Environmental factors controlling the interaction between benthic and pelagic microalgae in a groundwater fed marine environment of the Wadden Sea, Germany.

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Applied Limnology

Submitted by

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Abstract

The Wadden Sea is a highly productive and very dynamic ecosystem where shallow coastal areas provide hot spots for benthic and pelagic productivity. As part of the project “Beaches” from the ICBM, University of Oldenburg investigating biogeochemical cycles at the northern beach side of Spiekeroog Island in the Wadden Sea an experiment and a pre-sampling analysis were conducted. Different ways of nutrient supply in sediment and water column as well as distribution patterns of benthic and pelagic microalgae were analysed. A twenty-four hour incubation experiment could detect overall low productivity of the pelagic and benthic algae after nutrient enrichment of nitrate, phosphate or nitrate plus phosphate. Whereas phytoplankton showed a slight response to nitrogen alone, microphytobenthos reacted most to nitrate plus phosphate enrichment in the water column and in the sediment indicating a co-limitation and a more competitive advantage in nutrient uptake. With the help of a transect experiment we were able to detect that strong mixing conditions due to tidal movement and wave action play a major role for nutrient availability in the water column and as well for the surface area of the sediment. Our results suggest that increasing alteration of nutrient flow can become an impacting factor by growing biomass of microphytopbenthos. However, microphytobenthos growth depends on the one hand on the availability of phosphate and on the other hand on protected areas like tideways having the potential of lowering the degree of disturbances. Groundwater influence from the lens located below the Island on the microphytobenthos distribution could not be clearly confirmed.

Zusammenfassung

Das Wattenmeer ist ein sehr produktives und dynamisches Ökosystem wo flache Küstengebiete optimale Bedingungen für benthische und pelagische Mikroalgen darstellen. Als Teil des Projektes „Beaches“ vom ICBM der Universität Oldenburg in dem biogeochemische Zyklen untersucht werden, wurde einerseits ein Laborexperiment und andererseits eine Voruntersuchung direkt am Strand durchgeführt, um die Nährstoffverfügbarkeit im Strandsediment und im Wasserkörper sowie um die Verteilung von benthischen und pelagischen Mikroalgen am Nordstrand der Insel Spiekeroog im deutschen Wattenmeer genauer zu untersuchen. Mit einem 24 Stunden Inkubationsexperiment war es möglich die Produktivität dieser Mikroalgen zu testen, die unter Zugabe von Nährstoffen wie Nitrat, Phosphat oder beiden Nährstoffen zusammen relativ gering ausfiel. Phytoplankton reagierte leicht auf die Zugabe von Nitrate und das Mikrophytobenthos reagierte vermehrt auf die Zugabe von Nitrat plus Phosphat im Sediment als auch im Wasserkörper. Diese Reaktion könnte ein Hinweis auf eine Co-Limitierung der benthischen Algen sein sowie eine wesentlich bessere Nährstoffverwertung, die zu einer erhöhten Konkurrenzfähigkeit führen kann.

Das zweite Transekt- Experiment konnte aufzeigen wie wichtig die Durchmischung durch beispielsweise den Tidengang und die Wellenbewegung für die Nährstoffverfügbarkeit im Wasser aber auch im Sediment ist. Die Ergebnisse zeigen ebenso, dass die Veränderung und Beeinflussung des Nährstoffflusses ein wichtiger Faktor werden kann mit wachsender Biomasse des Mikrophytobenthos. Das Wachstum hängt einerseits von der Phosphatverfügbarkeit ab und andererseits, ob Turbulenz geschützte Regionen wie ein Priel mit geringer Strömung und damit weniger Störung vorhanden sind. Ein direkter Einfluss von Grundwasser von der Süßwasserlinse unterhalb der Insel konnte mit diesem Experiment nicht eindeutig festgestellt werden.

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1 Introduction

Shallow water systems are highly productive habitats in freshwater and in marine aquatic ecosystems (Tillmann et al., 2000; Engelsen et al., 2008; Pasternak et al., 2009). Coastal shallow zones, beaches, deltas or tidal inlets are examples for areas of intense exchange between water column and sediment compartments acting as hot spots for benthic microalgae and phytoplankton competing for nutrients and light (Hansson, 1988; Carlton & Wetzel, 1988; McClain et al., 2003).

