Input and fate of dissolved nitrogen compounds via submarine groundwater discharge into the Puck Bay (Poland)

Diplomarbeit

am
Leibniz Institut für Ostseeforschung Warnemünde (IOW)
an der
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vorgelegt von
Sabine Nestler

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Gutachter:
Dr. habil. Maren Voß
Dr. habil. Stefan Forster

Abbreviations

BC   benthic chamber

C   carbon

DIN   dissolved inorganic nitrogen

DON   dissolved organic nitrogen

IN   inorganic nitrogen

L   groundwater lance

N   nitrogen

NH_4^+ ammonium

NO_3^- nitrate

NO_3^- nitrite

$NO_{2/3}^-$ sum of NO_3^- and NO_2^-

POM   particulate organic matter

SGD   submarine groundwater discharge

O_2 oxygen

OM   organic matter

T   push pull lance

TDN   total dissolved nitrogen

Abstract

The aim of this study was the investigation of nitrogen input to the Puck Bay (Poland) via submarine groundwater discharge (SGD) and its ecological impact. Thus concentrations of dissolved organic nitrogen (DON), nitrate, nitrite and ammonium were measured in pore waters of SGD impacted and unimpacted sites at Hel Penisula (Poland). Furthermore the δ^{15}N-NH$_4^+$ values as well as the δ^{15}N and δ^{13}C values of various organisms were determined. Nitrate and nitrate were nonexistent in the discharging groundwater and DON of pore water showed concentrations about 20 µmol L^{-1}, similar to the water column concentrations, but could not be associated with SGD. The dominant nitrogen species in the SGD was by far ammonium with concentrations ranging from 200 to 5000 µmol L^{-1}. This high range in concentrations also indicates the variability of nitrogen input in time and space.

In order to identify the source of the ammonium in the SGD a deep and a shallow well were sampled on Hel Peninsula. Since both these wells contained only relatively low ammonium concentrations about 30 µmol L^{-1} the corresponding aquifers can not be the source of the high ammonium load of the SGD. It was therefore hypothesized that the ammonium may originate from organic rich sediment layers overlying a deep aquifer and that the ammonium is dissolved in groundwater from a deep aquifer seeping upwards through this layer prior to submarine discharge. The relatively low δ^{15}N-NH$_4^+$ values between 0 and 2 ‰ support such a hypothesis indicating a terrigenous source of nitrogen like degradation of soil organic matter. The high ammonium load of the SGD would therefore not be of anthropogenic origin.

Ammonium from SGD was mostly conservatively mixed into the water column without any significant transformation. Extrapolations from ammonium flux rates of the SGD to the whole Puck Bay indicate a high overall nitrogen load from SGD compared to other nitrogen sources. However, the ammonium load from SGD did not seem to have a significant impact on the Puck Bay ecosystem since organisms sampled on the SGD impacted site showed the same δ^{15}N values as organisms sampled from the SGD unimpacted Baltic Sea side and the two food webs looked quite similar.

Finally, to exactly understand the sources and sinks of ammonium from SGD on Hel Penisula and its ecological significance further investigations of the hydrogeological conditions and the ecosystem of the Puck Bay are necessary.

Zusammenfassung

Das Ziel dieser Arbeit war es den Stickstoffeintrag und damit den ökologischen Einfluss durch submarine Grundwasseraustritte (SGD) in die Puck Bay (Polen) zu untersuchen. Dafür wurden die Konzentrationen von organischem gelösten Stickstoff (DON), Nitrat, Nitrit und Ammonium im Porenwasser gemessen, sowohl in Grundwasser beeinflussten als auch in unbeeinflussten Gebieten auf der Halbinsel Hel. Außerdem wurden die $\delta^{15}N$ Werte im Ammonium sowie die $\delta^{15}N$ und $\delta^{13}C$ Werte von verschiedenen Biota bestimmt. Nitrat und Nitrit kamen nicht im austretenden Grundwasser vor. DON Konzentrationen von ca. 20 µmol L^{-1} im Porenwasser waren ähnlich den Konzentrationen, die in der Wassersäule gemessen wurden und konnten nicht mit den submarinen Grundwasseraustritten in Verbindung gebracht werden. Die Stickstoffspezies, die mit Abstand in den höchsten Konzentrationen von 200 bis 5000 µmol L^{-1} im Grundwasser auftrat war Ammonium. Die große Spanne in den Ammoniumkonzentrationen zeigte auch die große räumliche und zeitliche Variabilität.

Um die Quelle des Ammoniums aus den submarinen Grundwasseraustritten ausfindig zu machen wurden ein tiefer und ein flache Brunnen auf Hel beprobt. Da allerdings die Grundwässer beider Brunnen nur relative geringe Ammoniumkonzentrationen von ca. 30 µmol L^{-1} enthielten, können die beiden entsprechenden Grundwasserleiter nicht die Quelle für die große Ammoniumfracht sein, die in den Grundwasseraustritten gefunden wurde. Auf Grund dessen wurde die Hypothese aufgestellt, dass das Ammonium aus Organik reichen Schichten stammt, die über einem tiefen Grundwasserleiter liegen. Danach wird das Ammonium im Grundwasser gelöst bevor es in die Puck Bay austritt, während dieses durch eben diese Schichten aufsteigt. Die relativ niedrigen $\delta^{15}N$ Werte im Ammonium zwischen 0 und 2 ‰ sprechen für diese Hypothese, da sie auf eine terrigene Stickstoffquelle wie den Abbau von organischem Material im Boden hindeuten. Demnach wäre das Ammonium aus den submarinen Grundwasseraustritten nicht anthropogenen Ursprungs.

Das austretende Ammonium wurde hauptsächlich konservativ in die Wassersäule eingemischt ohne vorherige Umwandlung. Extrapolationen von Ammoniumflussraten der Grundwasseraustritte auf die ganze Puck Bucht deuten auf eine hohe Stickstofffracht hin verglichen mit anderen Quellen. Allerdings scheint das Ammonium keinen deutliche Einfluss auf das Ökosystem der Bucht zu haben, da die Organismen, die im Grundwasser beeinflussten Gebiet gesammelt wurden, die selben Isotopenwerte Werte zeigten, wie Organismen von der Ostseeseite der Halbinsel Hel ohne SGD.

Um die Quellen und Senken für das Ammonium aus dem Grundwasser richtig zu verstehen und damit auch seine ökologische Bedeutung für die Puck Bucht sind weitere Untersuchungen der hydrogeologischen Bedingungen und des gesamten Ökosystems nötig.

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1   Introduction

Eutrophication of coastal waters due to nonpoint source land-derived nitrogen (N) loads is perhaps the greatest agent of change altering coastal ecology (National Research Council, 2000). Global river-derived nutrient inputs into the ocean have tripled since the 1970's (S. V. Smith et al., 2003). However, little is known how much of this originates from groundwater input into rivers and estuaries. Submarine groundwater discharge (SGD) to the coastal ocean is a worldwide phenomenon. But since it occurs mostly only in a diffusive and temporal and spatial very heterogeneous way, localization and quantification is difficult. Hence SGD and its impact on geochemical cycling in the coastal ocean have been neglected for a long time. In addition groundwater flow is much slower than riverine flow and therefore the volume discharged is lower. Most estimates of terrestrially derived SGD range from 6 to 10 % of surface water inputs (Burnett et al., 2003).

However, the exchange of groundwater between land and sea is a major component of the hydrological cycle (Moore, 2010). Groundwater may be a major route of transport from land to sea for freshwater and associated land-derived nutrient loads in coastal watersheds where soils have a high hydraulic conductivity and permeable coastal sediments (Valiela et al., 1990). SGD-derived nutrient loads may even rival local surface water nutrient inputs in many coastal areas (Moore, 1996; Kim et al., 2003; Kim et al., 2008; Santos et al., 2008). It may therefore have an important ecological impact on productivity, biomass and species composition (Johannes, 1980). Seasonal fluctuation in SGD may influence initiation of algae blooms (Sewell, 1982) and thus anthropogenic nutrient concentrations may support eutrophication (Johannes, 1980; LaRoche et al., 1997). The input of inorganic nitrogen via submarine groundwater may also impact the benthic species composition. (Maier & Pregnall, 1990) found that elevated nitrate input via SGD is giving an advantage to macroalgal species over marine plants like the eelgrass *Zostera marina*, which leads to a dominant algal growth. Something similar was observed on coral reefs in Jamaica and Florida. In this case an increase in near bottom dissolved inorganic nitrogen due to SGD stimulated the growth of epilithic macroalgae. This was to the disadvantage of the corals these macroalgae grow on. In Jamaica macroalgae are now dominant (Lapointe, 1997). Furthermore groundwater residence times can range from years to decades and are much longer than surface run-off. One such example is the groundwater in Florida, USA, which was contaminated by fertilizer and sewage disposal about 60 years ago. This groundwater provides nitrogen that fuels widespread modern harmful algae blooms (Hu et al., 2006).

As already mentioned, SGD occurs mostly as slow and diffuse flow, but can also be a point source like a submarine spring. The flow rate depends thereby on the permeability of the sediments overlying the seeping aquifer (Valiela et al., 1990). SGD, as defined by (Burnett et al., 2003), is any and all flow of water on continental margins from the seabed to the coastal ocean, regardless of fluid composition and driving force. In addition, submarine groundwater recharge (SGR) occurs: Tides, waves, currents, sea level fluctuations and density differences force seawater into the sea floor. Therefore driving forces for SGD are not only the terrestrial hydraulic gradients but also oceanic processes (Figure 1.1) which leads to the high spatial and temporal variability. In the transition zone between fresh and saline groundwater exists a brackish mixing zone with a salinity gradient from land to sea. (Moore, 1999) therefore introduced the term "subterranean estuary".
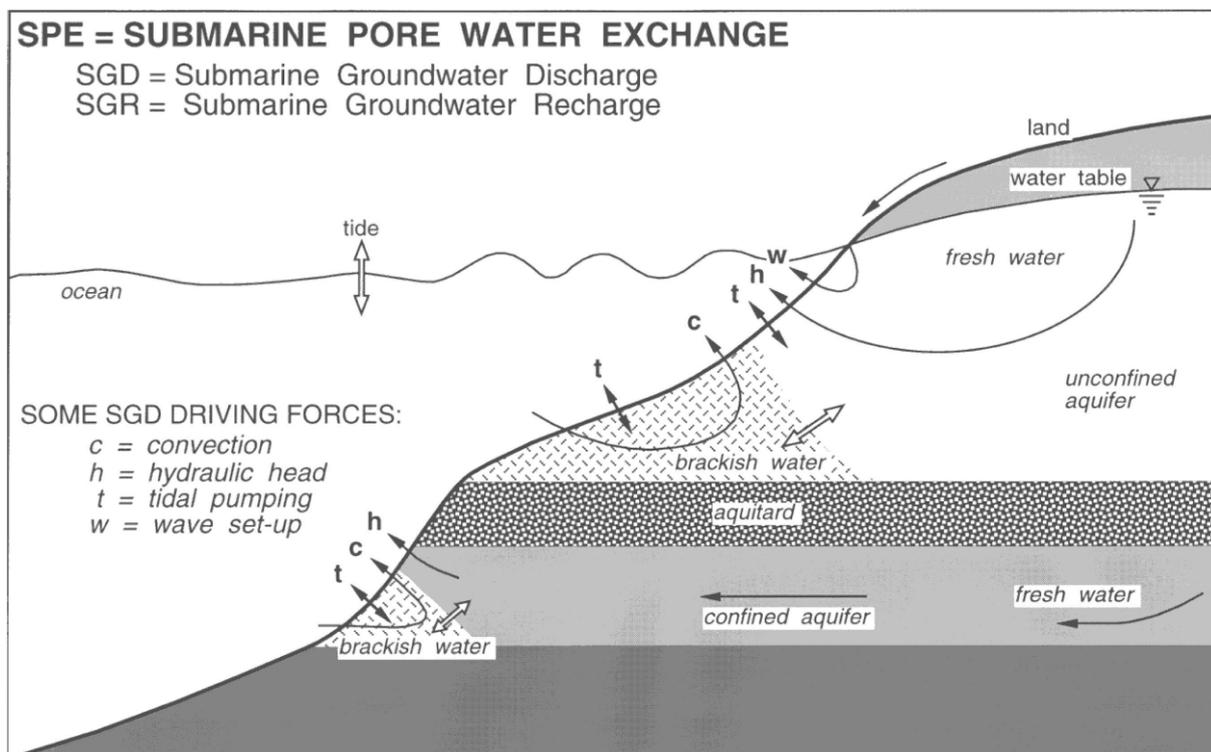
Figure 1.1: Nomenclature of fluid exchange and schematic depiction (no scale) of processes associated with submarine groundwater discharge and recharge. Arrows indicate fluid movement. Modified by Burnett et al. (2003) from Thibodeaux and Boyle (1987)

From 2002 to 2005 the EU project COSA was conducted on the island Sylt (North Sea, Germany) and Hel Penisula (Baltic Sea, Poland). The aim was to investigate the role of "COastal SAnds as biocatalytical filters". During this project SGD was found on the beach of the village Hel (outer Puck Bay). The present diploma thesis was conducted within the scope of the BONUS project AMBER (Assessment and Modelling of Baltic Ecosystem Response),

where one aspect deals with the biogeochemistry of the SGD in Hel and its impact on the coastal ecosystem. In most studied cases nitrate is the dominant N species found in groundwater (R. L. Smith et al., 2006). However, first measurements during the autumn campaigns on Hel Peninsula in 2009 showed very high ammonium concentrations in the groundwater seepage.

Ammonium in groundwater may naturally be generated by the anaerobic degradation of organic matter or artificially as a result of organic waste disposal. Anthropogenic ammonium sources may be wastewater disposal, sewage systems and agricultural practices. The transport of ammonium in groundwater may be retarded by physical-chemical processes such as sorption or by biological processes like microbially induced transformations, depending on aquifer geochemistry and the nature of the groundwater flow system (Böhlke et al., 2006). Ammonium may therefore have much longer flushing times than other more mobile aqueous species (Ceazan et al., 1989; van Breukelen et al., 2004). Ammonium is an N source for phytoplankton and is highly bio-available thus being assimilated by such organisms. In addition to assimilation, transformation of ammonium may also occur by nitrification of microorganisms. In this process ammonium is oxidized with O_2 to NO_3^-. In the transition zone of oxic-anoxic conditions nitrate may be removed from the system by denitrification which transforms nitrate to gaseous N_2. Alternatively, ammonium may be oxidized anaerobically with reduction of nitrite to form N_2, called the anammox process (Van de Graaf et al., 1995; Thamdrup & Dalsgaard, 2002). Inorganic N (nitrate and ammonium) is immediately available to primary producers. Also dissolved organic nitrogen (DON) from terrestrial sources may show substantial biological availability, but mineralization and assimilation occurs relatively slowly (Qualls & Haines, 1992; Seitzinger et al., 2002).

To study N altering processes stable isotopes are often used. The two stable isotopes of N are ^{14}N and ^{15}N. They both have the same number of protons and electrons but the heavier ^{15}N contains one more neutron. N in the atmosphere consists of 99.63 % of ^{14}N and 0.37 % of ^{15}N. The ratio in abundance of these two natural N isotopes can give information about sources and sinks of N (Peterson & Fry, 1987; Sulzman, 2007) because the isotope ratio $^{15}N/^{14}N$, or R, varies among different N pools. Since those differences are very small the isotopic composition is reported as the deviation of R from a sample from R of a standard in parts per thousand:

$$\delta^{15}N(\text{‰}) = \left(\frac{R_{sample}}{R_{s\,\tan dard}} - 1 \right) * 1000 \qquad [1.1]$$

It is possible to discriminate the N source of a sample if the pools to be considered are distinct in their δ^{15}N values.

Stable isotopes may also be used to identify N altering processes because of the occurring fractionation during a reaction. This is because more energy is needed to break bonds in molecules with the heavier ^{15}N isotope. Since ^{15}N therefore has a lower reaction rate than ^{14}N, it is discriminated over ^{14}N in biochemical reaction leaving the remaining substrate enriched in ^{15}N compared to the product. This can be expressed in the following way, where $\varepsilon_{p/s}$ is the isotope enrichment factor:

$$\delta^{15}N_{product} \cong \delta^{15}N_{substrate} + \varepsilon_{p/s} \qquad [1.2]$$

Processes altering NH_4^+ concentration, like nitrification, show different fractionations. Simple mixing of NH_4^+ into a NH_4^+ free solution would not change the isotope ratio and ε is therefore 0 ‰, while ε for the assimilation of NH_4^+ by marine diatoms was found to be -20 ± 1 ‰ (Waser et al., 1998). The isotope enrichment factor for nitrification may range from -17 to -38 ‰ (Mariotti et al., 1981). Sorption of NH_4^+ in sediments to clay for instance leads to an opposite fractionation. NH_4^+ remaining in solution gets enriched in ^{14}N with ε being +1 to +11 ‰ (Delwiche & Steyn, 1970; Karamanos & Rennie, 1978).

Isotope ratios can also be helpful for analyses of food webs. In this case the carbon (C) isotopes can give information about the food source of organisms. The two stable C isotopes are ^{12}C and ^{13}C and the δ^{13}C values of animals reflect there diets within about 1 ‰ (DeNiro & Epstein, 1978; Rau et al., 1983; Peterson & Fry, 1987). N on the other hand shows a more significant enrichment of ^{15}N between a consumer and its diet (DeNiro & Epstein, 1981). Isotope ratios of N can therefore be used to identify the trophic level of animals in a food web. Minagawa & Wada (1984) found a mean ^{15}N enrichment of +3.4 ± 1.1 ‰ per trophic level independent of the habitat and according to Peterson & Fry (1987) animals are 3 to 5 ‰ heavier in the isotopic composition of N than their diets. On average field studies have shown an enrichment of 3.2 ‰ per trophic level (Post, 2002). Stable isotopes of organisms may also reflect differences in the N source of primary producers. McClelland et al. (1997) found that

producer and consumer $^{15}N/^{14}N$ ratios were both shifted due to isotopically heavy wastewater N inputs.

In the present diploma thesis DIN concentrations as well as $\delta^{15}N$ values of DIN and organic forms of N have been used to understand the ecological importance of SGD to the Puck Bay. Therefore the following hypotheses are worked out:

1. $\delta^{15}N-NH_4^+$ values are different to all other N sources..

2. The entry of nitrogen via SGD is temporally, seasonally and spatially very variable and enters the coastal waters unmodified. SGD at Hel Peninsula contributes significantly to the N input into the Puck Bay.

3. The $\delta^{15}N$ signal can be detected in the trophic network.

2 Material and Methods

2.1 Sampling Site
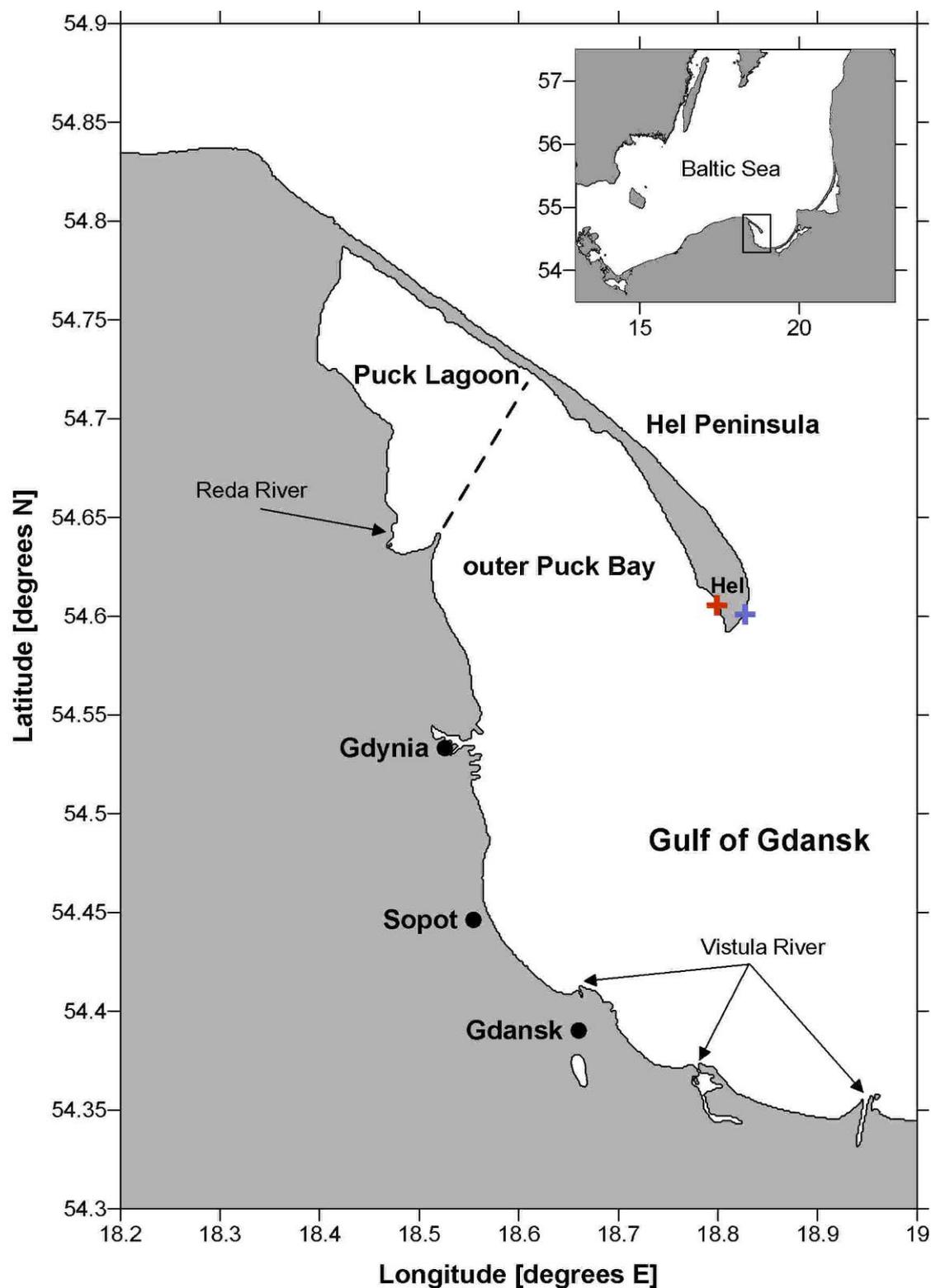
Figure 2.1: Map of the western part of the Bay of Gdańsk with Puck Bay. The broken line indicates the underwater sandy bank separating Puck Lagoon from the outer Puck Bay. Arrows indicate the river mouths of Vistula and Reda. Sampling sites were the beach of the village Hel (**+**) and a reference station at the Baltic Sea side of Hel Peninsula (**+**).

Sampling took place on Hel Peninsula in Poland. It is a 36 km long sandy spit which forms Puck Bay, the south western part of the Bay of Gdańsk (Baltic Sea) (Figure 2.1).

Puck Bay is a semi-enclosed gulf characterized by low average salinities of 7.6 (Nowacki, 1993). Depths range from 2 m in the western part of the Bay to 50 m in the eastern part (Nowacki, 1984). Puck Bay is divided by an underwater sandy bank into the inner shallower Puck Lagoon (average depth 3.1 m) and the outer Puck Bay (average depth 20.5 m). This bank is divided by two straits where intensive water exchange between outer Puck Bay and Puck Lagoon occurs.

The bay is influenced by marine waters from the Gulf of Gdańsk as well as by terrestrial waters. 76.3% of the whole Puck Bay catchment area drains into Puck Lagoon. Puck Bay is classified as eutrophic. It is polluted with wastewaters from three sewage treatment facilities and seven rivers (Kruk-Dowgiałło & Szaniawska, 2008) the largest being the Reda River. The annual N input into Puck Bay is 2,275 t a^{-1} (Pempkowiak, 1994). The average inflow of wet nitrogen from the atmosphere was estimated to be 306,040 t (Bolałek et al., 1993). Furthermore high flux rates up to 1434 µmol NH$_4$-N m^{-2} day^{-1} from sediment to bottom water were found within the Puck Bay (Bolałek & Graca, 1996) leading to an amount of about 825 t NH$_4$ per year passing from the sediment to near-bottom water. Approximately 205,400 t inorganic N (IN) flow from the Gulf of Gdańsk into Puck Bay annually. Outflow of substances occurs mainly in winter being 197,600 t IN a^{-1} (Kruk-Dowgiałło & Szaniawska, 2008).

