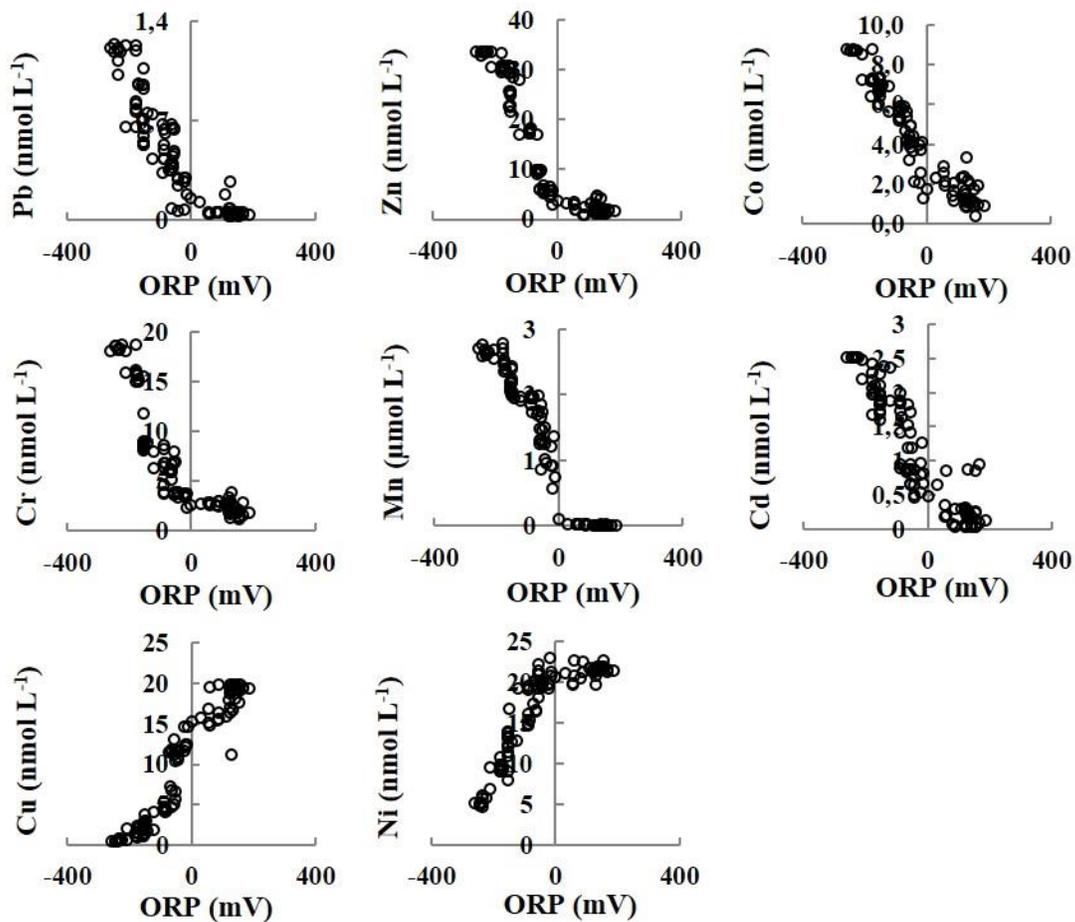


Figure 5. The dependences between dissolved Pb, Cd, Co, Mn, Cr, Cu, Ni and ORP in the subterranean estuary.