While in the past benthic and pelagic algae are often studied separately despite of their trophic interaction and energy flows (Vadeboncour et al., 2003), several studies of freshwater and marine systems (Hansson, 1988, 1992; Sundbäck & Granéli, 1988; Vadeboncoeur et al., 2003; Pasternak et al., 2009; Grunwald et al., 2010) showed that the trophic state and the depth play an important role for the primary production of benthic and pelagic algae. The interaction between these primary producer groups is especially important in shallow, coastal systems, generally in systems with a high environmental variability. Whereas benthic micro algae are able to take up nutrients from sediments and the water column (Carlton & Wetzel, 1988; Nilsson et al., 1991; Blumenshine & Vadeboncour, 1997), phytoplankton is mainly using nutrients from the water column (Hein et al., 2004). A high availability of nutrients in the water column can therefore increase the abundance of phytoplankton, which can lead to a decrease in light available for benthic micro algae. By taking up phosphate, ammonium and nitrate from the sediment, microphytobenthos is additionally able to regulate and to reduce the nutrient flow from the sediment to the water column (Sundbäck et al., 1991). Furthermore, the utilization of nutrients from the water column (Blumenshine & Vadeboncour, 1997) can make benthic algae more competitive against phytoplankton on condition that enough light is available, which was suggested to be a major limiting factor for phytoplankton growth (Colijn & Cadeé, 2003). One resulting effect can be a lower impact of shading by pelagic algae on the benthic communities (Pasternak et al., 2009). On the other hand Vadeboncour et al. (2003) also showed that eutrophication leads to a dominance of pelagic algae even in shallow lakes and therefore a significant reduction of benthic algae.

The productivity of pelagic and benthic algae and their competition for nutrients and light in freshwater as well as in marine environments is highly influenced by the availability of abiotic factors such as temperature, light, nutrients as well as biotic factors such grazing and bioturbation (Hillebrand et al., 2002; Hillebrand & Kahlert, 2002; Sundbäck et al., 1991, Colijn & Cadeé, 2007; Hansson, 1992). As a

consequence a temporary dominance of the pelagic or benthic community can develop due to the individual ability of taking the most out of the current conditions.

Marine and coastal marine ecosystems are generally nitrogen and light limited (Vitousek, & Howarth, 1991; Smith, 1984; Collijn & Cadeé 2003). Groundwater and freshwater coming from rivers entering these ecosystems are influencing the pelagic food web by nutrient input especially nitrate from catchment including anthropogenic sources. Eutrophication signs in such coastal and estuarine waters are one of the consequences seen nowadays (Slomp & Capellen, 2004; Collijn & Cadeé, 2007; Pearl, 1997; Burnett et al., 2006). Additionally, freshwater inflow is impacting the salinity in the water column and shows salinity drops and layers of brackish water in sediments. Another factor is the sediment composition where sandy or muddy sediment is affecting the nutrient as well as the oxygen availability (Beck et al., 2011; Beck & Brumsack, 2012, Sundbäck et al., 1991, Kotwicki et al., 2014).

The coastal area of the German North Sea, called Wadden Sea, contains a chain of islands acting as a boundary between the coastal area and the open North Sea separated by tidal inlets, channels and marshes. Such tidally influenced water exchange with biological and chemical compounds affects the biogeochemistry of the whole North Sea ecosystem (Beck & Brumsack, 2012, Beck et al., 2012). Such a highly productive environment with typical mixing characteristics such as tidal movement, wave induced circulation, wind and resuspension are extremely influencing the nutrient distributions and their availability for algal productivity (Cloern, 1991; Pearl, 1997; Cedeé & Hegeman, 2002; Vadeboncour et al., 2003; Burnett et al., 2006; et al., 2007; Waska & Kim, 2010). The microbial food web is additionally favoured by nutrients entering coastal systems by groundwater inflows. However, the composition of nutrients is depending on the individual groundwater composition and land uses within the catchment area (Garcés et al., 2012; Blumenshine & Vadeboncour, 1997; Hagerthey and Kerfoot, 1998). Waska & Kim (2010) analysed the impact of groundwater discharge on the Wadden Sea area of the southern and western coast of Korea showing that groundwater contains not just a large amount of nutrients but plays additionally a protective role against salt stress, desiccation and heat. Consequently, groundwater discharge can positively influence the primary production of pelagic and benthic algae (Waska & Kim, 2010; Hagerthey & Kerfoot, 1998). Still the environmental and biogeochemical consequences of a groundwater inflow in a tidal influenced marine ecosystem were not often and detailed analysed so far (Beck & Brumsack, 2012).