Hel Peninsula has evolved during the Holocene. Its coast consists basically of recent alluvial and littoral zone Holocene sediments (Furmanczyk, 2007). Pleistocene deposits are present in the substratum of the whole spit (Tomczak, 1995). In the eastern part of the spit where sampling took place, the Holocene series is fully developed with a thickness up to 100 m (Figure 2.2). The surficial bottom sediments of the coast around the head of the spit (study area) consist mainly of medium-grained sands (Kramarska, 1995).

The bottom sediments of Puck Bay consist mainly of sand and mud (Krzymiński et al., 2004). There are at least three main ground water horizons underlying Puck Bay: One upper Cretaceous, one Tertiary and one Quaternary horizon. Puck Bay is the main drainage area for those aquifers (Dowgiałło & Kozerski, 1975; Sadurski, 1986).

Seismoacoustic profiling showed a series of permeable deposits under the sea floor (Jankowska et al., 1992). Since the groundwaters of the three aquifers are fresh, the existence of drainage zones is indicated by changes in the salinity of the sediment-water interface. SGD into the Puck Bay occurs mainly by ascensic seepage through the seabed (Figure 2.2). On Hel

Peninsula the Cretaceous aquifer, which is generally isolated from the overlying horizons, is in direct contact with the Pleistocene sandy series and constitutes a joint groundwater horizon (Jankowska et al., 1994). The cross-section in Figure 2.2 presents a relatively simple illustration of the existing conditions. The actual hydrogeology might be far more complicated.

Winds from north northwest are the most important physical process that causes erosion along Hel Peninsula and create a transport of sediments along the shore towards the end of spit. North-easterly winds, perpendicular to the spit, create currents that transport sandy material eroded from the coast into deep water (Furmanczyk & Musielak, 1999). The eastern part of Hel Peninsula with the sampling area is predominantly accumulating (Furmanczyk, 1994).

There are on. Besides built-up areas and railway there are forests, meadows and wastelands on Hel Penisula but no arable fields. The three important sectors of economy on Hel Peninsula are fishery and fishing industry, tourist industry and defence and military services (Furmanczyk, 2007).
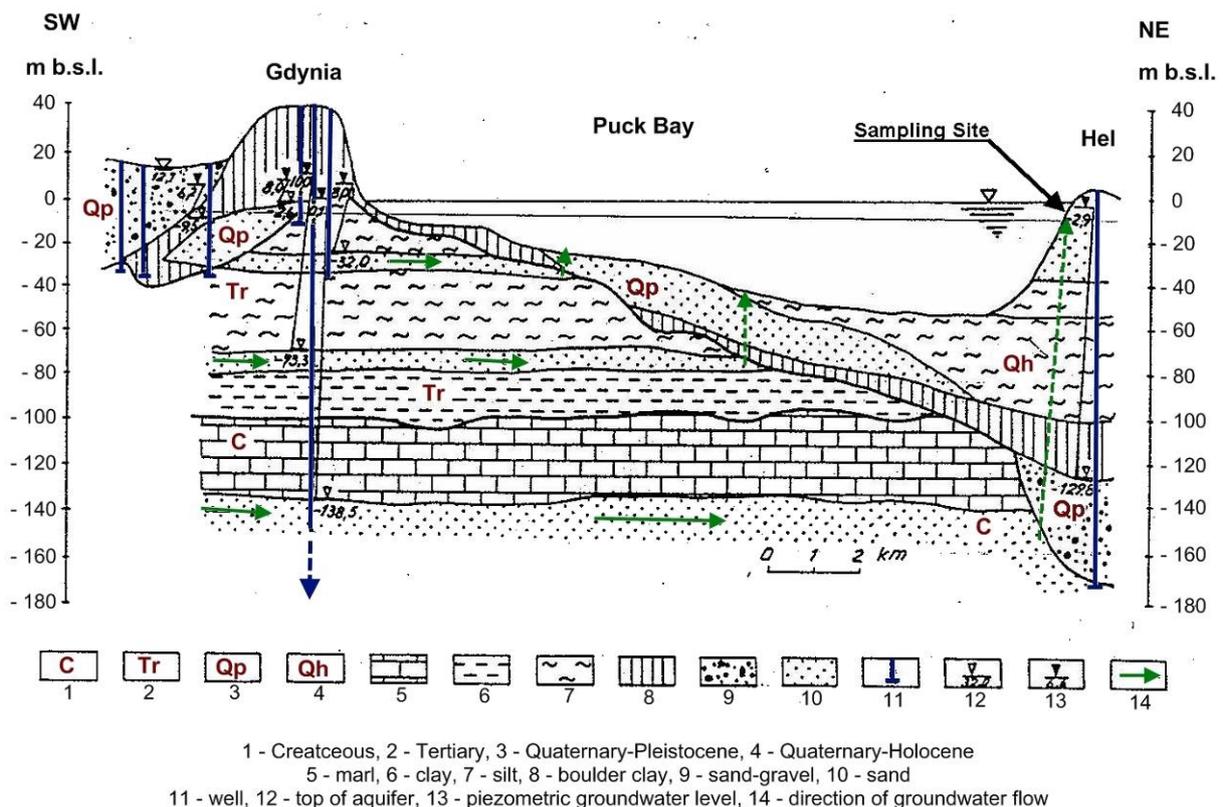
Figure 2.2: Hydrogeological section through Puck Bay from Gdynia to Hel. Sediment depth is given as meter below sea level (m b.s.l.). The three aquifers with the direction of the groundwater flow are indicated by the green arrows. From bottom up: Cretaceous, Tertiary and Quaternary horizon. Vertical green arrows indicate potential submarine groundwater discharge. The sampling site in Hel and the 180 m deep sampled well are shown. (modified from Piekarek-Jankowska (1996))

The main sampling site was on the beach of the village Hel on Hel Peninsula. Altogether 5 sampling campaigns were conducted: Two in September and November 2009, one in the end of February till the beginning of March 2010 and two in May and October 2010. During October 2010 samples were taken from the Baltic Sea side of Hel Peninsula as a reference station (Figure 2.1), too.

2.2 Sampling

Pore water salinity was tested at first in the research area to find spots with SGD. This was done with the help a push pull lance (Figure 2.3). Such a lance is very thin (about 1 cm in diameter), has only one port at the lower end and can be pushed into the sediment and sampled immediately.

At spots with low pore water salinities larger groundwater lances were buried in the sediment (Figure 2.3) to sample submarine groundwater. These groundwater lances had each 8 ports all located in different heights. The difference in height between the ports constitutes 4 cm, respectively, except for the two lowest ports (7 and 8) where the difference was 8 cm (Figure 2.3). Since the burial disturbed the sediment this lances could not be sampled immediately. Only after at least 24 hours the sediment was thought to be readjusted and samples could be taken from different depths with syringes via the Teflon tubes. It was not possible to plunge the lances completely into the sediment. Thus only the lower five to six ports were connected to the pore water and could be sampled (Figure 2.3). Groundwater lances were sampled on two to three different days. From every port 100 to 200 ml could be sampled (Table 2.1).

In September and November 2009 samples for N measurements were taken by S. Vogler (Institute for Baltic Sea Research, Working Group: Geochemistry and Stable Isotope Geochemistry) from one groundwater lance, respectively. For the February/March campaign no samples were available. The May and October campaigns were planned and conducted by myself as well as all N measurements.
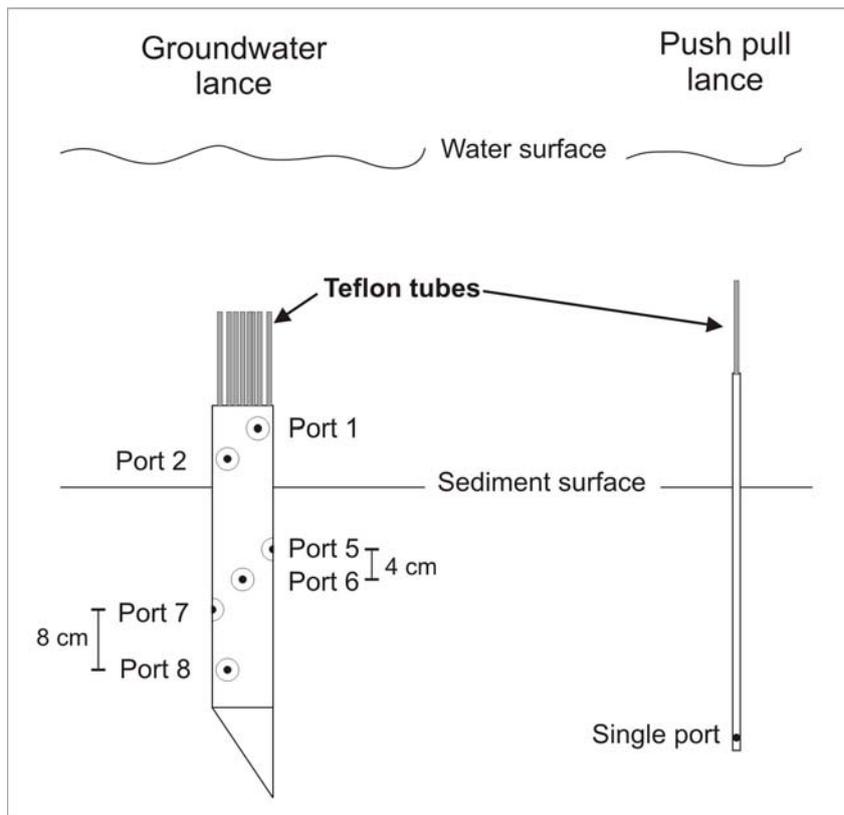
Figure 2.3: Sampling lances used in Hel. Each port is connected to one Teflon tube. Pore water was taken from the Teflon tubes with the help of syringes. The groundwater lances had 8 sampling ports in different heights. The thinner push pull lance had only one port at the lower end.

During May and October 2010 transects were sampled in addition to the groundwater lances within the SGD impacted area perpendicular to the beach line (Figure 2.4). Since only two groundwater lances were available, this was done using the thinner push pull lances (Figure 2.3). During the last two campaigns in May and October bottom and surface water was taken at each pore water sampling site.

In October 2010 the Baltic Sea side of Hel peninsula was sampled in addition. Pore water samples were taken with a push pull lance together with water column samples. Only one sediment depth (30 cm) was sampled at two adjacent spots.
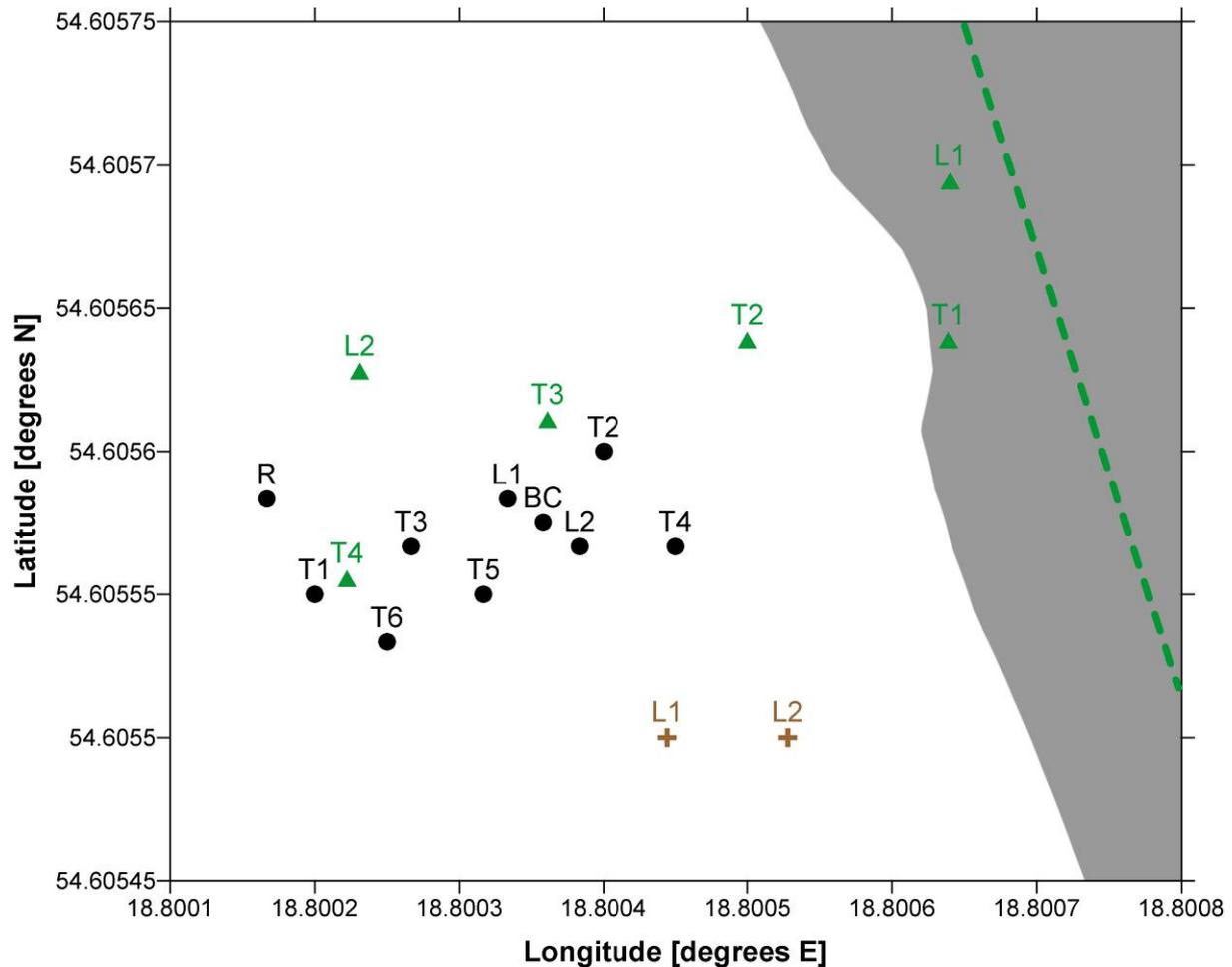
Figure 2.4: Sampling sites on the beach of the village Hel. Beach with shoreline as existent during October 2010. During May the shore line was farther east as indicated as the broken green line. Ground water lances (L) and push pull lances (T). Rope from which organisms were collected (R). Benthic chambers (BC) Locations during September 2009 (**+**), May 2010 (▲) and October 2010 (●). No location coordinates were available for November 2009 and February/March 2010, here two ground water lances were placed each time similar to the sites during September 2009.

Two wells were sampled in addition: One 3 m deep well at the Fokarium Stacji Morskiej in Hel as well as a 180 m deep well at the drinking water treatment plant in Hel.

In October 2010 six benthic chambers were positioned in a circle (ca. 1 m in diameter) between the two groundwater lances (Figure 2.4). They were used to measure the groundwater and ammonium fluxes between the sediment and the water column. Chambers were 330 mm in height and 190 mm in diameter (Figure 2.5). They were placed on the sediment-water interface by pushing them about 15 to 20 cm deep into the sediment. Height of the enclosed water column above the sediment was about 15 cm. A stirrer was installed to create an advective flow within the chamber. Water samples were taken with syringes from the sampling valves. Incubation was conducted from October 6th at 15.45 till the next day at 16.30. Sampling took place at the start and stop of the incubation. In addition samples were

taken on October 7th at 08.05 marking the end of the dark incubation (from 15.45 till 08.05) and the start of the light incubation (from 08.05 till 16.30). At every sampling point 50 ml were taken from each chamber.

Table 2.1: Samples taken during the different campaigns from groundwater lances (L), push pull lances along transects (T) benthic chambers (BC) and wells. The range of sampled sediment depths is given for all lances as well as the number of sampling days for the groundwater lances. *There were no samples available for February/March, but ammonium concentrations were provided by S. Vogler.

Sampling Campaign	Groundwater lances						Transects			Sample V per port (ml)
	L1	depths (cm)	sampl. days	L2	depths (cm)	sampl. days	Nb.	T	depths (cm)	
Sepember 2009	-	-	-	x	4 to 24	2	-	-	-	100
November 2009	x	4 to 28	1	-	-	-	-	-	-	100
Feb/March 2010*	-	-	-	x	4 to 28	2	-	-	-	-
May 2010	x	4 to 40	2	x	4 to 40	2	1	T1 to T4	5 to 30	100
October 2010	x	4 to 28	2	x	4 to 28	3	2	T1 to T3	5 to 20	200
								T4 to T6	5 to 20	200

Sampling Campaign	Baltic Sea side			BC		Wells	
	Nb. of lances	depths (cm)	Sample V per port (ml)	Nb. of BC	Sample V per BC (ml)	3 m deep	180 m deep
Sepember 2009	-	-	-	-	-	-	-
November 2009	-	-	-	-	-	-	-
Feb/March 2010*	-	-	-	-	-	-	-
May 2010	-	-	-	-	-	x	-
October 2010	2	30	200	6	50	x	x

All water samples were filtered and salinity and NH_4^+ concentration were measured immediately. Subsamples for NO_x and DON concentration measurements as well as for the determination of $\delta^{15}N$ in NH_4^+ were stored frozen in PE bottles at -20°C. Water column samples were filtered on GF/F filters and stored frozen until analyses.
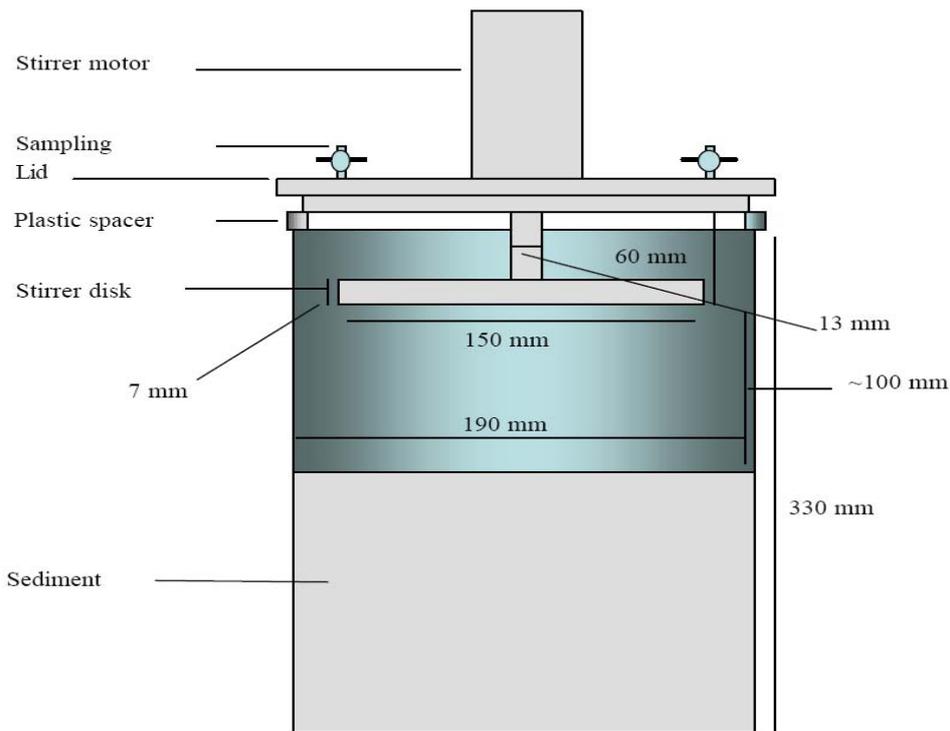
Figure 2.5: Schematic diagram of the benthic chambers used to measure the groundwater and ammonium fluxes between the sediment and the water column during the October campaign. The chamber depicted shows the experimental set-up during pre-incubations. Plastic spacers were removed before incubation start and chambers closed with Lids. (from Cook et al. (2005))

Organisms were sampled during October 2010. Plankton was sampled from the SGD impacted site of the beach in Hel as well as from the Baltic Sea side of Hel peninsula. Phytoplankton was collected with a 10 µm mesh size net and filtered on GF/F. Zooplankton samples were collected with a 55 µm net and living zooplankton was separated from seston and phytoplankton. Therefore the whole net sample was filled in an opaque dark chamber which was connected via a pipe with a transparent light chamber filled with filtered seawater. The living zooplankton was moving into the light chamber and thus separated from the rest of the sample. All plankton samples were stored frozen at -20°C until analyzing. Benthos was collected from the same sites as plankton using a brailer. In addition ropes anchored in the sediment were found on the beach of Hel near the groundwater lances (Figure 4) and on the Baltic Sea side. Parts of them were cut off and epiflora and epifauna were hand picked. Benthic animals were held in filtered seawater for 24 hours to allow their guts to clear. All benthos samples were classified and stored frozen separately at -20°C till analyzing.

Sediment from the first 20 cm was taken at the SGD impacted site for a lab experiment. It was transported in a bucket with some supernatant seawater from the Puck Bay. At IOW it was

kept at a 4°C cooling chamber spread in a basin with supernatant seawater until conduction of the experiment.

2.3 Laboratory experiment with artificial sediment cores

To investigate the potential for nitrification at the sampling site a core experiment was conducted. Sediment cores were streamed with nutrient-poor seawater with added ammonium. The experiment was set up in the following way. Eight PE tubes (length 25 cm, diameter 2.4 cm) were closed on both ends with plugs, which were perforated with Tygon hoses (Figure 6). A perforated washer was placed over the lower plug with a GF/F filter on top to avoid sediment to fall through. The PE tubes were half filled with nutrient-poor seawater through the Tygon hose at the lower end with the help of a peristaltic pump (MCP Standard). Afterwards the PE tubes were filled with the homogenized sediment taken from Hel. The Sediment cores were 18 cm high. Before the start of the experiment the water in all cores was exchanged with nutrient-poor seawater (pump velocity 2ml min^{-1} for 1 hour). After this the experiment was started. Two control experiments were performed with nutrient-poor seawater only. The other six cores were performed with nutrient-poor seawater with added ammonium chloride. In three cores NH_4^+ concentration of the solution was 200 µmol L^{-1} in the other three 500 µmol L^{-1}. The experiment was carried out until the pore water in the sediment was exchanged once. The time needed for that was calculated prior to the start of the experiment by determination of the pore volume:

$$t = \frac{V_P}{v} \qquad\qquad \text{[2.1.a]}$$

$$V_P = V_K * \phi \qquad\qquad \text{[2.1.b]}$$

$$\phi = \frac{Vol\%}{100} \qquad\qquad \text{[2.1.c]}$$

$$Vol\% = \frac{\dfrac{WW - DW}{1.011} * 100}{\dfrac{WW - DW}{1.011} + \dfrac{DW}{2.65}} \qquad\qquad \text{[2.1.d]}$$

t indicates the time needed for one pore water exchange at a certain pump velocity v for the pore volume V_P in the sediment core. V_K depicts the volume of the sediment core and ø the porosity of the sediment which is calculated from the water content in volume % (Vol%). Equation 2.1.4 gives the calculation of Vol% for sandy quartz sediments and seawater. WW indicates the wet weight and DW the dry weight.

For the experiment this results in the following:

ø = 0.38

$V_K = 163,4$ cm^3 (area A = 9.1 cm^2, height l = 18 cm)

$V_P = 62.6$ cm^3 (= 62.6 ml)

v = 0.108 ml min^{-1} → t = 580 min = 9.7 h 40 min

v = 0.05 ml min^{-1} → t = 1252 min = 20 h 52 min

The experiment was conducted twice at the two different pumping velocities 108 µl min^{-1} and 50 µl min^{-1}. These velocities were chosen because they were similar to the seepage rates measured in Hel. The exact pumping velocities were determined by the pump and the diameter of the pumping hoses.