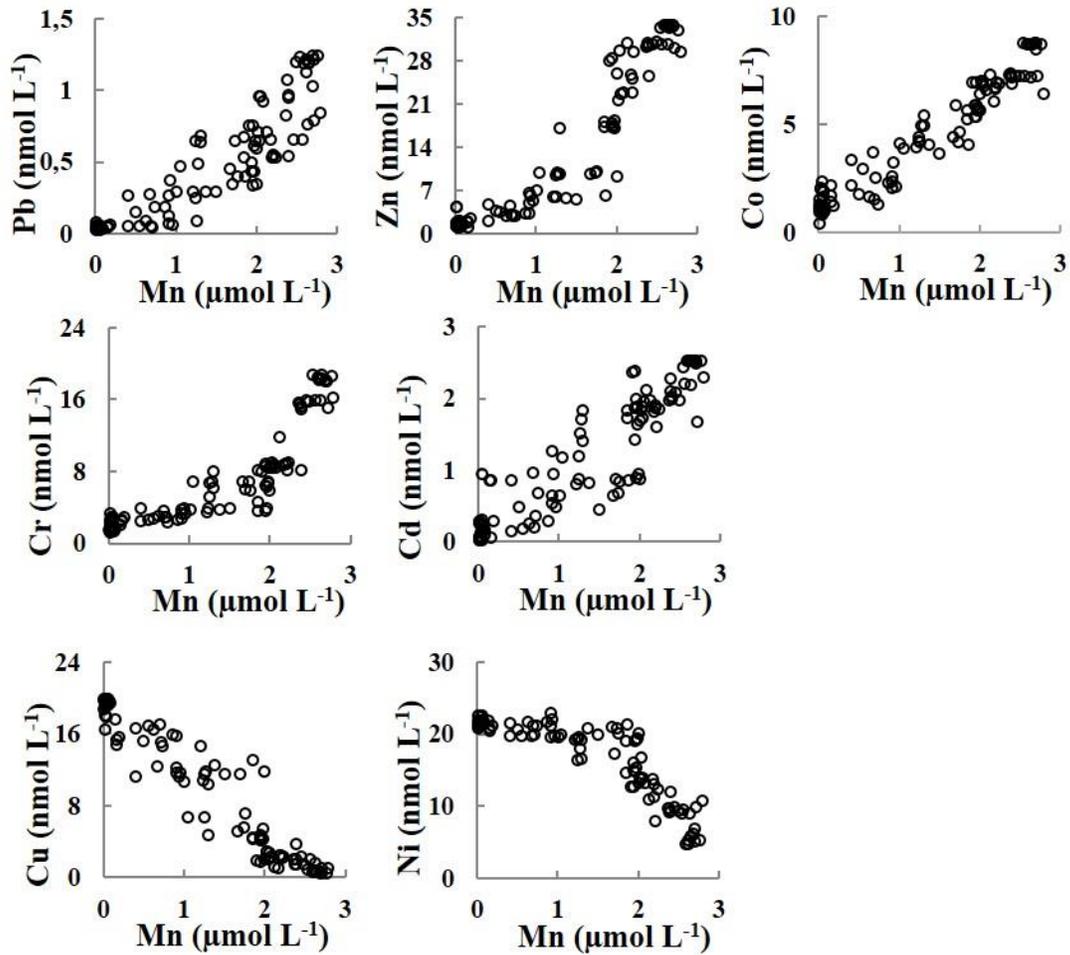


Figure 6. The dependences between dissolved Pb, Cd, Cu, Cr, Co, Ni and Mn in the subterranean estuary.

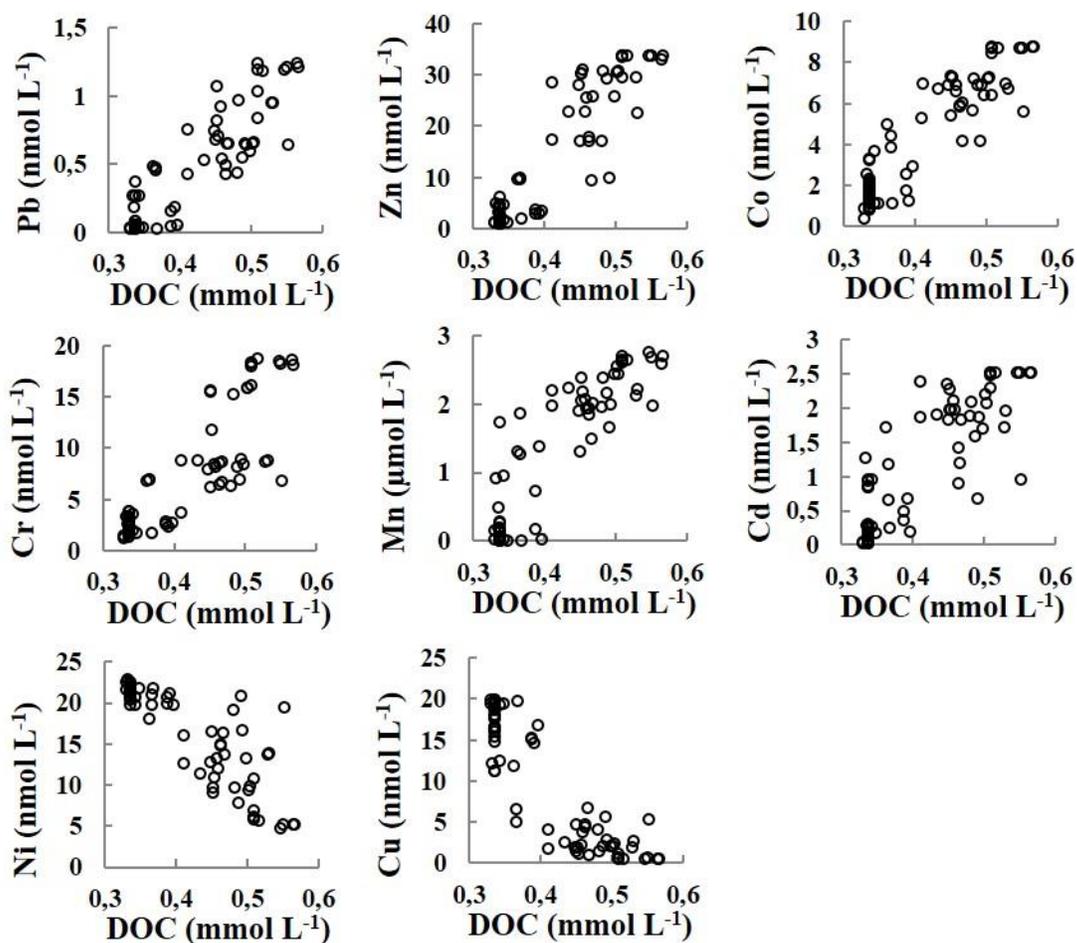


Figure 7. The dependences between dissolved Mn, Cu, Cr, Co, Zn, Cd, Ni and DOC in the subterranean estuary.