The experiments were stopped after the water exchange. The water above the sediment cores was completely collected. In the end of the experiment the pore water of the sediment was pumped downwards and collected as well. During each experiment oxygen saturation was measured continuously with an oxygen microelectrode (Figure 2.6) in the water above the upper end one of the eight cores. NH_4^+ and NO_x concentrations as well as δ^{15}N-NH_4^+ values were measured in all samples from the core experiments. δ^{15}N-NH_4^+ of the ammonium chloride solution used was measured, too.
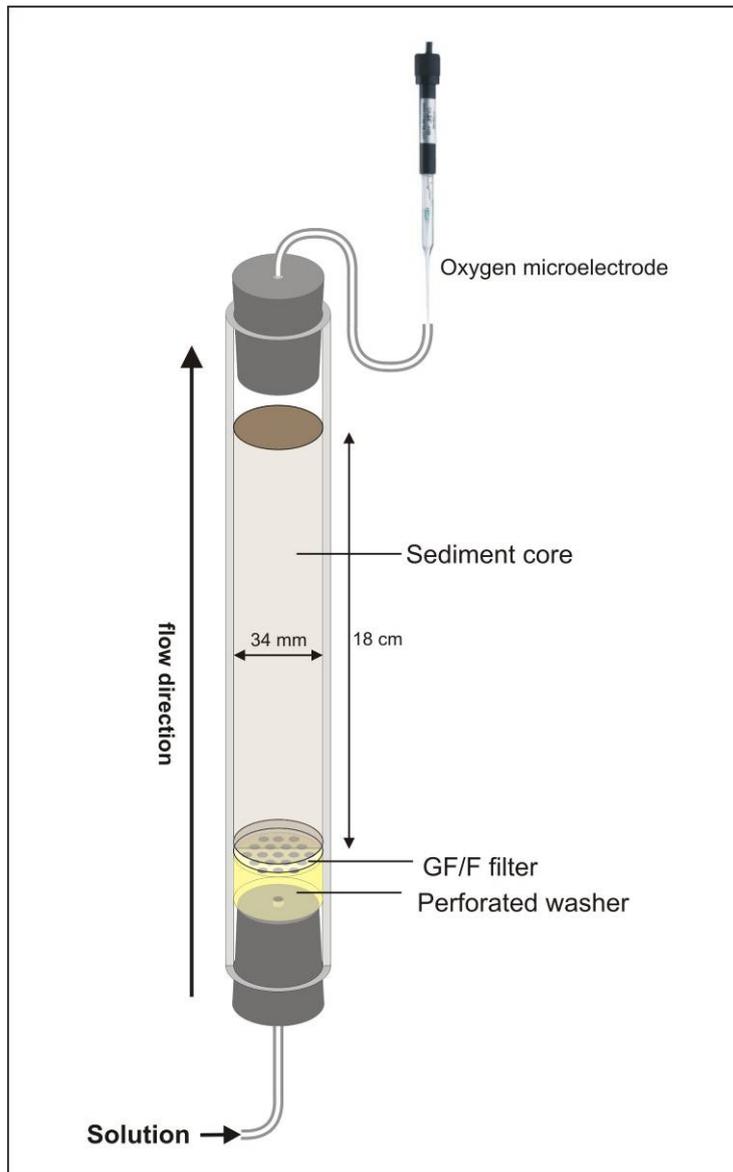
Figure 2.6: Experiment set up. Shown is one core. 18 cm of Sediment was filled into the PE tube. Solution was pumped with a tubing pump through the sediment. Flow direction is indicated. Oxygen saturation was measured at the end of one of the eight cores.

The isotopic enrichment factor for nitrification can be calculated after (Mariotti et al., 1981).

The following calculations were applied:

$$\delta_s = \varepsilon_{p/s} * \ln f$$

[2.2.a]

δ_s denotes for the $\delta^{15}N\text{-}NH_4^+$ value of the sample. $\varepsilon_{p/s}$ is the isotopic enrichment factor.

$$f = \frac{N_s}{N_{s,0}}$$

[2.2.b]

$N_{s,0}$ is the NH_4^+ concentration at the start in the solution. N_s is the NH_4^+ concentration of the sample.

For every δ_s three data points were available with each three parallels: One from the starting solution, one from the cores and one from the supernatant solution on top of the cores.

2.4 Analytical methods

2.4.1 Determination of DIN

All DIN measurements of the samples from September and November 2009 were conducted by F. Korth (Institute for Baltic Sea Research, Working Group: Stable Isotopes). NH_4^+ concentrations from additional samples during these campaigns were measured by S. Vogler and were also available. For the February/March campaign no samples were available but NH_4^+ concentrations measured by S. Vogler are presented in the results part.

For measurements of DIN concentrations the colorimetric determination of NO_2^-, NO_3^- and NH_4^+ after (Grasshoff et al., 1983) was applied.

The determination of NH_4^+ was carried out photometrically as indophenol blue. NH_4^+ reacts in moderately alkaline solution with Trione (dichloroisocyanuric acid) to monochloramine leading to indophenol blue in presence of phenol. After six to 18 hours the extinction was measured at 630 nm. As sulphide concentrations higher than 2 mg/l interfere with this method, pore water samples were diluted accordingly.

NO_2^- was determined with 5 ml for each water column sample. NO_2^- reacts with Sulphanilamide hydrochloride forming a diazonium compound. This couples with N-(1-naphtyl)-ethylenediamine dihydrochloride leading to the formation of a red azo dye. The colour intensity is thereby proportionally to the NO_2^- concentration. After 15 minutes in the dark the extinction was measured photometrically within a 5 cm semi micro cell at 543 nm. NO_3^- within water column samples was reduced to NO_2^- in copper-plated cadmium columns at a pH between 7.5 and 8.4. The samples were then further treated as explained for NO_2^-. NO_3^- and NO_2^- concentration in pore water samples were determined with the "Spongy Cadmium method" (Jones, 1984). Samples are buffered at pH 8.5 and shaken for 90 minutes

with spongy cadmium. NO_3^- is reduced to NO_2^-. Color reagent B is added and after 15 minutes in the dark extinction for combined NO_3^- and NO_2^- is measured at 543 nm.

2.4.2 Determination of DON

Dissolved organic nitrogen (DON) was measured indirectly by determination of total dissolved nitrogen (TDN) in filtered samples applying the persulfate oxidation method after (Grasshoff et al., 1983). 40 ml of the water sample was transferred into PTFE-tubes, respectively and 10 ml of potassium peroxide solution was added. All nitrogen within the sample was then digested to nitrate in a microwave (CEM, MarsXpress) for 30 minutes at 180 to 200°C. Nitrate representing TDN was determined after oxidation with the Spongy Cadmium method as described in the section above. DON was then calculated by the difference of TDN minus DIN of the sample measured before. For DIN/TDN ratios >0.85 the standard deviation on DON measurements increases greatly (Vandenbruwane et al., 2007). Hence, NH_4^+ had to be removed from pore water samples with high NH_4^+ concentrations before digestion. This was done by applying NH_4^+ diffusion method (see below). Afterwards the filter was removed and the solution was filtered prior to DON measurements. To eliminate the filtering step after the diffusion it was tried to raise pH with NaOH instead of MgO. But since the pH was sinking below 9.7 in the presence of NaOH and without MgO during incubation, this method was abandoned again. Due to time issues it was not possible to measure DON concentrations in all samples and the error of the DON measurement due to the removal of ammonium could not be determined exactly.

2.4.3 Stable Isotopes

Ammonium

Isolation of NH_4^+ from the samples to determine $\delta^{15}N$ values was conducted in two different ways. For pore water samples the NH_4^+ diffusion method (Sigman et al., 1996) was applied. Samples were transferred into Schott flasks and MgO was added to increase pH as well as a pack of Teflon membranes containing an acidified GF filter. The Schott flask is closed immediately and held in a shaking water bath for 5 days. At pH higher than 9.7 the acid-base pair, NH_4^+-NH_3 is present as the gas NH_3 which then diffuses through the Teflon membranes onto the acidified filter. NH_3 is converted to NH_4^+ at low pH and remains on the filter which is stored in a desiccator for at least two days. Prior to analysis the filters were removed from the Teflon membranes, dried at 60 °C over night and then folded into tin cups.

Due to low NH_4^+ concentrations in water column samples the diffusion method was not suitable and therefore the NH_4^+ distillation method after (Velinsky et al., 1989) was applied. As explained for the diffusion method MgO is added to the sample to shift the equilibrium of NH_4^+-NH_3 towards NH_3. During distillation the NH_3 evaporates from the sample and is collected in a measuring cylinder containing a weak acid which traps NH_3 as NH_4^+ again. This distillate is then mixed with a molecular sieve which collects all NH_4^+ within the solution. The molecular sieve was filtered onto a precombusted GF/F filter (450 °C for 3 h) and dried at 60 °C over night. The molecular sieve was removed from the filter and transferred into a tin cup. For the benthic chambers 4 to 6 $\delta^{15}N$ values are missing due to low NH_4^+ concentrations and sample volumes for the samples from the start of incubation.

POM and Organisms

Benthos samples were dried and homogenized with mortar and pestle before measurements on the mass spectrometer. Small animals were measured as a whole directly after drying. From calcareous organisms like mussels and barnacles the shells were removed and the remains acidified prior to measurements. Filters for particulate organic matter (POM) and plankton samples were dried and measured directly. All samples were transferred into tin cups for analyses of $\delta^{15}N$, $\delta^{13}C$ and C/N values.

2.5   Mass spectrometric analyses

Tin cups were pressed into pellets and measured in an elemental analyser (flash EA) coupled to an isotope ratio mass spectrometer (IRMS, Finnigan Delta S). The samples are combusted with additional oxygen at 1020°C (flash combustion) converting all inorganic and organic nitrogen and carbon into gases. The carrier gas helium transports these combustion gases through a reduction furnace (650°C) where NO_x is reduced to N_2. To remove water before transporting the gases to a gas-chromatographic column which separates N_2 from CO_2, the helium flow passes a water trap. A subsample (~ 1%) is transferred into the IRMS were the gases are ionized and accelerated before entering the magnetic sector. The ions are separated depending on their charge ratio and hit a collector. A detector transforms the electric signal. All isotope values are noted relative to reference gases (N_2, CO_2,):

$$\delta^{15}N[\text{‰}] = \left[\frac{\left(\dfrac{^{15}N}{^{14}N} \right)_{sample}}{\left(\dfrac{^{15}N}{^{14}N} \right)_{reference}} \right] * 1000 \qquad [2.3]$$

This way the mass spectrometer measures the difference in ^{15}N abundance between sample and reference. The reference gasses are calibrated against international standards of the International Atomic Energy Agency (Table 1).

Table 1: Overview over IAEA standards and internal lab standards.

Standard	$\delta^{15}N$ (‰)	$\delta^{13}C$ (‰)
international standards		
IAEA N1 (Ammonium sulphate)	0,43 ± 0,07	
IAEA N2 (Ammonium sulphate)	20,32 ± 0,09	
IAEA N3 (Potassium nitrate)	4,69 ± 0,09	
IAEA C6 (Saccharose)		-10,43 ± 0,13
NBS22 (Oil)		-29,74 ± 0,12
internal laboratory standards		
Peptone	5,8 ± 0,2	-22,11 ± 0,17
Acetanilid	-1,7 ± 0,2	-29,81 ± 0,19

2.6 End-member mixing calculations

To investigate mixing patterns of groundwater and marine NH_4^+ the conservative mixing equations by (Fry, 2002) were applied. The concentrations of NH_4^+-N were modelled as mixture (C_{MIX}) of groundwater and Puck Bay water column end-members:

$$C_{MIX} = f * C_{GW} + (1 - f) * C_P \qquad [2.4a]$$

C denotes the NH_4^+ concentration. The subscript GW indicates the groundwater end-member and the subscript P the Puck Bay water column end-member. f is the fraction of freshwater calculated from salinity (S):

$$f = \frac{S_P - S_{MIX}}{S_P} \qquad \text{[2.4b]}$$

Water column end-members were calculated from the means of all water column samples during each campaign. As groundwater end-member the well samples were used. In addition mixing was calculated with pore water samples with the lowest salinity during each sampling campaign as groundwater end-member. However, pore water samples present no true groundwater end-members. As they all had salinities >0, f had to be adapted as followed:

$$f = \frac{S_P - S_{MIX}}{S_P - S_{GW}} \qquad \text{[2.4c]}$$

The conservative mixing of $^{15}N\text{-}NH_4^+$ values (δ_{MIX}) was calculated as well:

$$\delta_{MIX} = \frac{f * C_{GW} * \delta_{GW} + (1 - f) * C_P * \delta_P}{C_{MIX}} \qquad \text{[2.4d]}$$

δ denotes the NH_4^+ isotopic values. End-members were achieved in the same way as for concentration mixing.

Deviations of actual samples from the theoretical conservative mixing lines indicate additional sources or sinks in the mixing gradient. For the concentration mixing that means higher values than predicted point towards additional sources and lower values towards additional sinks.

3   Results

3.1   Seasonal and temporal variability

For the characterization of the submarine groundwater discharge salinities and nitrogen compounds are presented. In addition sulphide was measured during the May and October campaigns and provided by Susann Vogler.

Seasonal variations are shown in depth profiles of the groundwater lances sampled during all campaigns (Figure 3.1). The number of parallels for each sampling campaign varied between one and five (Table 3.1).
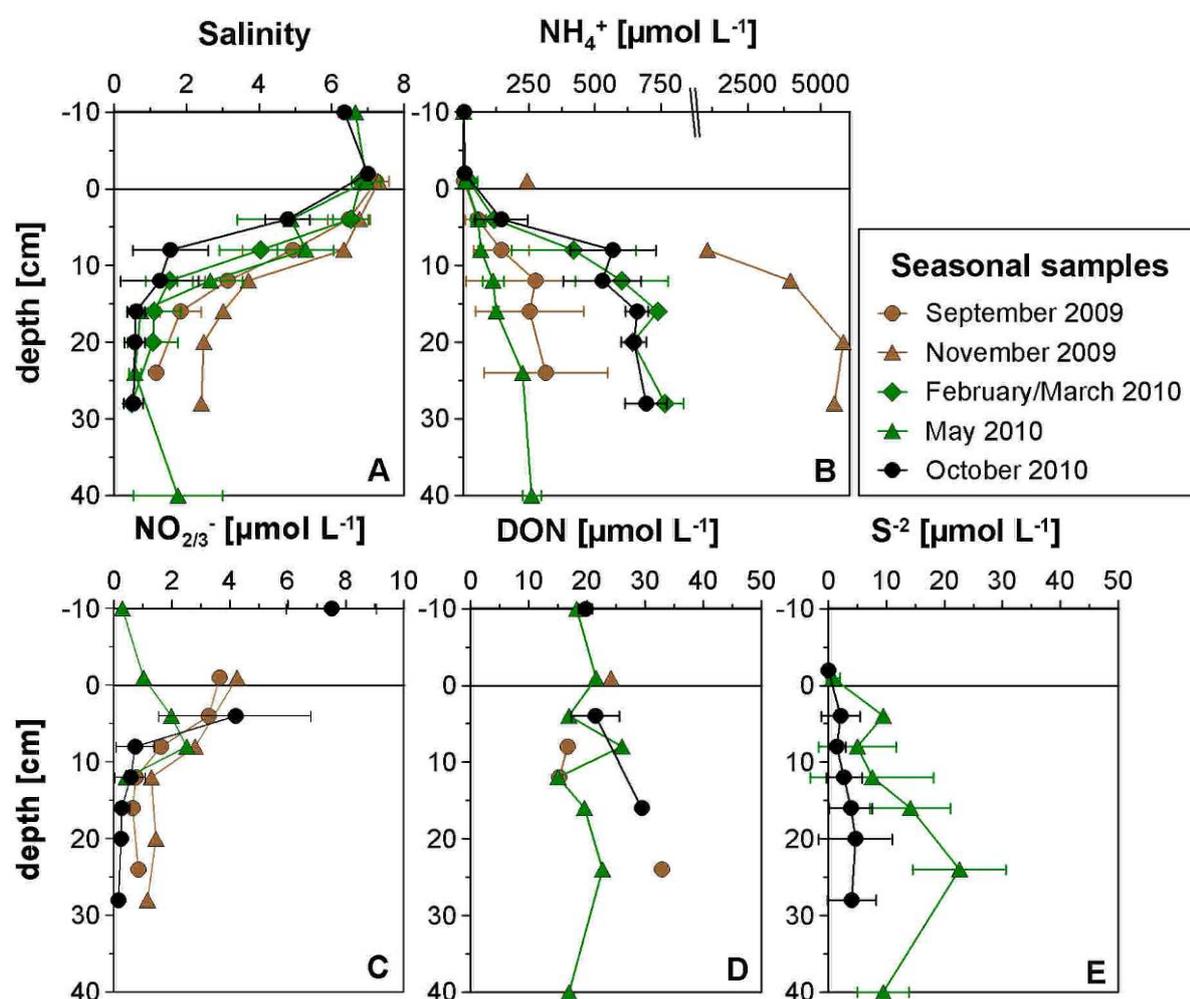
Figure 3.1: Depth profiles from pore water and water column samples of groundwater lances during the different sampling campaigns. Horizontal lines at 0 cm depth indicate the sediment surface. Salinity (A), ammonium (NH_4^+) (B), sum of nitrite and nitrate ($NO_{2/3}^-$) (C), dissolved organic nitrogen (DON) (D) and sulphide (S^{-2}) (E) from the different seasons. Means and standard deviations are given. September 2009 (●), November 2009 (▲), March 2010 (◆) May 2010 (▲), October 2010 (●). Note break in x-axis of 3.1B.

Table 3.1: Number of sampling parallels from groundwater lances during each sampling campaign.

Sampling Campaign	Nb. of groundwater lances	Nb. of sampling days	Overall sampling parallels
September 2009	1	2	2
November 2009	1	1	1
February/March 2010	1	2	2
May 2010	1	2	2
October 2010	2	2, 3	5

Highest salinities of 6 to 7 were measured in the water column and decreased below 2 with increasing depth. Only in November 2009 the lowest measured salinity was 2.4. The strongest decrease down core occured within the first 10 to 15 cm. In this zone the highest variability between sampling days was encountered. Ammonium concentrations were lowest in the upper water column ranging from 1 to 4 μmol L^{-1}. They were increasing with depth and decreasing salinity. Highest values were measured during November 2009 reaching 5.8 mmol L^{-1} in 20 cm depth. Ammonium depth profiles from March and October 2010 showed much lower concentrations of 600 to 800 μmol L^{-1} at 28 cm depth but were quite similar to each other. Lowest concentrations were measured during September 2009 (on average 310 μmol L^{-1} at 24 cm depth) and May 2010 (235 μmol L^{-1} at 40 cm depth). The sum of nitrite and nitrate ($NO_{2/3}^-$) concentrations were low at the sediment surface (3 to 5 μmol L^{-1}) and decreased mostly below 1 μmol L^{-1} within the first 10 cm in the sediment. Values around 8 μmol L^{-1} were only found in the water column during October 2010. A peak of 2.5 μM $NO_{2/3}^-$ was found in May at 8 cm sediment depth. DON concentrations ranged between 10 and 40 μmol L^{-1} but showed no trends with depth. Sulphide values measured during May and October 2010 increased with depth. In May they reached a maximum of 23 μmol L^{-1} at 24 cm depth. In October sulphide values were lower reaching only 9 μmol L^{-1} at 20 cm depth.

Ammonium concentrations plotted over the salinity showed the mixing behaviour of ammonium from SGD (Figure 3.2). The theoretical conservative mixing lines (after Fry 2002) for the two sampled wells and the pore water samples are given (for calculations see equations 2.4 to 2.7). The mean values from all water column samples taken during each campaign were used as saline end-members, respectively. Values from the well samples as well as from pore water samples with the lowest salinity during each campaign were used as groundwater end-members (Table 3.2). Both wells contained relatively low ammonium concentrations, 26.8 μmol L^{-1} in the 3 m deep well and 32.6 μmol L^{-1} in the 180 m deep well. The data from the pore water samples did not fit those two mixing lines. Despite some scatter

the mixing of ammonium concentrations was mostly conservative as predicted by each pore water mixing line. For the data points from pore water samples the linear regression lines (y = a*x + b) were calculated and compared to the respective conservative mixing lines, which were also linear with the simple equation y = a*x + b (Table 3.3). Samples from November 2009 and February/March 2010 showed fewest scatter and the linear regression had the highest r_r^2 of 0.99 and 0.95, respectively. The conservative mixing lines and the sample regression lines were quite similar for those two campaigns. In November 2009 the slope (a) of the sample regression line was slightly steeper than that of the conservative mixing line (a_r/a_m = 1.05). In February/March 2010 it was the other way around (a_r/a_m = 0.92). Most data were available from the October 2010 campaign. They varied mostly between salinities of 0 to 2 with differences in ammonium concentrations of about 400 µmol L^{-1} at salinity 1. However r_r^2 of the sample regression line were still relatively high with 0.93. The conservative mixing line and the sample regression line of October 2010 showed the highest similarity (a_r/a_m = 1.01) between all sampling campaigns. There was also scatter in the May 2010 data. r_r^2 was only 0.71 for the sample regression line. a_r/a_m for this month was only 0.87 showing a steeper slope of the conservative mixing line than of the sample regression line. The highest variations between data were found in September 2009. The sample regression line had the lowest of all r_r^2 (0.57). For this month also the maximum difference between conservative mixing line and sample regression line (a_r/a_m = 0.70, b_r/b_m = 0.71) was found.

Table 3.2: End-members for the calculations of conservative mixing of ammonium (NH_4^+) concentrations. Seasonal samples. Sediment depths of all groundwater end-members are given as well as the distances from the sediment surface of the respective water column samples for the Puck Bay end-members.

	Samples	Groundwater end-member			Puck Bay end-member		
		Sediment depth (cm)	Salinity	NH_4^+ (µmol L^{-1})	cm above the Sediment	Salinity	NH_4^+ (µmol L^{-1})
Groundwater lances	September 2009	24	1.1	479	1	7.2	3
	November 2009	28	2.4	5478	1	7.3	242
	February/March 2010	28	0.4	816	1	6.9	1
	May 2010	24	0.5	226	10 to 60	6.9	2
	October 2010	28	0.3	678	10 to 80	6.3	4
	Well 3m (Oct. 2010)	300	0.0	27	10 to 80	6.3	4
	Well 180m (Oct. 2010)	18,000	0.0	33	10 to 80	6.3	4
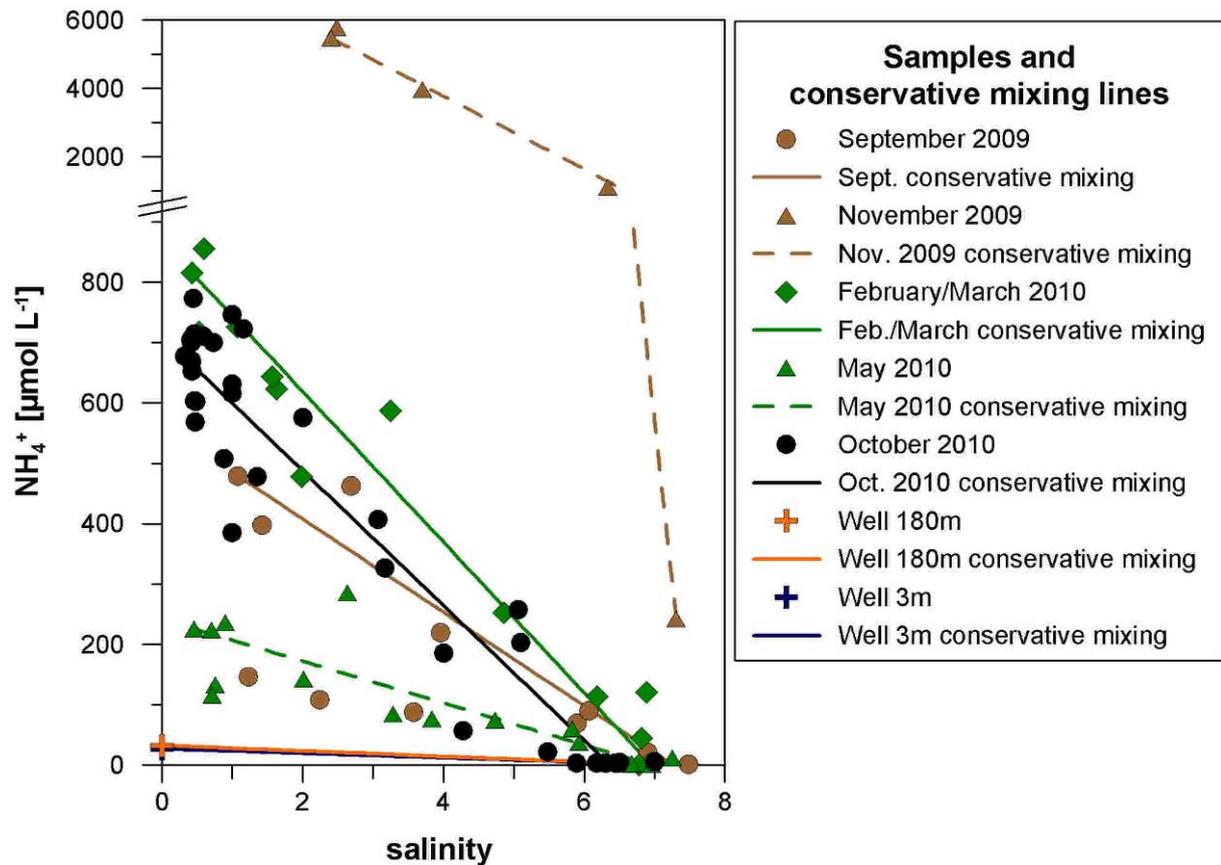
Figure 3.2: Ammonium (NH_4^+) concentrations over salinity. Two wells sampled in October 2010 (3 m deep **+**, 180 m deep **+**) and groundwater lances sampled in September 2009 (●), November 2009 (▲), March 2010 (◆) May 2010 (▲) and October 2010 (●). Conservative mixing lines for pore water of every month and the two wells. For end-members see Table 3.2. Note break in y-axis.

Table 3.3: Comparison of regression lines calculated from conservative end-member mixing and sample data for groundwater lances. Equation for regressions: $y = ax + b$. a (slope) and b are given for all equations. Subscript m indicates the mixing calculation and r the sample regression line. For sample regression lines r^2 and number (nb.) of samples are given in addition. r^2 for all end-member mixing regressions is 1. a_r/a_m shows the relation of the slope of the sample regression to that of the mixing calculation.

	Samples	Mixing calculation		Sample regression line				a_r/a_m	b_r/b_m
		a_m	b_m	a_r	b_r	r_r^2	nb. of samples		
Groundwater lances	September 2009	-77.4	562.5	-54.5	398.7	0.57	12	0.70	0.71
	November 2009	-1067.5	8041.2	-1116.5	8275.0	0.99	5	1.05	1.03
	February/March 2010	-124.9	869.1	-114.9	835.8	0.95	13	0.92	0.96
	May 2010	-34.7	241.6	-30.3	219.1	0.71	16	0.87	0.91
	October 2010	-111.7	711.5	-112.9	718.4	0.93	38	1.01	1.01
Well 3m (Oct. 2010)		-3.7	26.8						
Well 180m (Oct. 2010)		-4.6	32.6						

3.2 Spatial variability

The depth profiles of lances sampled in transects perpendicular to the shore line during May and October 2010 showed the spatial variability (Figures 3.3 and 3.4). The May transect was about 30 m long whereas the two October transects were each about 15 m long. For positions of lances see Figure 2.4.
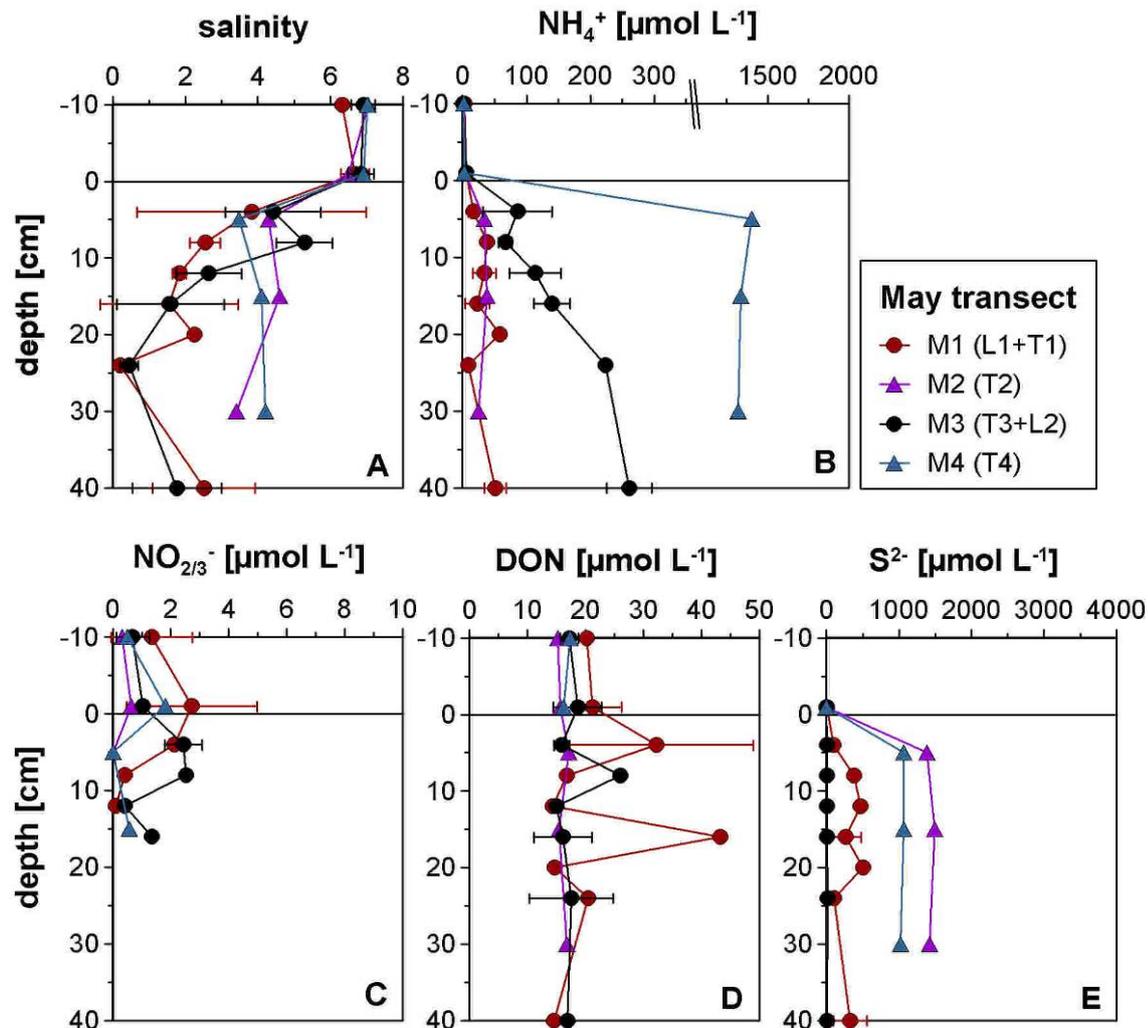
Figure 3.3: Depth profiles of lances sampled in a transect perpendicular to the shore line in May 2010. Salinity (A), ammonium (NH_4^+) (B), sum of nitrite and nitrate ($NO_{2/3}^-$) (C), dissolved organic nitrogen (DON) (D) and sulphide (S^{2-}) (E). Horizontal lines at 0 cm depth indicate the sediment surface. Adjacent lances with similar values were pooled. Means and standard deviations are given. For positions of lances see Figure 2.4. M1=T1+L1 (●), M2=T2 (▲), M3=T3+L2 (●), M4=T4 (▲). Note break in x-axis of 3.3B.

Adjacent lances with similar depth profiles were pooled for illustrations. *M* depicts for areas of pooled lances during May 2010, *O* for those areas during October 2010. M1 contains lances L1 and T1 and M3 is the mean of lances L2 and T3 sampled in May 2010. M2 includes only the push pull lance T2 and M4 only T4. The two groundwater lances L1 and L2 sampled in October 2010 are combined to O2. O1 includes the two push pull lances T2 and T4

positioned closest to the shore line. O3 is the mean of the push pull lances T1, T3, T5 and T6 which were positioned farthest away from the shore line.
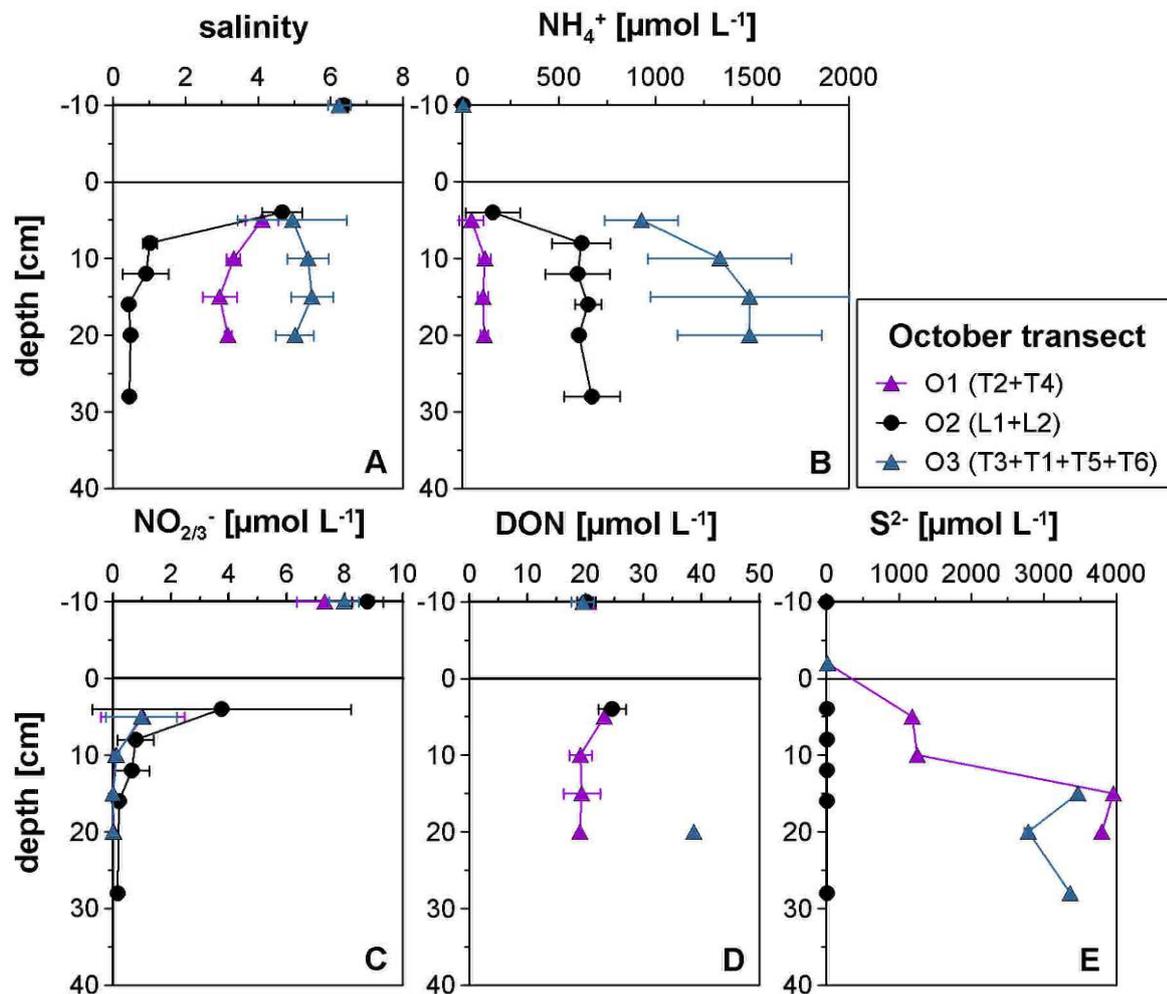
Figure 3.4: Depth profiles of lances sampled in two transects perpendicular to the shore line in October 2010. Water column samples were taken on every position from 10 cm above the sediment. Salinity (A), ammonium (NH_4^+) (B), sum of nitrite and nitrate ($NO_{2/3}^-$) (C), dissolved organic nitrogen (DON) (D) and sulphide (S^{2-}) (E). Horizontal lines at 0 cm depth indicate the sediment surface. Adjacent lances with similar values were pooled. Means and standard deviations are given. For positions of lances see Figure 2.4. O1=T2+T4 (▲), O2=L1+L2 (●), O3=T3+T1+T5+T6 (▲)

During May 2010 (Figure 3.3) salinities decreased at station M1 and M3 down to 0.2, whereas at station M2 and M4 lowest salinities were 3.4. M4 showed highest ammonium concentrations to 1400 µmol L^{-1} within the first 5 cm of the sediment. Highest concentrations in samples from M3 reach 220 µmol L^{-1}. Concentrations in M1 and M2 were lower, reaching only 11 and 38 µmol L^{-1}, respectively. $NO_{2/3}^-$ concentrations remained under 5 µmol L^{-1}. The highest concentrations were found in the first centimetres of the sediment. DON concentrations showed a high variability over depth and no linear trend with increasing depth. Values range from 10 to 50 µmol L^{-1}. Sulphide concentrations exceeded 1000 µmol L^{-1} at M2

and M4 at sites with salinities >3.4. Samples of M1 also contained high sulphide concentrations of up to 500 µmol L^{-1} while concentrations at M3 did not exceed 10 µmol L^{-1}. In general, transects sampled during October 2010 (Figure 3.4) showed a similar pattern as the one in May. Over all there was a decrease of salinity with increasing depth. The lowest salinity of 0.4 was found at site O2. At site O1 the salinity decreased down to 3 and at site O3 to 5. The ammonium concentrations were increasing with depth and from O1 (50 µmol L^{-1}) to O3 (on average 1500 µmol L^{-1}). They are altogether higher than during May 2010. $NO_{2/3}^{-}$ concentrations were very similar at all sampling sites. They were about 8 in the water column and decreased with depth being smaller than 1 µmol L^{-1} 10 cm deep in the sediment. DON has only been analyzed of a few samples. At O1 and O2 samples varied between 17 and 27 µmol L^{-1}. The only available pore water DON concentration for site O3 at 20 cm depth was 39 µmol L^{-1} and two fold higher than the water column concentration of 19 µmol L^{-1}. Sulphide concentrations were below 10 µmol L^{-1} in samples from O2, but reach 2 to 4 mmol L^{-1} at sites O1 and O3.

Table 3.4: End-members for the calculations of conservative mixing of ammonium (NH_4^+) concentrations. Transects in May and October 2010. Sediment depths of all groundwater end-members are given as well as the distances from the sediment surface of the respective water column samples for the Puck Bay end-members. *Groundwater end-member is the 180 m deep well sampled in October 2010 since this well was not sampled in May 2010.

Samples	Groundwater end-member			Puck Bay end-member		
	Sediment depth (cm)	Salinity	NH_4^+ (µmol L^{-1})	cm above the Sediment	Salinity	NH_4^+ (µmol L^{-1})
M1 (L1+T1)	28	0.2	8	10 to 60	6.9	2
M2 (T2)	30	3.4	25	10 to 60	6.9	2
M3 (L2+T3)	30	0.2	222	10 to 60	6.9	2
M4 (T4)	5	3.5	1404	10 to 60	6.9	2
O1 (T2+T4)	15	2.6	125	10 to 80	6.3	4
O2 (L1+L2)	28	0.3	678	10 to 80	6.3	4
O3 (T1+T3+T5+T6)	5	2.7	1181	10 to 80	6.3	4
Well 3m (May 2010)	300	0.0	40	10 to 80	6.9	2
Well 180m (May 2010)	18,000	0.0*	33*	10 to 80	6.9	2
Well 3m (Oct. 2010)	300	0.0	27	10 to 80	6.3	4
Well 180m (Oct. 2010)	18,000	0.0	33	10 to 80	6.3	4

(Transect sites: M1–O3 grouped under "Transect sites")

The mixing behaviour of the ammonium concentrations from the lances in transects was shown in the same way as for the seasonal samples (Figures 3.5 and 3.6). Puck Bay end-members were calculated from the mean values of all water column samples taken in May and October 2010, respectively. As groundwater end-members values from both wells and pore water samples with the lowest salinity at each site M and O were used (Table 3.4). The 180 m deep well was not sampled during May 2010. Therefore the conservative mixing line was calculated with the values from October 2010 as groundwater end-member for the 180 m deep well. At no site ammonium concentrations were mixed as predicted from the conservative mixing lines using one or the other well as groundwater end-member.

Table 3.5: Comparison of regression lines calculated from conservative end-member mixing and sample data for transects of May and October 2010. Equation for regressions: $y = ax + b$. a (slope) and b are given for all equations. Subscript m indicates the mixing calculation and r the sample regression line. For sample regression lines r^2 and number (nb.) of samples are given in addition. r^2 for all end-member mixing regressions is 1. a_r/a_m shows the relation of the slope of the sample regression to that of the mixing calculation. *Groundwater end-member from well sample taken in October 2010.

Samples	Mixing calculation		Sample regression line				a_r/a_m	b_r/b_m
	a_m	b_m	a_r	b_r	r_r^2	nb. of samples		
M1 (L1+T1)	-1.0	8.6	-3.6	35.2	0.22	19	3.72	4.10
M2 (T2)	-6.6	47.5	-9.2	67.8	0.77	6	1.39	1.43
M3 (L2+T3)	-32.8	228.6	-31.1	226.0	0.77	22	0.95	0.99
M4 (T4)	-409.2	2827.8	-431.6	3037.9	0.99	6	1.05	1.07
O1 (T2+T4)	-32.7	210.6	-32.6	206.5	0.74	12	1.00	0.98
O2 (L1+L2)	-111.7	711.5	-112.9	718.4	0.93	38	1.01	1.01
O3 (T1+T3+T5+T6)	-323.9	2055.2	-510.9	3723.3	0.39	24	1.58	1.81
Well 3m (May 2010)	-5.5	39.8						
Well 180m (May 2010)*	-4.4	32.6						
Well 3m (Oct. 2010)	-3.7	26.8						
Well 180m (Oct. 2010)	-4.6	32.6						

(The first seven data rows are labelled "Transect sites" on the left, split into M sites and O sites.)

In the same way as for the seasonal samples above, the linear regression lines for the data points from transects were calculated and compared to the respective conservative mixing lines (Table 3.5). During May the sampling regression lines and conservative mixing lines were quiet similar with a_r/a_m and b_r/b_m close to 1. However, data of M3 scattered a lot with r_r^2 being 0.77. Also data of M1, the site nearest to the shore line, showed high variations. The

respective sample regression line had an r_r^2 of only 0.22 and differed greatly from the calculated conservative mixing line.
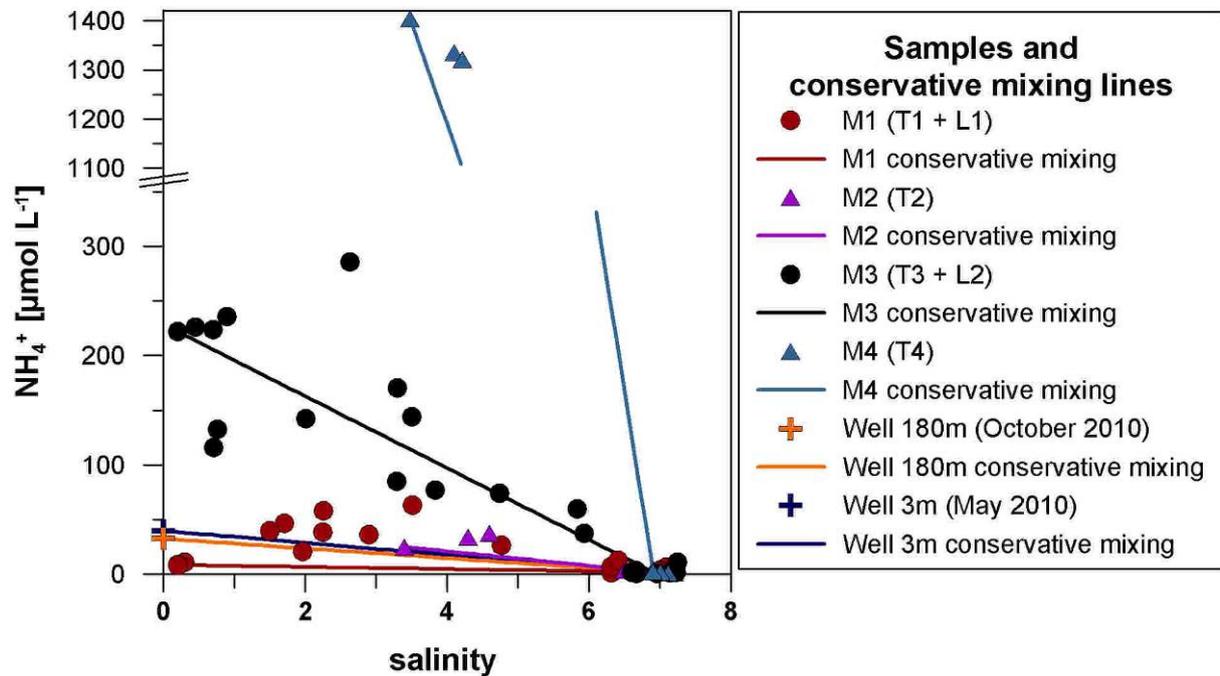
Figure 3.5: Ammonium (NH_4^+) concentrations over salinity. Lances sampled in a transect perpendicular to the shore line in May 2010. M1 (●), M2 (▲), M3 (●) and M4 (▲).3m deep well sampled in May 2010(+), 180 m deep well sampled in October 2010(+).For positions of lances see Figure 2.4. Conservative mixing lines for pore water of every site M and the two wells. For end-members see Table 3.4. Note break in y-axis.

During October the mixing of ammonium concentrations was mostly conservative at site O1 and O2 despite some scatter. They both showed the highest similarities of sample regression and conservative mixing lines of all sites in transects sampled during May and October 2010. O2 had the best r_r^2 of 0.93 in October. At O3, the site farthest away from the shore in October, the slope of the sampling regression line was steeper than that of the conservative mixing line and b_r is greater than b_m. Therefore ammonium concentrations were higher than the values calculated from the pore water with the lowest salinity.
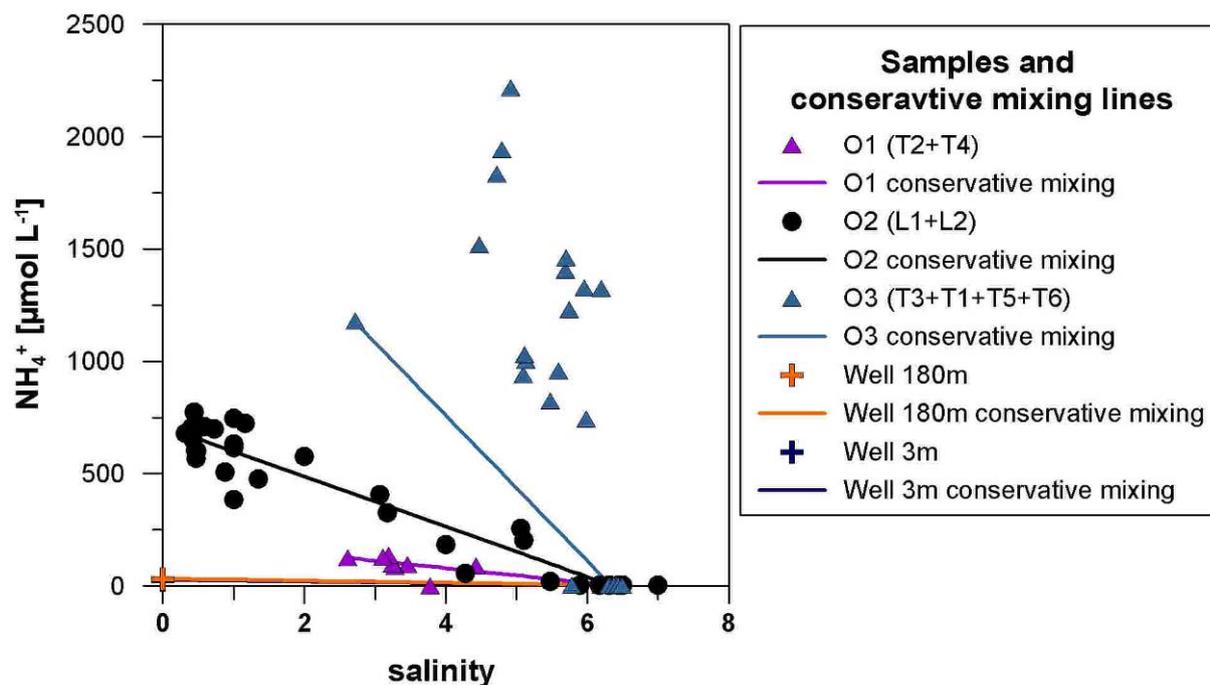
Figure 3.6: Ammonium (NH_4^+) concentrations over salinity. Lances sampled in two transects perpendicular to the shore line in October 2010. O1 (▲), O2 (●) and O3 (▲).3m deep well (+) and 180 m deep well (+) both sampled in October 2010. For positions of lances see Figure 2.4. Conservative mixing lines for pore water of every site O and the two wells. For end-members see Table 3.4.

3.3 $\delta^{15}N$ values of ammonium

To specify the source of $\delta^{15}N$-NH_4^+ values are presented and seasonally (Figure 3.7) and spatially (Figure 3.8 and 3.9) compared.

Table 3.6: End-members for the calculations of conservative mixing of $\delta^{15}N$-NH_4^+ values. Seasonal samples. Sediment depths of all groundwater end-members are given as well as the distances from the sediment surface of the respective water column samples for the Puck Bay end-members. There were no $\delta^{15}N$-NH_4^+ values available for February/March 2010.

	Samples	Groundwater end-member			Puck Bay end-member		
		Sediment depth (cm)	Salinity	$\delta^{15}N$ (‰)	cm above the Sediment	Salinity	$\delta^{15}N$ (‰)
Groundwater lances	September 2009	24	1.1	1.9	-4	6.1	2.5
	November 2009	28	2.4	1.0	1	7.3	1.3
	February/March 2010	-	-	-	-	-	-
	May 2010	24	0.5	5.4	10 to 60	6.9	10.6
	October 2010	28	0.3	1.4	10 to 80	6.3	7.1
Well 3m (Oct. 2010)		300	0.0	9.6	10 to 80	6.3	7.1
Well 180m (Oct. 2010)		18,000	0.0	0.2	10 to 80	6.3	7.1
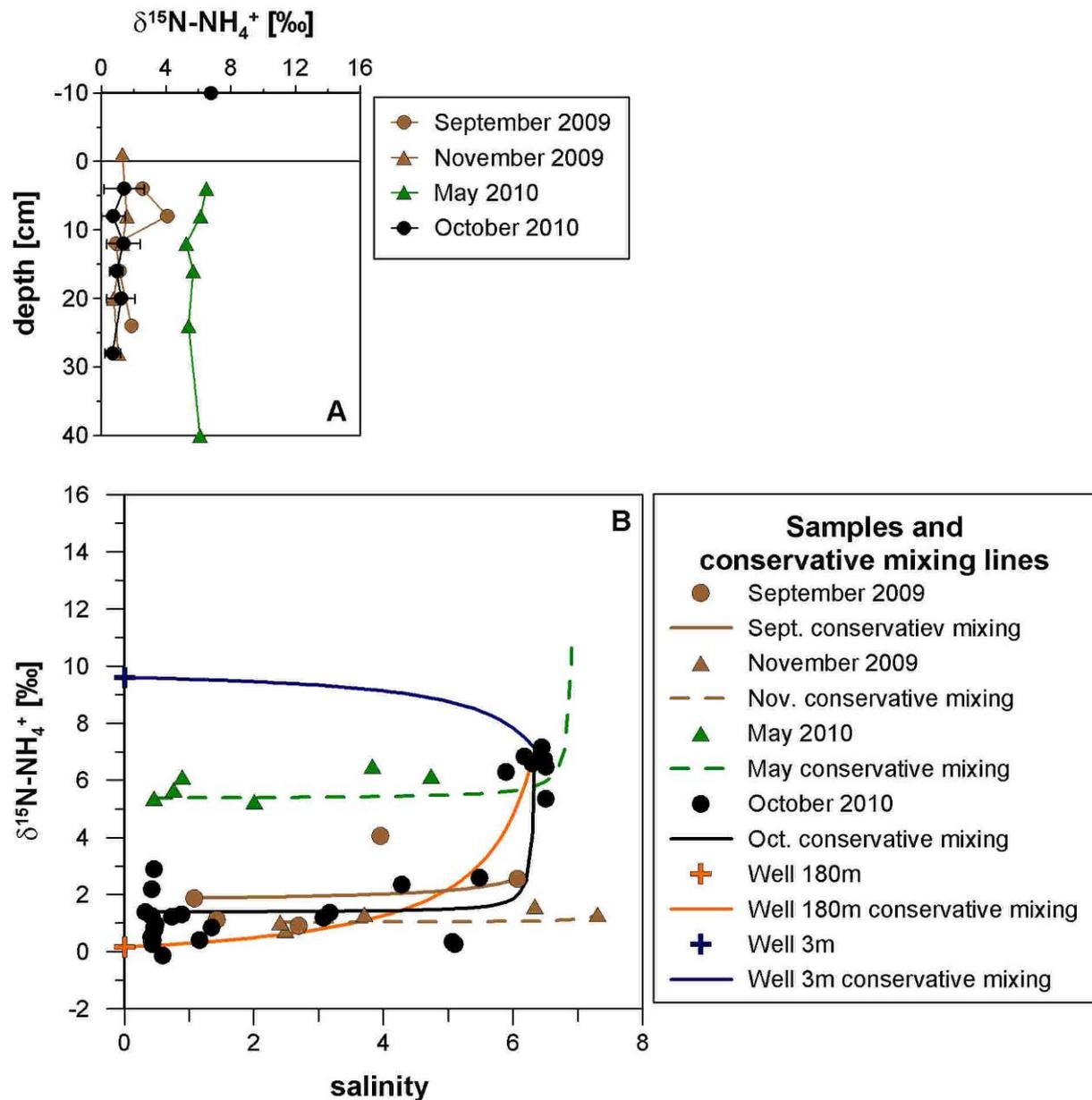
Figure 3.7: δ^{15}N-NH$_4^+$ values for September 2009 (●), November 2009 (▲), May 2010 (▲), October 2010 (●). **A:** Depth profiles. **B:** δ^{15}N-NH$_4^+$ over salinity. Samples and conservative mixing lines for the different seasons and the two sampled wells.

The seasonal comparison of all depth profiles of δ^{15}N-NH$_4^+$ values showed little differences with values mostly between 1 and 2 ‰ in the sediment (Figure 3.7A). Only the May depth profile showed higher δ^{15}N-NH$_4^+$ values of about 6 ‰. δ^{15}N-NH$_4^+$ value measured in the water column during October 2010 was higher than in the pore water with a value of 6.8 ‰. There were no δ^{15}N-NH$_4^+$ values available for the February/March campaign. δ^{15}N-NH$_4^+$ values plotted over salinity can give additional information about the mixing behaviour of ammonium from SGD and the source (Figure 3.7B). The theoretical conservative mixing lines were calculated with end-members in a similar way as for the mixing of ammonium concentrations (Table 3.6). The δ^{15}N-NH$_4^+$ value of the 3 m deep well was the highest of all

values found in the seasonal groundwater samples (9.6 ‰). The 180 m deep well had a δ^{15}N-NH_4^+ value of 0.16 ‰, more similar to the pore water samples. However, as shown above the ammonium concentrations of both wells were much lower than those of the pore water. Thus the mixing behaviour could not be described using one of the wells as groundwater end-member. δ^{15}N-NH_4^+ values of the SGD were conservatively mixed with low salinity pore water as end-member. There was some scatter in the September 2009 data (at salinities of 2 to 5) and also in the October 2010 data (at salinities of 0 to 2 and 4 to 6).

Table 3.7: End-members for the calculations of conservative mixing of δ^{15}N-NH_4^+ values. Transects in May and October 2010. Sediment depths of all groundwater end-members are given as well as the distances from the sediment surface of the respective water column samples for the Puck Bay end-members. *Groundwater end-member is the 180 m deep well sampled in October 2010 since this well was not sampled in May 2010.

	Groundwater end-member			Puck Bay end-member		
Samples	Sediment depth (cm)	Salinity	δ^{15}N (‰)	cm above the Sediment	Salinity	δ^{15}N (‰)
M1 (L1+T1)	40	1.5	12.4	10 to 60	6.9	10.6
M2 (T2)	30	3.4	13.4	10 to 60	6.9	10.6
M3 (L2+T3)	30	0.2	4.6	10 to 60	6.9	10.6
M4 (T4)	5	3.5	1.4	10 to 60	6.9	10.6
O1 (T2+T4)	15	2.6	6.2	10 to 80	6.3	7.1
O2 (L1+L2)	28	0.3	1.4	10 to 80	6.3	7.1
O3 (T1+T3+T5+T6)	5	2.7	0.7	10 to 80	6.3	7.1
Well 3m (May 2010)	300	0.0	9.8	10 to 60	6.9	10.6
Well 180m (May 2010)	18,000	0.0*	0.2*	10 to 60	6.9	10.6
Well 3m (Oct. 2010)	300	0.0	9.6	10 to 80	6.3	7.1
Well 180m (Oct. 2010)	18,000	0.0	0.2	10 to 80	6.3	7.1

(Transect sites: M1, M2, M3, M4, O1, O2, O3)

δ^{15}N-NH_4^+ values are also shown for the transects sampled in May and October 2010 (Figures 3.8 and 3.9, for end-members see Table 3.7). In May δ^{15}N-NH_4^+ values along the transect were decreasing from M1 to M4 (Figure 3.8A). They remained mostly the same over sediment depth. δ^{15}N-NH_4^+ values of sites M1 and M2 were similar to values of the water column (10.8 ‰). M2 was not conservatively mixed (Figure 3.8B). Data from M1 and M3 were very scattered around their conservative mixing lines. δ^{15}N-NH_4^+ values of M4 samples were conservatively mixed as calculated using low salinity pore water as end-member.
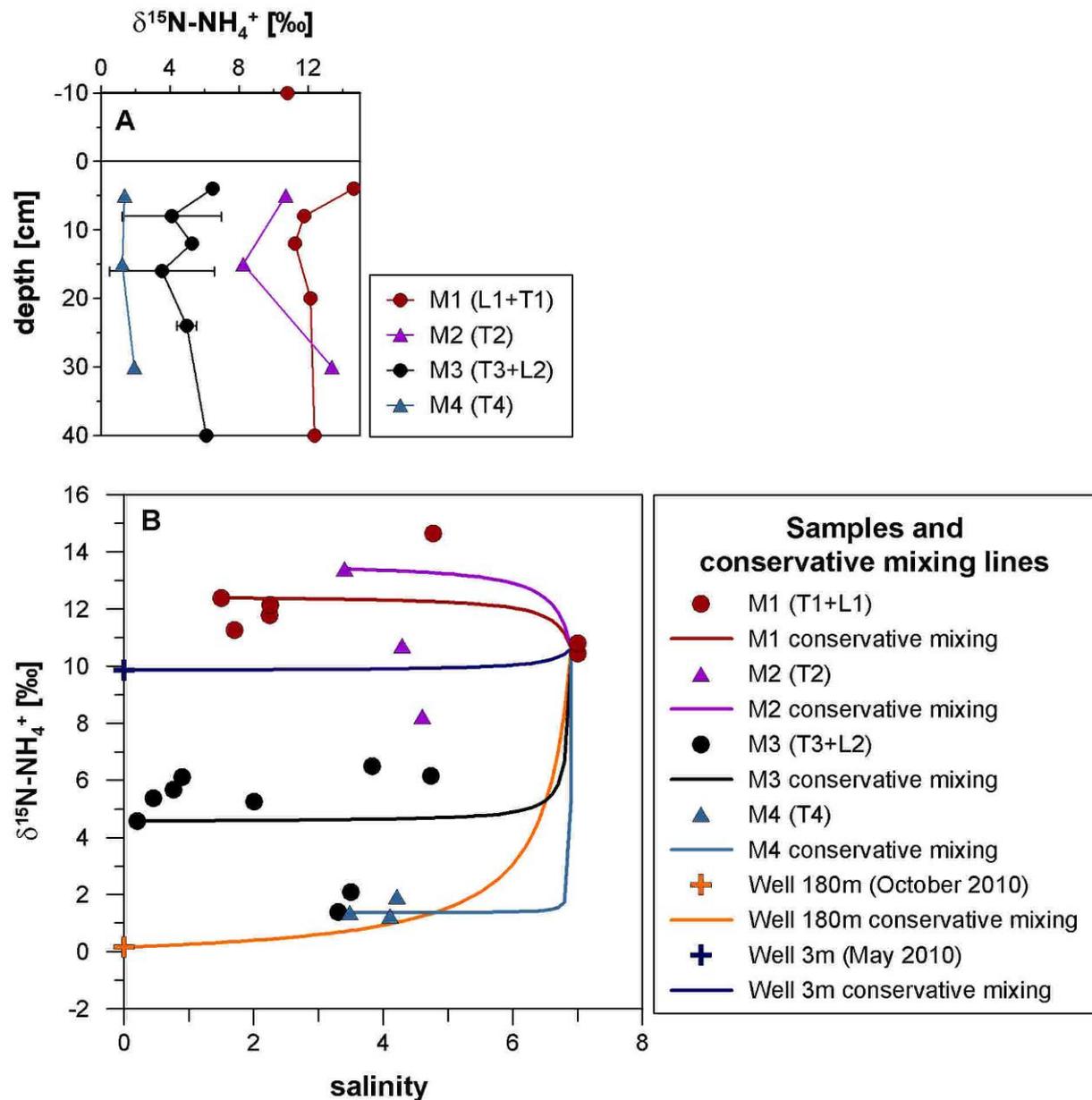
Figure 3.8: $\delta^{15}N$-NH_4^+ values of sampled May transect. Adjacent lances with similar values were pooled. M1 (●), M2 (▲), M3 (●) and M4 (▲). **A:** Depth profiles. **B:** $\delta^{15}N$-NH_4^+ over salinity. Samples and conservative mixing lines for pore waters and the two sampled wells.

Samples of sites O2 and O3 taken in transects in October contained ammonium with similar $\delta^{15}N$ values lower than 2 ‰ which remained constant over sediment depth (Figure 3.9A). $\delta^{15}N$-NH_4^+ values at site O1 were all higher than 3 ‰. They were on average 6.8 ‰ in the water column. $\delta^{15}N$-NH_4^+ values over salinity showed that samples from site O3 were conservatively mixed as calculated from O3 pore water (Figure 3.9B). The same accounts for site O2 although data were more scattered. $\delta^{15}N$-NH_4^+ values from site O1 seemed not conservatively mixed.

No data of any site M or O did fit the conservative mixing line calculated using the 3 m deep well as groundwater end-member. $\delta^{15}N$-NH_4^+ values from M4 were very similar to the

conservative mixing line of 180 m deep well (Figure 3.8B). Also data of O2 and O3 were relatively close to that mixing line (Figure 3.9B) However ammonium concentrations of that sites were much higher than that of the deep well (Figures 3.5 and 3.6).
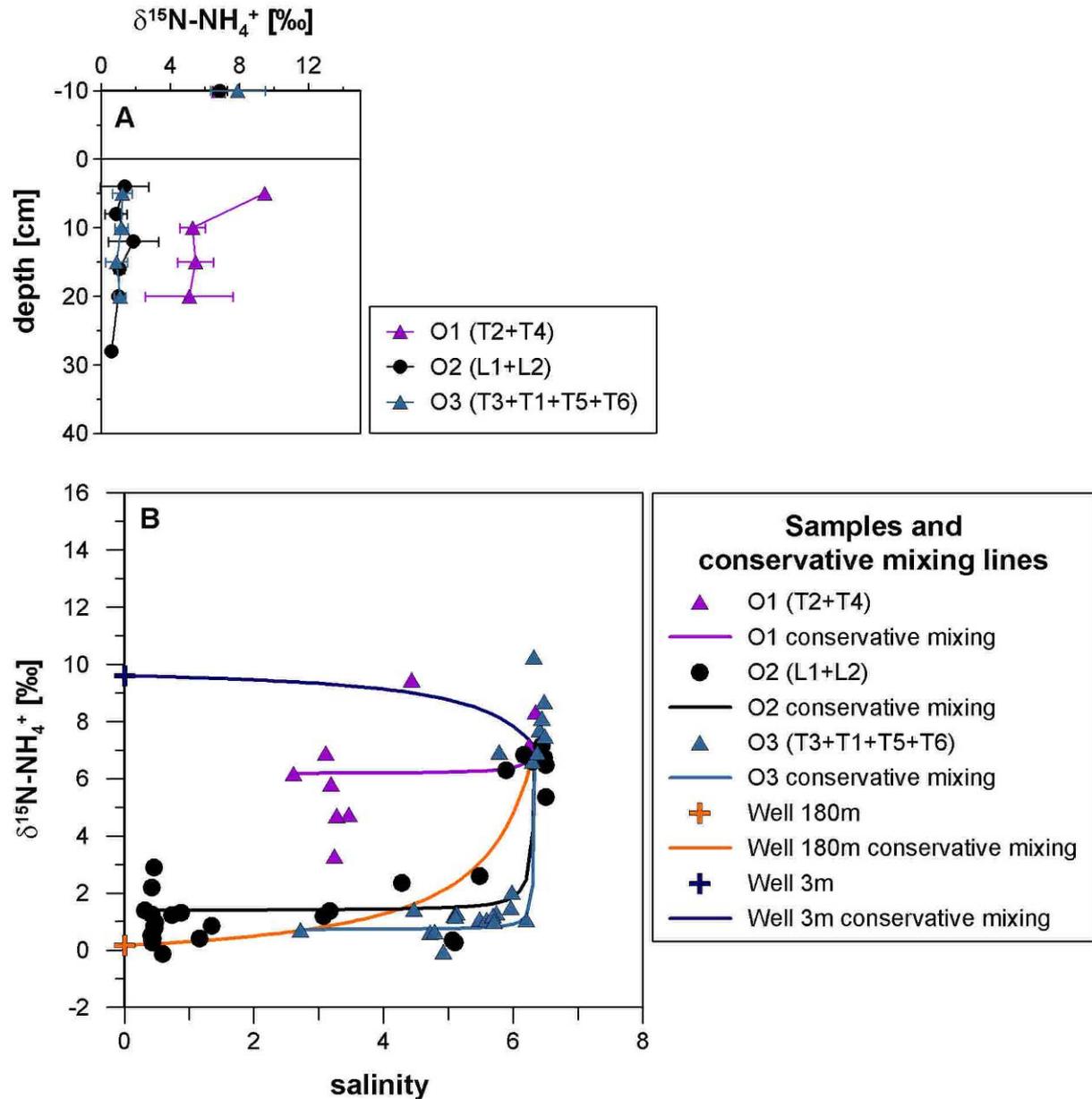
Figure 3.9: δ^{15}N-NH$_4^+$ values of sampled October transects. Adjacent lances with similar values were pooled. O1 (▲), O2 (●) and O3 (▲). **A:** Depth profiles. **B:** δ^{15}N-NH$_4^+$ over salinity. Samples and conservative mixing lines for pore waters and the two sampled wells.

3.4   Comparison of SGD influenced sites with a Baltic Sea station
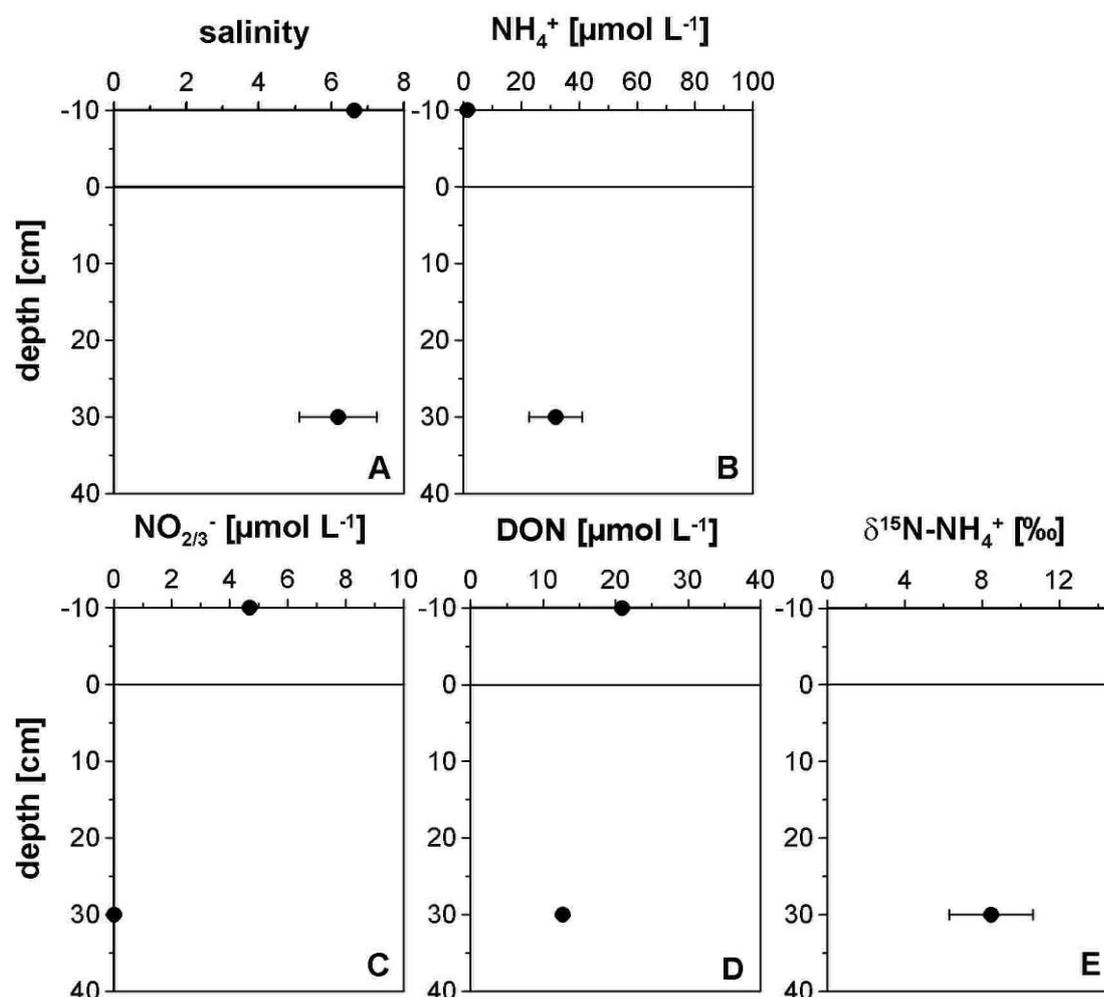
Figure 3.10: Depth profiles of salinity (A), ammonium (NH_4^+) (B), sum of nitrite and nitrate ($NO_{2/3}^-$) (C), dissolved organic nitrogen (DON) (D) and $\delta^{15}N$-NH_4^+ values (E) from the Baltic Sea side taken during October 2010. Horizontal lines at 0 cm depth indicate the sediment surface.

During October 2010 samples were taken from the Baltic Sea side of Hel for comparison with a potentially groundwater unaffected site (Figures 1.2 and 3.10). Pore water samples were taken only from 30 cm depth at two different spots about 5 m apart from each other. Salinities at the surface waters and in the sediment were very similar. Ammonium concentrations remained low, only reaching a mean of 32 μmol L^{-1}. $NO_{2/3}^-$ concentrations in the water column were with 4.7 μmol L^{-1} lower than in the Puck Bay water column (7.5 μM). No $NO_{2/3}^-$ was found in 30 cm depth of the sediment. DON concentrations were lower in the sediment (12.6 μmol L^{-1}) than in the water column (20.8 μmol L^{-1}). $\delta^{15}N$-NH_4^+ values in the sediment were about 8.5 ‰ and therefore higher than in the water column of the Puck Bay during October 2010 (6.8 ‰).

3.5 Benthic Chambers

To estimate the rate of SGD in Hel and the associated input of ammonium, experiments with benthic chambers were carried out during October 2010.
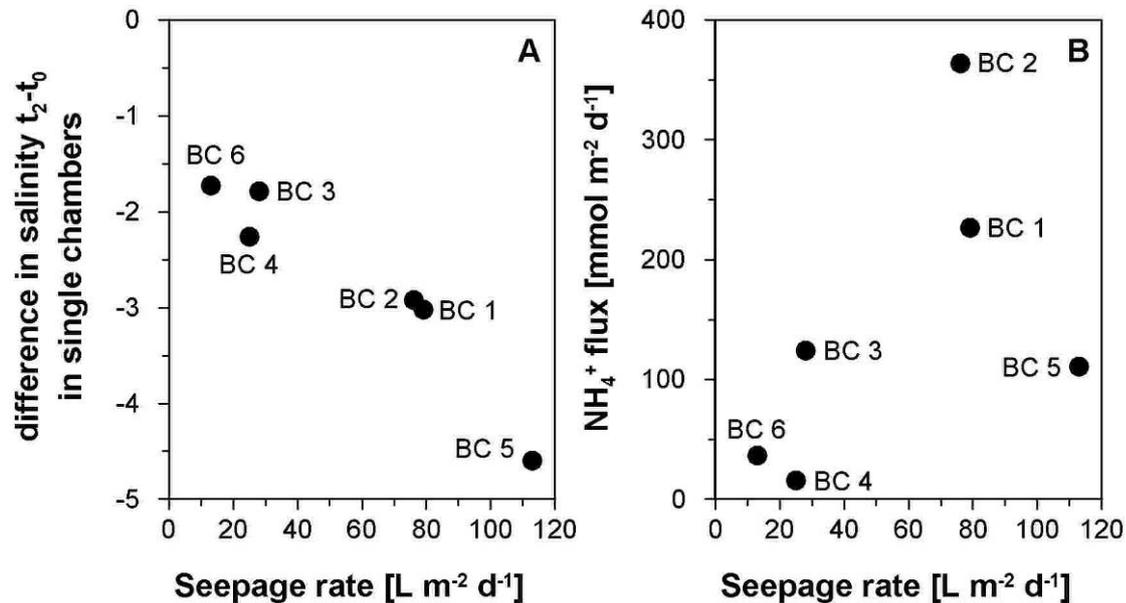
Figure 3.11: Difference in salinity t_2-t_0 [units d^{-1}] (**A**) and ammonium (NH_4^+) flux at the sediment water interface [mmol m^{-2} d^{-1}] (**B**) over seepage rates [L m^{-2} d^{-1}] from 6 benthic chamber experiments during October 2010. Number of benthic chamber (BC) is given for every data point. Start of incubation t_0: October 6th at 15.45. End of incubation t_2: October 7th at 16.30.

Seepage rates, calculated by Susann Vogler, occurred with a high variability differing from 13 to 113 L m^{-2} d^{-1} (Table 3.8). Salinities in the benthic chambers were stronger decreasing with higher seepage rates (Figure 3.11A). At the highest seepage rate salinity decreased about 4.6 units. Ammonium concentrations were increasing in the benthic chambers during the experiment (Figure 3.11B). However they did not show such a clear relation to seepage rates as salinities. Lowest flux rates of 15.8 and 36.3 mmol m^{-2} d^{-1} were measured at the lowest seepage rates of 25 and 13 L m^{-2} d^{-1}. The highest ammonium flux of 363.8 mmol m^{-2} d^{-1} occurred at a seepage rate of 76 L m^{-2} d^{-1}. At the highest seepage rate of 113 L m^{-2} d^{-1} the ammonium flux was relatively low being only 110.6 mmol m^{-2} d^{-1}.

Table 3.8: Seepage rates of the 6 benthic chambers (BC) from October 2010.

	L m^{-2} d^{-1}
BC 1	79
BC 2	76
BC 3	28
BC 4	25
BC 5	113
BC 6	13
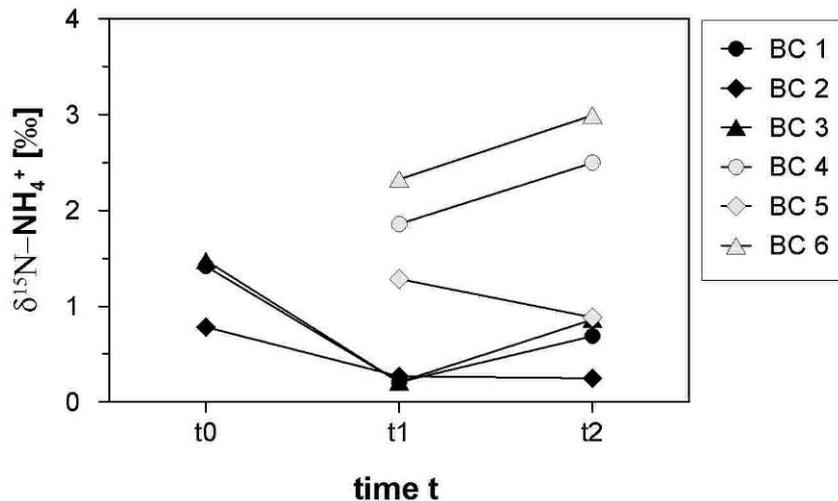
Figure 3.12: Changes in ammonium δ^{15}N values in the benthic chambers (BC) during the incubation. BC 1 (●), BC 2 (■), BC 3 (▲), BC 4 (○), BC 5 (□) and BC 6 (Δ). For respective seepage rates see table 3.8. Start of incubation t_0: 6th of October at 15.45. End of incubation t_2: 7th of October at 16.30.

δ^{15}N-NH$_4^+$ values during the benthic chamber incubations were measured as well (Figure 3.12). δ^{15}N-NH$_4^+$ values in the chambers 1 to 3 were between 0.8 ‰ and 1.5 ‰. Those three chambers also showed the highest ammonium flux rates (table 3.8, figure 3.11B). δ^{15}N-NH$_4^+$ values were further decreasing during the dark incubation t_0 to t_1 (from 15.45 till 08.05) to about 0.2 ‰. During the subsequent light incubation t_1 to t_2 (from 08.05 till 16.30) δ^{15}N-NH$_4^+$ values were slightly increasing again in chamber 1 and 3. In chamber 2 the δ^{15}N-NH$_4^+$ values remained the same. This chamber had by far the highest ammonium flux rate (Figure 3.11B). In chamber 4 to 6 δ^{15}N-NH$_4^+$ values were higher at the end of the dark incubation at 08.05 am than in the other three chambers and more variable. Values were highest in chamber 6 (2.3 ‰) and 4 (1.9 ‰). Those two chambers also showed the lowest seepage rates and lowest ammonium flux (Table 3.8, Figure 3.11B). δ^{15}N-NH$_4^+$ values were increasing in both chambers during the light incubation from 08.05 to 16.30. Benthic chamber 5 had the highest seepage rates but low ammonium flux. The δ^{15}N-NH$_4^+$ value at the end of the dark incubation was 1.3 ‰ and decreased during the light incubation down to 0.9 ‰.

3.6   Core incubation experiment in the laboratory

To quantify the nitrification potential at the SDG in Hel core experiments were conducted (Figure 3.13, Table 3.9). Data points in Figure 3.13 are plotted according to Mariotti et al. (1981) to determine the isotope enrichment factor $\varepsilon_{p/s}$.
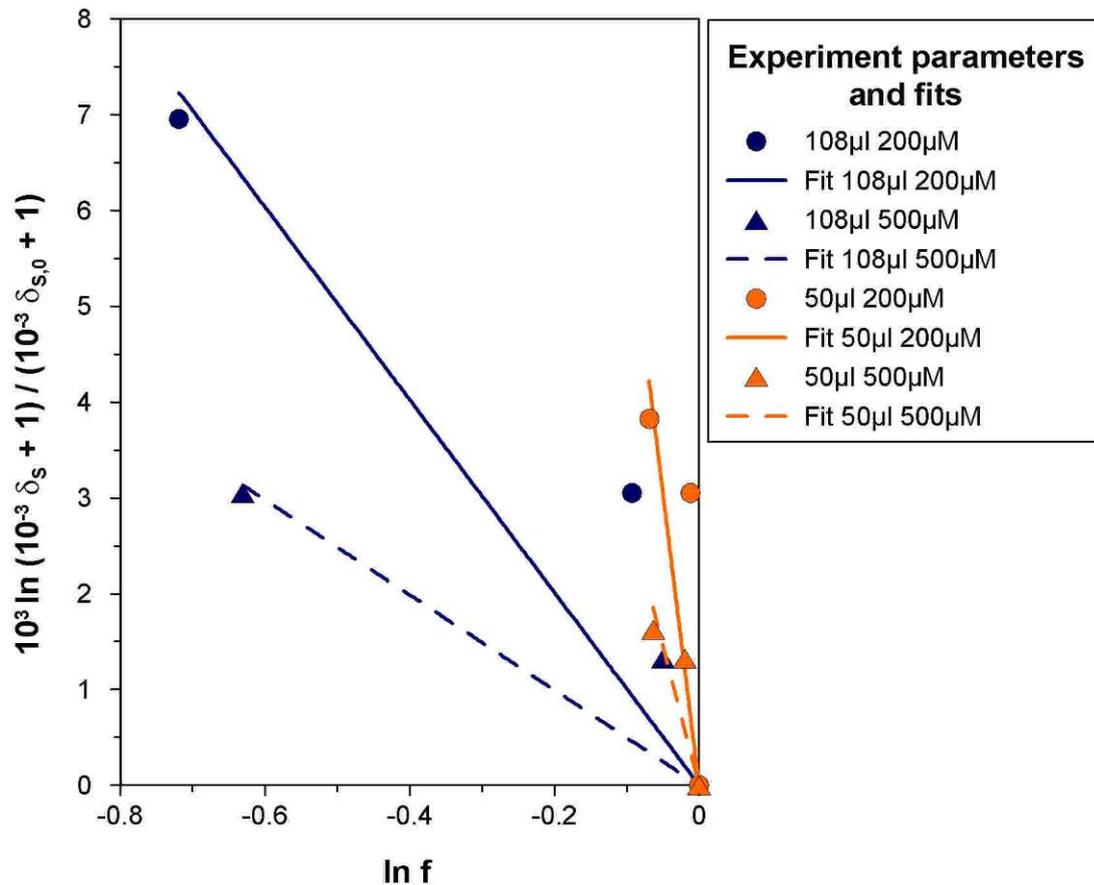
Figure 3.13: Change in ammonium $\delta^{15}N$ (substrate) as a function of ln f during the incubation experiments. Two different seepage rates (108 amd 50 µl min^{-1}) with two different ammonium concentrations (200 and 500 µmol L^{-1}) in each seeping solution are shown. The slopes in the regression line are the isotopic enrichment factors $\varepsilon_{p/s}$. Note that every regression line was calculated from only 3 data points, respectively. For f see Equation 2.2.b.

Table 3.9: Nitrate concentrations and O_2 saturation at the start and end of experiments and Enrichment factors $\varepsilon_{p/s}$ obtained from the core experiments. The mean $\varepsilon_{p/s}$ calculated from all data pints is given as well.

seepage rate (µl/min)	concentration of solution (µM)	Nitrate (µM) at the end	O_2 saturation at the start (%)	O_2 saturation at the end (%)	$\varepsilon_{p/s}$
108	200	> 1	91.3	31.5	-10.1
108	500	> 1	91.3	31.5	-5.0
50	200	> 1	85.9	12.6	-61.0
50	500	> 1	85.9	12.6	-29.1
over all					-8.2

The conducted experiments show very different results. The increase in ammonium δ^{15}N with decreasing concentrations is never linear. During the two experiments with a seepage rate of 108 µl min^{-1} the ammonium concentration declined by more than 50 %. δ^{15}N values of ammonium increased. The experiment conducted with a start concentration of 200 µmol L^{-1} ammonium showed the highest decrease in ammonium concentration and the highest increase in ammonium δ^{15}N values.

With a solution of 500 µmol L^{-1} at 108 µl min^{-1} the relative decrease in concentration is only slightly smaller but the increase in the δ^{15}N value is only half the value gained with the 200 µmol L^{-1} solution. During both experiments with a seepage rate of 50 µl min^{-1} ammonium concentrations decreased about less than 10 %. Still the δ^{15}N were increasing but less than during the experiments with the same concentrations but higher seepage rate. Again the experiment conducted with 500 µmol L^{-1} ammonium showed half the increase in δ^{15}N of the one conducted with 200 µmol L^{-1}. During all experiments less than 1 µM Nitrate was accumulated (Table 3.9).

Oxygen saturation at the end of the experiment was 31.5 % at seepage rates of 108 µl min^{-1} and 12.6 % at seepage rates of 50 µl min^{-1}. Calculated enrichment factors differed from -5 ‰ to -61.0 ‰. At a seepage rate of 108 µl min^{-1} conducted with 500 µmol L^{-1} ammonium the lowest enrichment factor of -5.0 was calculated. The highest enrichment factor was calculated for the experiment with a seepage rate of 50 µl min^{-1} with 200 µmol L^{-1} ammonium.

3.7   Isotope values in biota

The following figures and tables show stable isotope ratios of sampled organisms from the SGD impacted and potentially unaffected sites to identify the influence of the ammonium derived from the SGD for the food web.

At the SGD impacted site POM showed the lowest δ^{15}N (3.6‰) and δ^{13}C (-25.0 ‰) values (Figure 3.14, Table 3.10). δ^{13}C in zooplankton was only slightly higher (-24.8 ‰) compared to POM, but δ^{15}N values were much higher (8.2 ‰). Unfortunately there were no δ^{15}N and δ^{13}C values available for Phytoplankton at this site. Phytobenthos samples, containing *Cladophora* species, *Enteromorpha compressa* and *Ulva lactua*, had δ^{15}N values between 4.4 and 5.1 ‰. δ^{13}C, however, were higher than the POM values and differed greatly between -20.8 and -14.3 ‰. Benthic animals showed a similar spectrum in δ^{13}C as phytobenthos. All benthic animals had higher δ^{15}N values than phytobenthos. At least 4 different groups with similar δ^{15}N values could be distinguished in the zoobenthos. The lowest values about 7 ‰ were found in *Mytilus spp.*, Amphipoda and Isopoda. The last two contained relatively high

δ^{13}C values about -18 ‰ quite similar to the macroalgae *Cladophora rupestris*. *Mytilus spp.* on the other hand showed lower δ^{13}C values of -22.6 ‰ more similar to the POM values. The second group consisted of *Balanus spp.*, *Neomysis integer*, Nudibranchia and Polychaeta. Their δ^{15}N values were about 9 ‰. All organisms within that group except for Polychaeta showed very similar δ^{13}C values of about -21 ‰ being only slightly higher than values found in *Mytilus spp.*. Polychaeta showed higher δ^{13}C of -19.5 ‰. *Crangon crangon* and *Platichthys flesus* belonged to the third group with δ^{15}N values of about 10 to 10.5 ‰. *Platichthys flesus* showed δ^{13}C values of 18.6 ‰ similar to Amphipoda. *Crangon crangon* contained the highest δ^{13}C values in the zoobenthos samples being -16.1 ‰. They were, however, still lower than the values measured within the macroalgae *Cladophora sp.* (-14.3 ‰). The highest δ^{15}N value was measured within samples from *Neogobius melanostromus* forming thus the fourth group. δ^{13}C values from this species were quite similar to those of the second group.
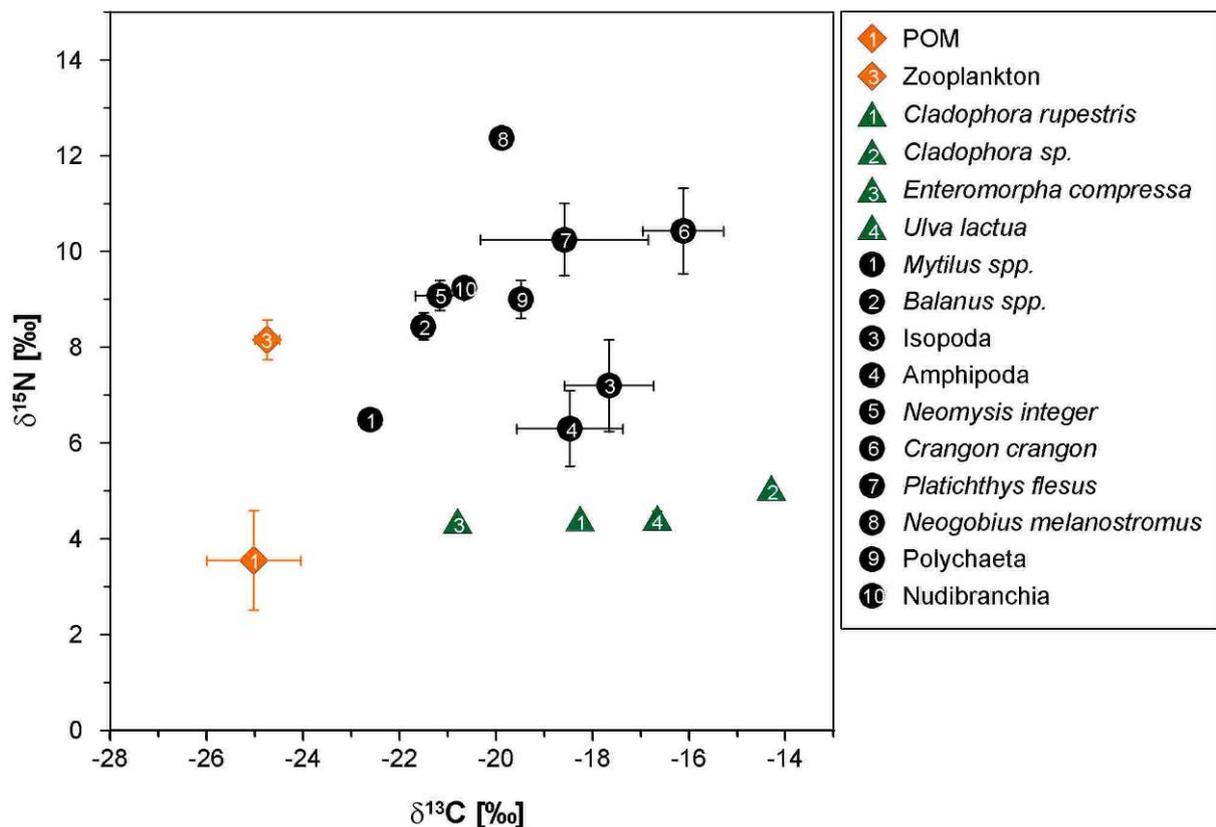
Figure 3.14: Isotope diagram (δ^{15}N vs. δ^{13}C) for organisms sampled during October 2010 in the submarine groundwater impacted area. Means with standard deviations are shown for particulate organic matter (POM) and plankton (◆), phytobenthos (▲) and zoobenthos (●).

Table 3.10: Organisms sampled during October 2010 in the submarine groundwater impacted area. Number of samples and means of isotope ratios with standard deviation are given.

Group/Species	nb.	δ^{15}N (‰)		δ^{13}C (‰)		C/N	
		mean	σ	mean	σ	mean	σ
POM	22	**3.5**	1.0	**-25.0**	1.0	**9.4**	0.6
Zooplankton (>55µm)	5	**8.2**	0.4	**-24.7**	0.3	**6.8**	2.4
Phytobenthos							
Cladophora rupestris	1	**4.4**		**-18.3**		**11.7**	
Cladophora sp.	1	**5.1**		**-14.3**		**16.1**	
Enteromorpha compressa	2	**4.4**	0.1	**-20.8**	0.0	**7.8**	0.1
Ulva lactua	2	**4.4**	0.1	**-16.7**	0.0	**7.7**	0.1
Zoobenthos							
Mytilus spp.	4	**6.5**	0.2	**-22.6**	0.2	**5.1**	0.3
Nudibranchia	2	**9.2**	0.0	**-20.7**	0.0	**5.0**	0.0
Polychaeta	2	**9.0**	0.4	**-19.5**	0.0	**4.9**	0.2
Balanus spp.	3	**8.4**	0.3	**-21.5**	0.1	**6.1**	0.3
Isopoda	6	**7.2**	1.0	**-17.7**	0.9	**7.2**	1.3
Amphipoda	14	**6.3**	0.8	**-18.5**	1.1	**5.4**	0.3
Neomysis integer	5	**9.1**	0.3	**-21.2**	0.5	**4.2**	0.1
Crangon crangon	8	**10.4**	0.9	**-16.1**	0.8	**4.5**	0.4
Platichthys flesus	4	**10.2**	0.8	**-18.6**	1.7	**3.9**	0.1
Neogobius melanostromus	1	**12.4**		**-19.9**		**5.2**	

POM values from samples of the Baltic Sea side had a lower δ^{13}C value but a higher mean δ^{15}N value than samples from the SGD impacted site (Figure 3.15, Table 3.11). Zooplankton showed very similar isotope values as in the samples from the SGD impacted site. The δ^{15}N values of phytoplankton were also very similar at both sites. δ^{13}C of phytoplankton in the Baltic Sea accounted for -22.9 ‰. The δ^{15}N of *Cladophora sp.*, the only macroalgae collected from the Baltic Sea was higher (6.3 ‰) than at the SGD impacted site (5.1 ‰). The δ^{13}C values were very similar being the highest of all samples on both sites. The lowest mean δ^{15}N value among Baltic Sea samples was found for *Mytilus spp.* (5.7 ‰). In contrast to the samples from the SGD impacted site, Amphipoda and Isopoda showed higher δ^{15}N values than *Mytilus spp.. Balanus spp.* belonging to the second group at the SGD impacted site showed only a slightly increased δ^{15}N value at the Baltic Sea side compared to Amphipoda and Isopoda. *Crangon crangon* and *Platichthys flesus* contained the highest δ^{15}N values measured within the Baltic Sea samples. δ^{13}C values of *Crangon crangon* were lower than in samples from the other site. Polychaeta, Nudibranchia and *Neogobius melanostromus* were not collected at the Baltic Sea side.
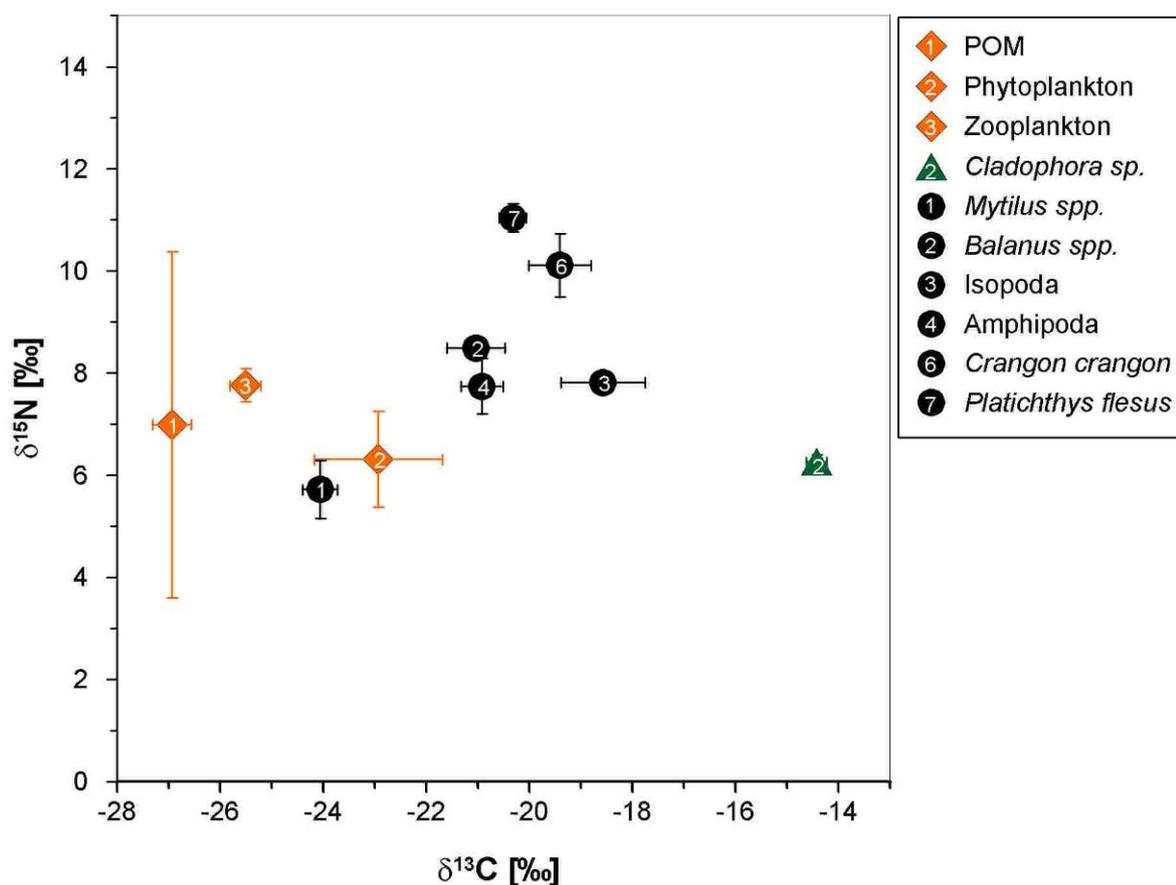
Figure 3.15: Isotope diagram (δ^{15}N vs. δ^{13}C) for organisms sampled during October 2010 from the Baltic Sea side of Hel. Means with standard deviations are shown for particulate organic matter (POM) and plankton (◆), phytobenthos (▲) and zoobenthos (●).

Table 3.11: Organisms sampled during October 2010 from the Baltic Sea side of Hel. Number of samples and means of isotope ratios with standard deviation are given.

Group/Species	nb.	δ^{15}N (‰)		δ^{13}C (‰)		C/N	
		mean	σ	mean	σ	mean	σ
POM	4	**7.0**	3.4	**-26.9**	0.4	**7.6**	0.1
Phytoplankton (10-100µm)	4	**6.3**	0.9	**-22.9**	1.2	**8.8**	1.0
Zooplankton (>55µm)	12	**7.7**	0.3	**-25.5**	0.3	**6.8**	2.3
Phytobenthos							
Cladophora sp.	1	**6.3**	0.1	**-14.4**	0.2	**14.4**	0.5
Zoobenthos							
Mytilus spp.	4	**5.7**	0.6	**-24.1**	0.3	**4.7**	0.0
Balanus spp.	4	**8.5**	0.2	**-21.0**	0.6	**5.5**	0.2
Isopoda	3	**7.8**	0.1	**-18.6**	0.8	**6.8**	0.0
Amphipoda	14	**7.7**	0.5	**-20.9**	0.4	**5.8**	0.7
Crangon crangon	8	**10.1**	0.6	**-19.4**	0.6	**4.7**	0.6
Platichthys flesus	4	**11.0**	0.3	**-20.3**	0.3	**3.9**	0.0

Table 3.12: Results from a student's t test conducted for Organisms sampled in both areas. Degrees of freedom (df), t value and probability of assuming null hypothesis are given. p values lower than 0.05 are bold.

Group/ Species	$\delta^{15}N$			$\delta^{13}C$			C/N		
	df	t	p	df	t	p	df	t	p
POM	23	-4.04	**0.001**	23	3.74	**0.001**	23	6.65	**>0.001**
Zooplankton	14	2.04	0.061	8	0.64	0.539	8	-0.02	0.986
Phytobenthos									
Mytilus spp.	6	2.52	**0.045**	6	7.01	**>0.001**	6	3.04	**0.023**
Balanus spp.	5	1.19	0.288	5	-2.09	0.090	5	3.53	**0.017**
Isopoda	7	-1.07	0.318	7	1.43	0.196	7	0.47	0.651
Amphipoda	26	-5.65	**>0.001**	26	7.82	**>0.001**	26	-1.74	0.094
Crangon crangon	14	0.83	0.423	14	8.99	**>0.001**	14	-0.82	0.425
Platichthys flesus	6	-1.97	0.096	6	1.97	0.096	6	0.21	0.837

For all species or groups which were found on both sites and were at least three parallels were available, a student's t test was conducted to see whether values showed significant differences. The null hypothesis was therefore that the two sites are not significantly different in $\delta^{13}C$ and $\delta^{15}N$ values. With a level of significance of 5 % the null hypothesis can be abandoned at p values lower than 0.05. Only POM samples and Amphipoda showed significantly lower $\delta^{15}N$ values at the SGD impacted site than in the Baltic Sea (Table 3.12). $\delta^{13}C$ values were significantly lower in those samples, too. *Mytilus spp.* showed lower $\delta^{15}N$ values in the Baltic Sea together with higher $\delta^{13}C$ values. In addition *Crangon crangon* had significantly lower $\delta^{13}C$ values at the SGD impacted site but showed no significant difference in $\delta^{15}N$ values between the two sites. In all other samples no significant difference between the two investigated areas could be found.

4 Discussion

4.1 SGD and its nitrogen load

4.1.1 Spatial distribution of SGD

The flux of terrestrially derived SGD is determined by different factors, mainly the hydraulic head and gradient as well as the porosity of the sediments. Those factors are influenced by topography and geomorphology. In addition the terrestrial groundwater recharge rate has an impact on SGD and is itself affected by precipitation and evapo-transpiration (Burnett et al., 2003). To assess the quantity of SGD different approaches are possible. One is modelling, for example with groundwater mass balance calculations; another is the use of chemical tracers like radium and radon isotopes which are enriched in groundwater. Finally direct physical measurements can be conducted like the use of seepage flux meters. This last technique was applied on Hel Peninsula in October 2010 with the help of benthic chambers. There are several possibilities to describe the rate of SGD. One is to indicate the specific volume flux across the sea floor like cubic meter water per square meter sea floor per year (m^3 m^{-2} a^{-1}) or equivalent terms. To calculate the equivalent velocity (e. g. cm s^{-1}) a correction for the porosity of the sediment has to be considered to obtain the actual travel rate of the groundwater in the sediment. It is also possible to express SGD as the total volume of discharge per unit length of shoreline per unit time (e.g., L m^{-1} d^{-1}). This indication is very useful for extrapolations to larger areas but requires a lot of measurements.

SGD is a composite of fresh terrestrial derived groundwater and recharged saline seawater. Thus the seepage rates obtained from seepage meter studies are higher than the actual freshwater discharge rate.

Seepage rates calculated by S. Vogler were used in a rough context to set the SGD and its nitrogen load into perspective with other freshwater sources of the Puck Bay. They are in accordance with other studies of SGD (Table 4.1) and indicated a slow flow of SGD.

Near-shore seepage typically has very diffuse and highly variable fluxes and the discharge can vary widely over time and space (Burnett et al., 2001; Burnett et al., 2003). This means that SGD does not occur on one small and confined area but discharges in patches on different spots with different seepage rates over a wide area. This phenomenon was also found on Hel Peninsula which could be seen from salinities measured along the shore line in two different depths in May 2010 (Figure 4.1, personal communication L. Kotwicki, Institute of Oceanology PAS (Polish Academy of Sciences, Sopot), Department of Marine Ecology). In May 2010 the two sampling spots M1 and M3 separated by about 20 m were characterized by low pore water salinities indicating discharging groundwater at those sites. Between those two

lay the site M2 with high pore water salinities. Also the high range in seepage rates measures in October 2010 from 13 to 113 L m^{-2} d^{-1} within two metres distance (Table 3.8) showed the high spatial variability, the highest seepage rate being nearly 9 fold higher than the lowest. The pore water salinities of samples taken along the transects showed the high spatial variability, too.
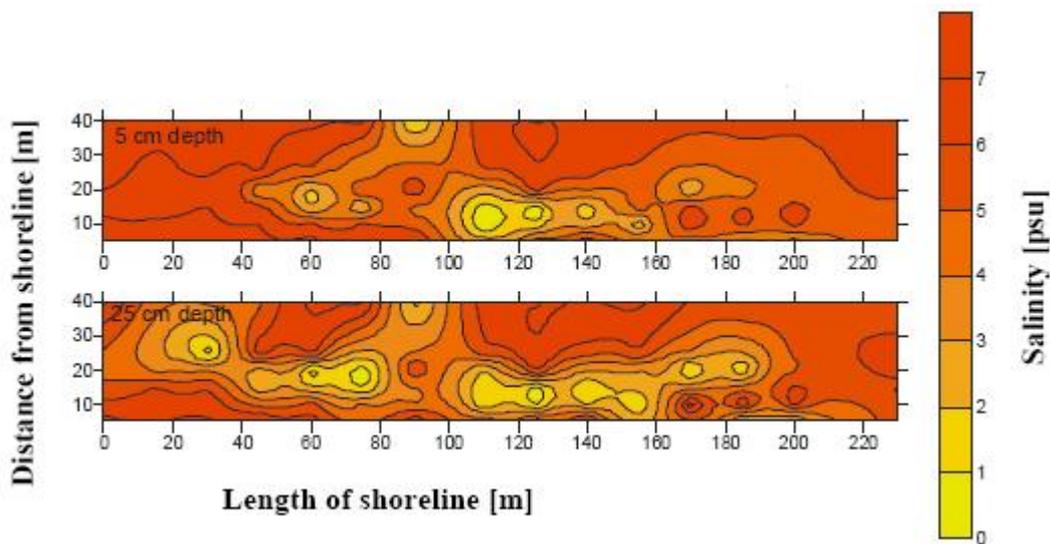
Figure 4.1: Salinity distribution along the shore line of the beach of Hel in May 2010. 5 and 25 cm depth. Yellow colour indicates salinity 0 and thus SGD. (from L. Kotwicki, personal communication)

Earlier studies of the SGD in the Puck Bay estimated a rate of only 0.4 L m^{-2} d^{-1} (Piekarek-Jankowska, 1994). This was, however, an average for the whole Bay. Therefore the much higher rates found at the specific sites in Hel are not contradicting. According to Taniguchi et al. (2002) one can expect the SGD to decrease with increasing water depth (and increasing distance from the shore line) due to increasing pressure from the water column. Based on that, SGD in the deeper central parts of the Puck Bay would be lower than near to the coast. Besides this the sediments of the central Puck Bay consist of clay and sandy clay with a lower permeability than the sandy coast leading to an even more diffusive SGD.

In comparison the submarine spring on Crescent Beach, Florida, constituting a point source of SGD, has a flow rate of >40 m^3 s^{-1} (Brooks, 1961). Located 4 km off the coast, it originates from a virtually confined aquifer. At the vent, however, the upper confining unit has been eroded away entirely leading to a direct contact of the groundwater with the seawater (Swarzenski et al., 2001) and thus to a submarine spring.

Table 4.1: Seepage rates of SGD obtained from seepage meter studies conducted on sites with similar conditions as the beach of Hel (shallow water close to the shore line with sandy sediments). Included are an estimated rate of SGD for the whole Puck Bay and rates from the benthic chamber incubations during the sampling campaign in October 2010.

Study area	Seepage rate	Water depth	Distance from shoreline	Soil	Reference
	$l\ m^{-2}\ d^{-1}$	m	m		
Great South Bay, NY	40	1.3	30	sand, silty sand	Bokuniewicz (1980)
Cape Cod, MA	43 - 50	<2	-	mud and sand	Giblin & Gaines (1990)
Northeast Gulf of Mexico, FL	14.4 - 115.2	0.5-2	<500	silty sand	Bugna et al. (1996)
NE coastal Gulf of Mexico, FL	1 - 10	0.5-2	<500	silty sand	Rasmussen (1998)
Chesapeake Bay, VA	0.5 - 88.6	-	0-50	sandy loam	Reay et al. (1992)
Chesapeake Bay, VA	15.1	1	5-9	sandy loam	Gallagher et al. (1996)
Coastal bays of New England	48 - 96	-	35-200	coarse sand	Valiela et al. (1990)
Puck Bay, Baltic Sea	0.4	<50	-	sand	Piekarek-Jankowska (1994)
Beach of Hel, Puck Bay (October 2010)	13 - 113	0.5	20	sand	pers. comm. S. Vogler

4.1.2 Temporal variability of SGD

The distribution of SGD was also varying in time. Spots with SGD, where the groundwater lances were positioned, were always slightly different during the different campaigns (Figure 2.4). The standard deviations in the depth profile of salinities in samples from groundwater lances (Figure 3.1A) show that there are differences between days. Those differences occurred mainly in the upper 10 to 15 cm, whereas standard deviations in the deeper sediment are lower. This may indicate changes of mixing conditions during SGD in the upper sediment layer. Lances were only sampled two days in a row. Standard deviations are therefore not statistically significant. However, such changes do not seem very unlikely. They may be induced by physical processes occurring in the Puck Bay which impact the mixing of fresh groundwater and saline seawater. There may happen a turnover of the sediment due to wind induced waves and advective transport (Furmanczyk & Musielak, 1999). This would change

the sorting of the sand grains and therefore also the permeability of the sediment. As a result the rate of SGD could increase or decrease and the groundwater may even change its route through sediments with a higher permeability. Furthermore discharge is driven by wave set-up or set-down (Li et al., 1999) which is changing in time. This means that for instance seawater may recharge the sediment thereby restraining groundwater discharge at the same spot. All this oceanic processes are very variable e.g. wind direction and intensity is changing over time. During the sampling campaign in October 2010 the wind was changing from a light breeze of about level 2 of the Beaufort scale from south west in the beginning of the campaign to west wind with Beaufort numbers 4 to 5 later on. This may therefore have an influence on the variability in SGD. Another observed phenomenon was the formation of methane bubbles in the sediments of Hel beach (Vogler et al., 2011). Those bubbles may have decreased the permeability at times and therefore also contributed to the high variability of SGD at the sampling site.

4.1.3   Extrapolating exercise for SGD

SGD may occur throughout the whole Puck Bay. To estimate the influence of SGD seepage rates were extrapolated to the whole Puck Bay area and compared to the surface freshwater input to the Puck Bay (8.1 km^3 a^{-1}; (Cyberski, 1993). Puck Bay covers an area of 359.2 km^{-2} (Bolałek & Graca, 1996). Seepage rates measured in the benthic chambers during October 2010 were extrapolated to one year and multiplied with the whole Puck Bay area. Assuming the largest seepage rate (113 l m^{-2} d^{-1}) the water input via SGD into the whole Puck Bay would be about 14.8 km^3 a^{-1} (Table 4.2). This would be as much as 65 % of the of the total water input (SGD plus surface runoff). Calculations with the lowest measured seepage rate of 13 l m^{-2} d^{-1} would still give 17 % SGD per total inflow of all surface water input and SGD. On a global scale, only about 6 to 10 % of the total freshwater runoff arises from groundwater seepage (Burnett et al., 2003). SGD may have a larger influence on a regional scale like for the Puck Bay area. However, the benthic chamber measurements gave the flux of combined saline and freshwater discharge because of the recirculating seawater component of SGD. The input of fresh SGD into the Puck Bay is therefore expected to be lower than the measured rates. Extrapolation with the highest measured seepage rate may give an idea for the maximal possible input but is not very realistic. Calculations with the lowest measured rate still give relatively high SGD fractions, since there are a lot of areas on the Beach of Hel where no salinity decrease and therefore SGD occurs (Figure 4.1). The six benthic chambers, which only covered a very small area of 0.03 m^2 each on a SGD impacted site, did not give enough

data to calculate a mean discharge rate for the beach of Hel let alone the whole Puck Bay.
Further measurements and combinations with modelling and tracer techniques are needed.
Using the estimated mean seepage rate for the Puck Bay of $0.4 \, l \, m^{-2} \, d^{-1}$ (Piekarek-Jankowska,
1994) the SGD portion would only be 1 % of the total water input. Based on that, the
influence of SGD on the Puck Bay seems rather low.

Table 4.2: Global discharge of freshwater and comparison of the water input via submarine
groundwater discharge (SGD) into Puck Bay and via surface freshwater inflow. The total
inflow is the sum of the surface run-off and the SGD. Input of SGD was extrapolated to the
whole area of Puck Bay ($359.2 \, km^2$; (Bolałek & Graca, 1996) for different seepage rates. The
SGD portion of the total water input is given in %.

	Seepage rate	Input flux	SGD per total inflow	Reference
	$l \, m^{-2} \, d^{-1}$	$km^3 \, a^{-1}$	%	
Global discharge				
Total runoff		37,400		(E. K. Berner & R. A. Berner, 1987)
Fresh groundwater seepage		2,400	6	(Zektser, 2000)
Puck Bay				
mean freshwater inflow		8.1		(Cyberski, 1993)
SGD	0.4	0.05	1	calculated from (Piekarek-Jankowska, 1994)
SGD in this study	13	1.7	17	calculated from the minimal seepage rate measured in October 2010 in Hel
	113	14.8	65	calculated from the maximal seepage rate measured in October 2010 in Hel

4.1.4 DON in the SGD

Although the actual water input of SGD to the Puck Bay may be of rather low significance
this may not be the case for the nitrogen input. Groundwater mostly contains higher
concentrations of organic and inorganic dissolved nitrogen than rivers or precipitation
(Johannes, 1980; Mulligan & Charette, 2006).

DON compounds in sediment pore waters can be produced as intermediates or end-products
of remineralisation or oxidation of sediment organic matter (SOM) (Hatcher & Spiker, 1988;
Burdige & Martens, 1990; Amon & Benner, 1996; Burdige & Zheng, 1998). According to
that sediments with low organic matter (OM) content should also contain low DON

concentrations. OM was not measured in the sediments of the sampling site in Hel. However, since they consist of sand OM concentrations should rather low. Shallow sandy areas in the Baltic sea contain only about 0.1 % particulate organic carbon (POC), which is a part of OM (Leipe et al., 2010) and thus a low content of 0 to 1 % organic carbon in coastal sandy sediments seems reasonable (Deutsch et al., 2010).

DON concentrations in pore water were mostly between 15 and 20 μmol L^{-1} in the pore water with some peaks of 40 to 50 μmol L^{-1}. Overall they did not change significantly with depth. Burdige & Zheng (1998) found a similar pattern with similar concentrations in marine sediments consisting of silty sands with low OM content. They found higher DON concentrations (>100 μmol L^{-1}) in sediments with higher OM content. DON concentrations were very similar on all sampling sites independent from SGD and they did not increase significantly with depth. Therefore SGD does not seem to be a significant source of DON, but DON seems to originate from the water column, which showed similar concentrations as pore water. Some experimental studies showed that anoxic conditions led to a decrease in pore water DON concentrations (Enoksson, 1993; Hansen & Blackburn, 1991). It has therefore been assumed that, under anoxic conditions, the mineralization of dissolved organic matter (DOM) may be less efficient (Hansen & Blackburn, 1991). This could be an explanation why the anoxic submarine groundwater in Hel did not contain higher DON concentrations.

4.1.5 DIN in the SGD

Only in the upper 10 cm of the sediment nitrite-nitrate was found mainly not exceeding 5 μmol L^{-1}. Nitrite-nitrate was overall decreasing with depth to 0 μmol L^{-1}. The absence of nitrate was not surprising since the SGD on the Beach of Hel was found to have highly reducing conditions (Vogler et al., 2011). Nitrate cannot occur in reducing conditions together with high ammonium concentrations and also nitrite was not found in the pore water either. The SGD is therefore no source for nitrite or nitrate.

Samples from groundwater lances show increasing ammonium concentrations with increasing depth correlating negatively with salinity. Therefore SGD at Hel is clearly a source of ammonium. Concentrations increased to amounts higher than 200 μmol L^{-1}. During November 2009 they even reached 5.8 mmol L^{-1}. Ammonium was therefore the dominant nitrogen species in the SGD. Studies on groundwater which also found high ammonium concentrations suggest a contamination (Böhlke et al., 2006). Investigations of Chincoteague Bay, Maryland, USA, also revealed ammonium as one major nitrogen species in both fresh and saline sub-estuarine groundwater next (Bratton et al., 2009). Ammonium concentration

maxima were approximately 760 µmol L^{-1}. The largest ammonium concentrations by far reported for groundwater globally with 21.6 mmol L^{-1} occurred in the basal sand Pleistocene aquifer of the coastal aquifer system in Pearl River Delta, China (Jiao et al., 2010). Since high ammonium concentrations were also found in other anoxic groundwaters, the SGD on the beach of Hel does not represent a unique phenomenon. However, according to (R. L. Smith et al., 2006) nitrate and not ammonium is mostly the dominant nitrogen species in groundwater. Therefore the study site in Hel is rather untypical.

4.1.6 Seasonality of ammonium from SGD

Ammonium concentrations found in the SGD differ between the sampling campaigns. They are lowest in spring (May) and late summer (September). The highest concentrations were measured in autumn (November). Late winter (February/March) and early autumn (October) showed medium concentrations compared to the other seasons. This may indicate seasonality in ammonium input via SGD being higher in autumn and winter than during spring and summer. Because investigations of SGD on the beach of Hel were conducted only during one year it is difficult to say whether there really was a seasonal signal in the ammonium input via SGD. However, seasonal changes of ammonium concentrations in near-bottom water with lower concentrations between March and July and higher concentrations between August and February are reported for the Puck Bay (Bolałek & Graca, 1996). Bolałek and Graca (1996) measured the flux of ammonium from the sediments into the bottom water, but it is not clear whether those fluxes were associated with SGD since they did not investigate this relationship. Therefore it remains unclear whether or not the ammonium input via SGD is subject to seasonality. To resolve this question, further measurements over a longer time period would be necessary. Similar to depth profiles of salinity ammonium concentrations showed differences between days in the upper sediment layers. During September 2009 samples taken from one lance during two different days had similar salinities but very different ammonium concentrations (Figures 6 and 7). This may indicate for instance a change of the seepage rate or the direction of SGD. Reasons for that have been discussed earlier. If one assumes more than one groundwater source (see chapter 4.2), the differences in the ammonium concentrations from one day to the other may even be du to a change in those sources. However, this cannot be further verified since there is a lack of additional data.

4.1.7   Spatial variability of ammonium from SGD

Samples taken along transects during May and October 2010 show high the spatial variability in ammonium concentrations. Ammonium concentrations were strongly negative correlated with salinity at sites with actual SGD. However, this was not the case on an overall spatial scale of the whole sampling area in Hel including site without SGD. Ammonium concentrations were always lowest in samples from lances nearest to the shore line (M1, M2 and O1) and concentrations were increasing with distance from the shore line. This might have been due to the fact that the sediments in the shallower waters are better mixed and regularly flushed by seawater because of higher wave stress. In deeper waters this wave stress should be lower and therefore ammonium could accumulate within the sediment. Lowest salinities indicating SGD where measured in M1, M3 and O2. Ammonium concentrations at these sites were increasing with depth and decreasing salinity. However highest of all concentrations were measured on spots showing no decrease in salinity with depth (M4, O3). Those sampling sites without SGD also contained high sulphide concentrations. This may indicate a different ammonium source than SGD namely degradation of organic matter in the bottom sediment under simultaneous sulfate reduction (Libes, 1992), which leads to the production of sulfide and ammonium. This may be a reason for the lack of correlations between ammonium concentrations and salinity in these areas. The stoichiometry of sulfate reduction is given in the following equation:

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 53\ SO_4^{2-} \rightarrow \qquad\qquad \textbf{[4.1]}$$
$$106\ CO_2 + 106\ H_2O + 16\ NH_3 + 53\ S^{2-} + H_3PO_4$$
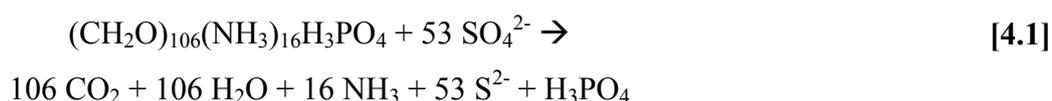
Sulphur measurements were not a part of my thesis but some data were provided by S. Vogler. The C:N:P ratio of organic matter is the average value for marine plankton (Redfield, 1958). In the absence of O_2 the remineralized nitrogen and sulphur remain in reduced form. Hydrolysis of CO_2 produces acid which causes the reduced forms to be almost completely converted to NH_4^+ and HS^- (Libes, 1992). The ratio of HS^- to NH_4^+ in the sediment should therefore be about 3.3 if the only source for sulphide and ammonium in the sediments is the degradation of organic material with sulphate reduction. In M4 maximum ammonium concentrations were 1400 μmol L^{-1} with sulphide concentrations of about 1000 μmol L^{-1} giving a ratio of HS^- to NH_4^+ 0.71. In O3 average ammonium concentrations of 1500 μmol L^{-1} occurred together with sulphide concentrations of about 3000 μmol L^{-1} with a HS^- to NH_4^+ ratio of 2.0. The ratios of HS^- to NH_4^+ are therefore lower than predicted for sulphate

reduction. This means that the net sulphate reduction exceeds the net sulphide production. Sulphide in the pore waters is mainly originating from the groundwater, which is essentially sulphate free. Sulphate in the pore water originates from seawater. This is also indicated by $\delta^{34}S$ values of sulphate and sulphide in pore waters.(Vogler et al., 2011). This is typical for marine sediments because of iron or manganese sulphide formations (Hammond, 2001) together with a massive re-oxidation of sulphide to finally sulphate due to deep mixing of oxic bottom water into the sediment at the study site in Hel (pers. comm. M. Böttcher, Institute for Baltic Sea Research, Working Group: Geochemistry and Stable Isotope Geochemistry).

However, sulphide concentrations in pore waters were much higher at SGD unimpacted sites like O1 and O3, exceeding 2000 µmol L^{-1}, than at sites showing SGD like O2 with <10 µmol L^{-1}. Therefore also the ammonium from SGD may have a different origin than ammonium in SGD free pore water.

Degradation of organic matter without sulphide production by also happen by another process e. g. denitrification (Equation 4.2).

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 84.8\ HNO_3 \rightarrow \qquad\qquad\qquad \textbf{[4.2]}$$
$$106\ CO_2 + 148.8\ H_2O + 42.4\ N_2 + 16\ NH_3 + H_3PO_4$$
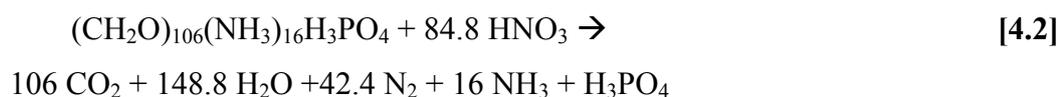
Nitrate is a stronger oxidizing agent than sulphate and would therefore be consumed first (Stumm & Morgan, 1981). At the study site nitrate was only found in low concentrations of <5 µmol L^{-1} in the upper centimetres of the sediment and was completely absent below 10 cm. Nitrate may have entered the anoxic sediment from above by recharge of seawater and supported nitrification. At the boundary of the recharging oxic seawater and the anoxic porewater denitrification may have occurred. Since denitrifying bacteria are mostly facultative anaerob (Ward et al., 2007) they are not negatively affected by oxygen and may even switch to oxic degradation of organic matter (>4-10 µmol $O_2\ l^{-1}$). The latter process would lead to the production of ammonium (Equation 4.3) and would explain ammonium generation independent of sulphide production.

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138\ O_3 \rightarrow \qquad\qquad\qquad \textbf{[4.3]}$$
$$106\ CO_2 + 122\ H_2O + 16\ NH_3 + H_3PO_4$$
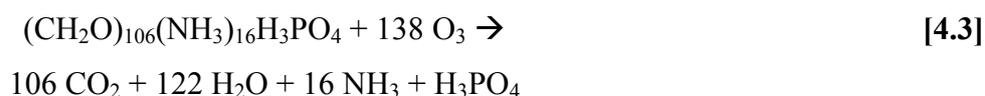
4.1.8 Estimate of ammonium input to the Puck Bay via SGD

A first estimate of ammonium input via SGD to the Puck Bay was done based on the area of 359.2 km^2 and the N loads measured in the benthic chambers. Assuming a flux rate of 363.8 mmol NH_4^+ m^{-2} d^{-1}, 668,080 t per year are estimated (Table 4.3). This is more than six times higher than the N input into the Gulf of Gdańsk via the Vistula River (106,945 t NO_3^- a^{-1}, Voss et al. (2005)), the largest river discharging to the Gulf of Gdańsk and more than three times higher than N input into Puck Bay from the Gulf of Gdańsk. Extrapolation with the lowest measured ammonium flux rate (15.8 mmol m^{-2} d^{-1}) still gave an annual nitrogen input of 29,013 t. This would still be nearly 13 times higher than the total N input to Puck Bay calculated by Pempkowiak (1994) and nearly 30% of the input via Vistula River. Ammonium from SGD seems to contribute substantially to the over all nitrogen load entering the Puck Bay. However, as discussed before, there were only six benthic chamber incubations conducted in very close vicinity, which can hardly be used for extrapolations for the whole Puck Bay. Still if ammonium input via SGD with the lowest measured seepage rate would occur only in one tenth of the Puck Bay sediments this ammonium load would still rival the load calculated by Pempkowiak (1994). The assumption of a high submarine nitrogen load is further supported by the study of (Bolałek & Graca, 1996). They estimated an ammonium flux of 825 t a^{-1} from sediments into bottom water. This is still a very high load compared to other nitrogen sources (Table 4.3). Bolałek and Graca (1996) measured flux rates from 0.005 to 1.4 mmol m^{-2} d^{-1}. These are much lower rates than those measured in the SGD on the beach of Hel. If rates from SGD were included in the extrapolation of Bolałek and Graca (1996) the ammonium load would be higher. It is not clear however, how much of the sediment flux measured in this study is due to SGD. The really estimate the fraction of nitrogen load from SGD into the Puck Bay further comprehensive investigations are necessary. Nevertheless, the present study showed that while the seepage rate of SGD may be small, discharge of nitrogen can be significant depending on the total discharge area and the concentration in the groundwater.

Table 4.3: Different nitrogen loads affecting the Puck Bay. Input of ammonium from submarine groundwater discharge (SGD) was extrapolated to the whole area of Puck Bay (359.2 km[2]; Bolałek and Graca, 1996) for lowest and highest flux rates measured in benthic chambers in October 2010.

	N flux rates	Nitrogen load	Reference
	mmol NH_4^+ m^{-2} d^{-1}	t N a^{-1}	
Vistula River		106,945	calculated from Voss et al. (2005) assuming 293 t NO_3^--N per day
Inflow to Puck Bay from Gulf of Gdańsk		205,400	(Kruk-Dowgiałło & Szaniawska, 2008)
Outflow from Puck Bay to Gulf of Gdańsk		197,600	(Kruk-Dowgiałło & Szaniawska, 2008)
Puck Bay			
total N input		2,275	(Pempkowiak, 1994)
Reda River		278	(Kruk-Dowgiałło & Szaniawska, 2008)
Dębogórze sewage treatment facility		548	(Kruk-Dowgiałło & Szaniawska, 2008)
NH_4^+ from sediment fluxes		825	Bolałek and Graca (1996)
SGD in this study	15.8	29,013	calculated from the lowest ammonium flux measured in October 2010
	363.8	668,080	calculated from the highest ammonium flux measured in October 2010

4.2   Source identification

4.2.1   Sources of the SGD

Tritium (^{3}H) values can be used as a tracer of the hydrological cycle and also to determine the age of groundwater. It is the radioactive hydrogen isotope and has a half live of 12.32 years (Lucas & Unterweger, 2000) its decay product beeing the noble gas helium-3 ([3]He). The activity of ^{3}H is given in tritium units (TU). 1 TU means one ^{3}H for every 10^{18} atoms of H. [3]H is produced in the atmosphere naturally and enters the water cycle via precipitation. However, this production is very low leading to low concentrations. [3]H activities in continental precipitation before the 1950s were in the range of 1 to 20 TU. This leaves an activity in surface waters of about 10 TU ($\sim 10^{-15}$ mol kg^{-1}). In the end of the 1950s and the early 1960s hydrogen bomb tests led to a large release of ^{3}H and activities increased by two to three orders of magnitude (Michel, 1989). The peak of ^{3}H input to groundwater was in 1963-1964. Due to a moratorium on atmospheric testing in late 1963 the ^{3}H activity in precipitation decreased again. Today they level values from before the 1950s again. Because of the testing

events ^{3}H can be used as an indicator for pre or post 1950s recharge of groundwater. The data from Hel Peninsula are from the group of M. Böttcher (Institute for Baltic Sea Research) and will only be used to roughly estimate the age of the groundwater. ^{3}H activity on Hel Penisula was relatively low in the SGD found in October 2010 (2.4 TU) compared to seawater at the sampling site (9.1 TU) (pers. comm. S. Vogler). This indicates that the ascending groundwater contains only a small fraction of post 1950s water (Vogler et al., 2011). Due to radioactive decay a ^{3}H activity of less than 0.6 TU would indicate a complete recharge of water prior to the 1950s assuming no mixing or dilution with other water (Bartolino, 1997). The ^{3}H activity of the SGD is not consistent with one of the sampled wells. In October 2010 they constituted 7.9 and 0.3 TU for the 3 m and 180 m deep well, respectively. Groundwater sampled from the deep well originated from the confined Cretaceous aquifer, which is the deepest aquifer underlying the Puck Bay (Figure 2.2). The groundwater from this aquifer was older than 60 years according to the very low ^{3}H activity. Samples taken from the other well originate presumably from a shallow unconfined aquifer on Hel Peninsula since the ^{3}H activity is relatively high. This means that the groundwater is much younger and maybe originating from local precipitation on Hel Peninsula. At least it is almost sure that the source of SGD can not be one of this two aquifers alone which were sampled with the wells since the ^{3}H activity in the SGD is higher than in the deep well but lower than in the shallow well (pers. comm.. S. Vogler). On Hel Peninsula the Upper Cretaceous sands are in direct contact with the Pleistocene sandy series and constitute a joint groundwater horizon (Jankowska et al., 1994). This means that the groundwater from the deep Cretaceous aquifer can seep upwards through permeable sediments and mix with groundwater from other overlying aquifers prior to submarine discharge. Therefore the SGD at the sampling site in Hel could be a composition of groundwater from the two sampled aquifers. Tritium values from the October campaign 2010 support this hypothesis (pers. comm. S. Vogler).

4.2.2   Sources of ammonium from SGD

Ammonium concentrations and δ^{15}N values, however, cannot be explained this way. Concentrations of ammonium in the groundwater are much higher than in the sampled wells (Figures 3.2, 3.5 and 3.6). End-member mixing calculations (Fry, 2002) with the two sampled wells as fresh water end-member (Table 3.2), respectively, cannot explain the ammonium concentrations in the pore water. Also a simple mixing of both aquifers would not lead to the high amounts of ammonium in the pore water. There has to be another or at least an additional source of ammonium.

Table 4.4: Different N pools and their range of $\delta^{15}N$ values.

N source	Compound measured	$\delta^{15}N$ values ‰	Reference
	N_2	0	Mariotti (1983)
Precipitation	NO_3^-	-9 to -2	Heaton (1986)
Fertilizer	NO_3^-	-7 to +3	Victoria et al. (2004)
Animal waste	NO_3^-	+10 to + 20	Kreitler (1975, 1979)
Soil	NO_3^-	-10 to 15	Kendall (1988)
Animal waste		+5	Kreitler (1975, 1979)
Precipitation	NH_4^+	-7 to +4	Heaton (1986)
Fertilizer	NH_4^+	- 8 to +7	Victoria et al. (2004)
Animal waste	NH_4^+	>20	Kendall et al. (2007)
Leaves		-8 to +3	Peterson and Fry (1987)
total soil N		-10 to 15	Kendall et al. (2007)
Soil organic matter		-4 to +14	Peterson and Fry (1987)
POM		-2 to 11	Peterson and Fry (1987)

To identify the source of ammonium $\delta^{15}N$ values were introduced. The use of stable isotopes can contribute both source-sink (tracer) and process information (Peterson & Fry, 1987). The occurrence of ammonium in pore water can have different reasons (Table 4.4). One source could be precipitation. Ammonium from this pool can have $\delta^{15}N$ values between -7 and +4 ‰. The range of $\delta^{15}N$ for the total N in precipitation in the Baltic Sea is -4.2 to 12.3 ‰ (Rolff et al., 2008). Unfortunately there were no $\delta^{15}N\text{-}NH_4^+$ values of precipitation available for the region of Puck Bay. However measurements of $\delta^{15}N\text{-}NO_3^-$ of atmospheric deposition in Mecklenburg Vorpommern gave values of 0.1 ‰ (Deutsch et al., 2006). Ammonium originating from artificial fertilizer has $\delta^{15}N$ values of around 0 ‰. The reason for this is the fertilizer production via the Haber Bosch process, where atmospheric N_2 with $\delta^{15}N$ values of 0 ‰ (Mariotti, 1983) is converted to ammonium (Freyer & Aly, 1974). If anthropogenic or animal waste water are the source of ammonium, they are usually more enriched in ^{15}N. Animal waste has a $\delta^{15}N$ value of about 5 ‰ (Kreitler, 1975; Kreitler, 1979). Ammonium is generated from urea. During early stages of degradation ^{14}N rich ammonia is lost due to volatilization (Macko & Ostrom, 1994). This leads to ammonium enriched in ^{15}N and therefore high $\delta^{15}N$ values. Ammonium can also be produced during the degradation of soil organic matter ($\delta^{15}N$ values of -4 to 14 ‰). In the course of degradation organic matter is getting depleted in ^{14}N. (Freudenthal et al., 2001) found an increase of $\delta^{15}N$ values in OM

with decreasing concentration. The ammonium released in the soil is therefore depleted in ^{15}N and shows lower $\delta^{15}N$ values than OM.

$\delta^{15}N$-NH_4^+ values of the SGD in Hel were relatively low between 0 and 2 ‰ (except for May 2010). It is therefore unlikely that the ammonium is wastewater derived. Possible sources of ammonium could be fertilizer, precipitation or degradation products of soil organic material. Ammonium from fertilizer can only originate from the mainland south-western of Puck Bay since there is no farmland on the Hel Peninsula (Furmanczyk, 2007). This leads to the overall suggestion that the high ammonium concentrations in the Puck Bay pore waters must therefore be present already in the seeping aquifer. This was, however excluded for the two sampled aquifers based on their ammonium concentrations. Precipitation as the source of the high ammonium concentrations in groundwater is also very unlikely because of lower concentrations in atmospheric deposition (Rolff et al., 2008). Ammonium may therefore originate from organic matter degradation. Jiao et al. (2010) found very high ammonium concentrations in a coastal Pleistocene aquifer (390 mg L^{-1} which is ~28mmol L^{-1}). According to their results this ammonium was natural and originated in the overlying Holocene-Pleistocene aquitard from degradation of organic material. It may therefore be possible that the high ammonium concentrations in the SGD in Hel are also originating from organic rich sediment layers. Most of the pore water samples contain high ammonium concentrations together with $\delta^{15}N$-NH_4^+ values between 0 and 2 ‰. There were, however, exceptions. Samples from lances nearest to the coast showed clearly lower ammonium concentrations with higher $\delta^{15}N$-NH_4^+ values. (Bratton et al., 2009) found something similar. In their studies ammonium was also one main nitrogen species in fresh and saline sub-estuarine groundwater. Samples with relatively high nitrogen concentrations had low $\delta^{15}N$ values (<2 ‰). In samples with relatively low nitrogen concentrations $\delta^{15}N$ values were generally lower. They explain this with different sources of organic matter. In their case low-N/high- $\delta^{15}N$ results come from estuarine sediments that likely contain mostly organic matter derived from phytoplankton whereas high-N/low- $\delta^{15}N$ samples are peats which contain a lot of organic material. Therefore organic material is an important ammonium source.

To define an aquifer underlying the sampling area as ammonium source for the SGD in Hel, $\delta^{15}N$- NH_4^+ values of the two sampled wells were determined. They showed very different values for the two aquifers. Samples from the 3 m deep well are more enriched in ^{15}N-NH_4^+ (9.6 ‰) compared to all other samples. The upper sediments in Hel consist of sand (Figure 2.2). The shallow well therefore presents an unconfined aquifer which may be influenced by anthropogenic wastewater from the village Hel which could explain the relatively high $\delta^{15}N$-

NH_4^+ values. The 180 m deep well represents the deepest freshwater horizon made of upper Cretaceous waters. $\delta^{15}N$-NH_4^+ were only 0.2 ‰. Ammonium may therefore originate from artificial fertilizer or organic matter sources. The isotope values of the deep well are more similar to the $\delta^{15}N$-NH_4^+ values of the pore water from the SGD impacted area. But since the ammonium concentrations received from the well sample are rather low (32.6 µmol L^{-1}) compared to those from low salinity pore water samples (100 to >5000 µmol L^{-1}) the deep aquifer can not be the main source of ammonium from SGD.

During May 2010 ammonium concentrations in samples from SGD were lower than during the other campaigns and $\delta^{15}N$-NH_4^+ values were higher. Ammonium values are more similar to those from samples from O1 in October and to the 3 m deep well. If two aquifers are mixing on the beach of Hel it may be that the shallow aquifer is dominant in close vicinity to the shore line. This could lead to lower ammonium concentrations combined with higher $\delta^{15}N$-NH_4^+ values. Further away from the shore line the deep aquifer is dominant in the mixing explaining the high ammonium concentrations and different $\delta^{15}N$-NH_4^+ values. It may be therefore possible that during May 2010 the upper unconfined aquifer was penetrating farther out into the Puck Bay maybe due to higher precipitation and the thawing of snow during spring.

Summarizing the findings there are at least two possibilities for the source of ammonium in the groundwater in Hel. First, the SGD occurring at the beach of Hel originates from another aquifer than the ones sampled. This aquifer may contain similar Tritium values as the pore water at the sites of SGD and may have accordingly high ammonium concentrations. The second possibility is that the SGD at Hel beach is indeed a mixture of the both sampled aquifers as assumed from Tritium values (pers. comm. S. Vogler). In this case the majority of ammonium found in the pore water does not originate directly from the two aquifers but from organic remains in the sediments. If water from the Cretaceous aquifer is seeping upwards to the seafloor it passes an at least 40 m thick Holocene layer (Jankowska et al., 1994). Holocene sediments can be rich in organic matter. Degradation of this organic matter could lead to high ammonium concentrations (Jiao et al., 2010) which could be washed out by the seeping groundwater from the deep aquifer. Anaerobic destruction of the organic matter in the deep sediment layers may have occurred under sulphate reduction (see above). To verify one or the other hypothesis investigations of all aquifers underlying the Puck Bay would be needed. It would be also necessary to take cores from the sediments in the Puck Bay to characterize the iron and sulphur content. The second hypothesis is more plausible provable with the present data. To verify the first hypothesis more measurements are necessary.

4.3   Reactions within the sediment

Ammonium concentrations plotted over salinity showed conservative mixing despite some scatter (Figures 3.2 3.5 and 3.6). This means that the ammonium was simply diluted with the seawater. There is no significant evidence for ammonium conversion such as nitrification since nitrate concentrations were very low and δ^{15}N-NH$_4^+$ values were not enriched. If nitrification (Equations 4.4a and b) occurred ammonium concentrations would have been decreasing faster than predicted by conservative mixing only. This is because nitrification removes ammonium from the system (Equation 4.4). Moreover the δ^{15}N-NH$_4^+$ indicated a conservative mixing since nitrification would lead to increasing δ^{15}N-NH$_4^+$.

$$NH_4^+ + 1.5\ O_2 \rightarrow NO_2^- + 2\ H^+ + H2O \qquad\qquad\qquad \textbf{[4.4a]}$$

$$NO_2^- + 0.5\ O_2 \rightarrow NO_3^- \qquad\qquad\qquad\qquad\qquad \textbf{[4.4b]}$$

During nitrification ammonium is oxidized under O_2 reduction (Anthonisen et al., 1976). Since the SGD was found to be highly anoxic no significant nitrification was been expected. In the upper centimetres of the sediment with oxic seatwater nitrification could be possible Nitrate, however, was not detected in high amounts in the sediment. The lack in nitrate accumulation in the sediment could be explained by a coupled nitrification:denitrification on the oxic:anoxic boundary. Thereby nitrated forming during nitrification would immediately be removed from the system by denitrification (Equation 4.2). Therefore there may have occurred nitrification at the sediment-water interface which may not have been recognized due to immediate removal and low sampling resolution. Shallowest pore water samples were taken from 4 cm depth and the bottom water from 5 to 10 cm above the sediment (Figures 3.1, 3.3 and 3.4).

To investigate the nitrification potential the core incubation experiments were conducted. They show a decrease of ammonium concentrations together with an increase in δ^{15}N values. This is the classical prove of nitrification. Ammonium concentrations can potentially be reduced by assimilation or nitrification. Both processes lead to enrichment in δ^{15}N. N isotope fractionation during the uptake and assimilation of ammonium by a marine diatom results in an isotope enrichment factor ε of -20 ± 1 ‰ for the remaining ammonium (Waser et al., 1998). The received values for the isotopic enrichment factors where very different. The mass balances of the experiments are difficult to explain. There was a substantial removal of

ammonium (more than 50 % at a seepage rate of 108 µl min^{-1}) but no significant formation of nitrate. Therefore it cannot be said whether the reduction in ammonium was due to assimilation or a coupled nitrification/denitrification. Oxygen saturation was decreasing in the course of the experiment which may have inhibited nitrification. It is questionable if the conditions within the core were favourable for a coupled nitrification:denitrification. A longer performance of the single experiments may have led to adaption of nitrifying organisms in the cores which may have led to clearer results. $\delta^{18}O$ values in Nitrate could have given information about nitrification. But since nitrate concentrations were very low (<0 µmol L^{-1}) this was not measured. Also a measurement of assimilation rates may have given more information about ammonium removal by this process. However, although the exact processes could not be distinguished the experiment did show a high potential of the sediments in Hel to oxidize ammonium.

4.4   Reactions after release to water

The ammonium released into the water column may have been assimilated by phototrophic organisms. Changes in $\delta^{15}N\text{-}NH_4^+$ values during the benthic chamber incubations support this assumption (Figure 3.12). They were first decreasing during the dark incubation showing the increasing fraction of groundwater with low $\delta^{15}N\text{-}NH_4^+$ values. During the light incubation, however, $\delta^{15}N\text{-}NH_4^+$ values were mostly decreasing again despite further ammonium input via SGD. This might have been due to fractionation during ammonium uptake by phytoplankton. Against this hypothesis stands the fact that high ammonium concentrations are toxic for many organisms. And indeed the highest $\delta^{15}N\text{-}NH_4^+$ values and therefore maybe the highest uptake rates were measured in benthic chamber 4 and 6 which also showed the lowest ammonium input (Figure 3.11B). Thus uptake of ammonium from SGD may occur if the high ammonium concentrations from the groundwater are sufficiently diluted.

The plankton species were not identified in the course of this study. However literature about species distribution in the Puck Bay can give some information. In the outer Puck Bay phytoplankton is dominated by diatoms in spring and autumn and by Cyanobacteria in summer (Pliński, 1993) while the contribution of green algae is insignificantly throughout the Year. Phytoplankton is composed of euryhaline species common to the Baltic Sea and fresh and brackish water species (Kruk-Dowgiałło & Szaniawska, 2008).

In the 1990 phytobenthos in the outer Puck Bay consisted mainly of Potamogeton spp. (30 %), Pilayella sp. (26 %) and Zostera marina (24 %). Chlorophyceae contributed only 9 %. The phytobenthos species found during the sampling campaign in October 2010 all belonged into

this last group. However, the amount of samples was not very high and could therefore not represent an overall distribution phytobenthos species. Bivalvia dominate the zoobenthos with 89 % of the biomass in the Puck Bay while Crustacea show the highest diversity in species in Puck Bay. This was also found during the October 2010 sampling campaign. *Mytilus spp.* were found in high numbers while the most species were found among the Crustacea like *Neomysis integer* and *Crangon crangon* as well as different species of Amphipoda, Isopoda and barnacles (*Balanus spp.*).

The stable Isotopes of N and C in organisms can give information about the food web structure. The $\delta^{13}C$ values in animals reflect their diet within about 1 ‰ (DeNiro & Epstein, 1978; Peterson & Fry, 1987; Michener & Kaufman, 2007). Therefore POM seems to be a food source for zooplankton at the SGD impacted site (Figure 3.14) since both groups showed $\delta^{13}C$ values of about -25 ‰. Similar values for POM in the Gulf of Gdańsk were also found in other studies (Hoffmann, 2003). POM consists amongst others of phytoplankton which can have $\delta^{13}C$ values ranging from -18 to -24 ‰ (Michener & Kaufman, 2007). Therefore phytoplankton may have been a food source for zooplankton in the Puck Bay. All benthic organisms found in the Puck Bay differ by more than 2 ‰ from zooplankton and POM samples. Therefore the latter two are not very likely to be a major food source for benthos. Instead phytobenthos with $\delta^{13}C$ values ranging from -21 to -14 ‰ seem to be the base of the food web. The benthic animals show a similar range from -23 to-16 ‰. This wide range indicates different food sources and therefore a diverse food web. $\delta^{15}N$ values can be used to determine the trophic level of consumers, since animals are on average enriched in $\delta^{15}N$ of 3.2 ‰ compared to their diet (Post, 2002). According to this Isopoda and Amphipoda were grazing on phytobenthos since their $\delta^{15}N$ values were 2 to 3 ‰ higher than that of for instance *Cladophora rupestris* ($\delta^{15}N$ 4.4 ‰). The next trophic level would constitute of *Crangon crangon* and the fish species *Platichthys flesus* with $\delta^{15}N$ values between 10 and 11 ‰. The molluscs *Mytilus spp.* showed the lowest $\delta^{13}C$ values (-22.6 ‰) of all benthic organisms together with relatively low $\delta^{15}N$ values (6.5 ‰). They may therefore represent another baseline for the benthic food web (Vander Zanden & J. B. Rasmussen, 1999).

The Baltic Sea side of Hel Penisula showed a similar composition of benthic organisms as the SGD impacted site (Table 3.12). The pore water samples of the Baltic Sea contained low ammonium concentrations with high $\delta^{15}N$-NH_4^+ values. If the ammonium from the SGD had a significant impact on organisms it would have been expected that $\delta^{15}N$ values would be lower in the SGD impacted area than in the Baltic Sea. Similar observations were made in other studies where waters with enriched $\delta^{15}N$ values were mirrored in organisms

(McClelland et al., 1997). $\delta^{15}N$ values of organism at both sides were very similar. They were not significantly lower in organisms from the SGD impacted area. Therefore, it seems that organisms are not significantly impacted by the SGD. The influence of the Baltic Sea seems to be greater then the one from SGD.

4.5 Conclusion

The source of the high ammonium concentrations in the SGD could not unequivocally be identified. The first hypothesis, that $\delta^{15}N$-NH_4^+ values of the groundwater are different to all other nitrogen sources did not apply. It is however very likely that the ammonium is originating from the anaerobic degradation of organic matter in the Holocene or Pleistocene sediment layers underlying Puck Bay. It would therefore not be anthropogenically derived. The SGD showed a high variability in time and space and the ammonium seems conservatively mixed into the water column. The first part of the second hypothesis, that the ammonium from SGD enters the coastal waters unmodified, is mainly be confirmed. It was also found from extrapolations that the ammonium input from SGD may contribute significantly to the nitrogen input to the Puck Bay despite the low discharge. This assumption remains however speculative, since there were not enough data available for an appropriate extrapolation. Furthermore a high impact of ammonium from SGD did not seem very likely if one looks at the ecosystem. There was no significant difference between the food web of the SGD impacted site and the Baltic Sea side of Hel and the $\delta^{15}N$ values did not differ within species of the affected and unaffected sampling sites. The $\delta^{15}N$ signal of the SGD could not be detected in the food web and distinguished from other nitrogen sources as stated in the third hypothesis. Processes like nitrification and denitrification at the sediment water interface may remove ammonium from SGD before it can enter the food web. Therefore the ammonium from SGD on the beach of Hel may not play an important role of the eutrophication in the Puck Bay ecosystem.

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Selbständigkeitserklärung:

Hiermit versichere ich, dass ich die vorliegende Arbeit selbständig verfasst und keine anderen als die angegebenen Quellen (siehe § 25, Abs. 7 der Diplomprüfungsordnung Biologie 2000) und Hilfsmittel verwendet habe.

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Rostock, Mai 2011

Sabine Nestler