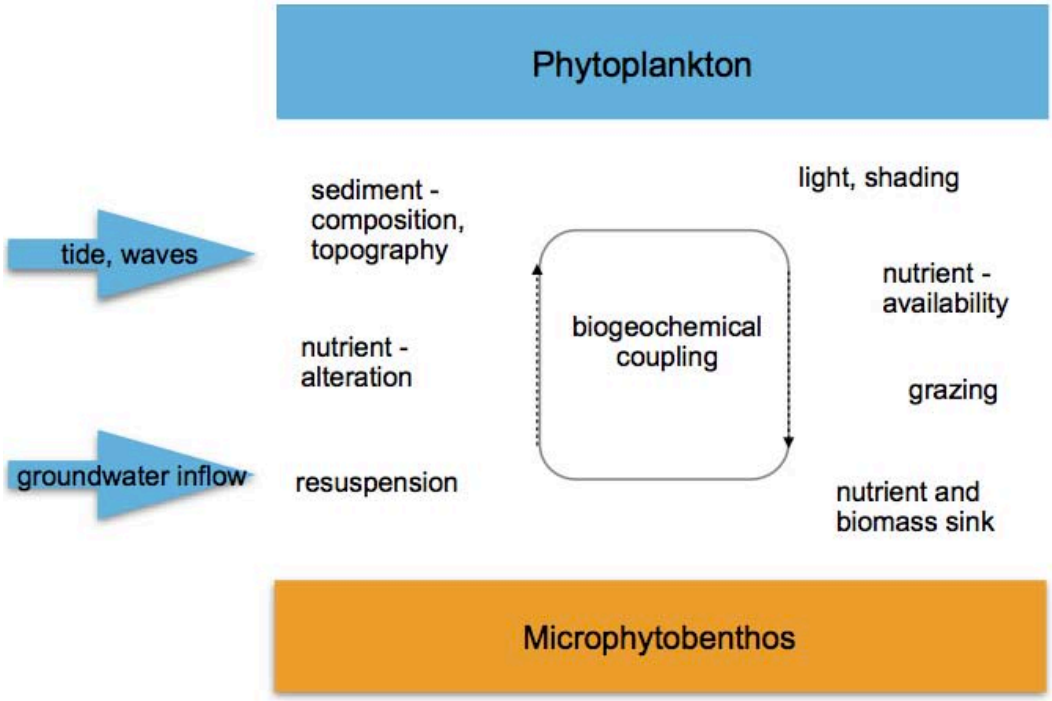

Figure 1: Interaction of biogeochemical coupling between benthic microalgae within and on top of sediment and pelagic microalgae within the water column including main controlling factors plus hydrological influences.

In this study the possible impact of groundwater discharge and nutrient enrichment in the sediment and in the water column will be analysed focussing on benthic and pelagic microalgae growth and productivity rates. Samples will be taken from the northern beach side of Island Spiekeroog in Germany. The following questions will be addressed:

- How strong does the microphytobenthos colonization of the sediment surface alter nutrient flow from the sediment to the water column?
- Which nutrient is most limiting for growth rates of benthic and pelagic algae?
- What is the role of groundwater nutrient transport for the growth rates and distribution of microphytobenthos?

2 Material and Methods

2.1 Experimental site

The Wadden Sea is a shallow coastal area reaching from Den Helder, Netherlands to Esbjerg in the North of Denmark covering almost 500 km of coastline (Flemming & Davis, 1994; Beusekom & Jonge, 2002). The Wadden Sea in Germany is located at the Frisian coastline and is confined by a chain of barrier islands only separated by the tidal inlets (Beck and Brumsack, 2012).

Our experimental study was carried out at the East-Frisian Island Spiekeroog with a length of 9.8 km, a maximum width of about 2 km resulting in an area of approximately 18.25 km^2. Spiekeroog contains mainly of fine sediment building a long beach and dune side at the northern part. This highly dynamic environment with rapid morphological changes is influenced by semi-diurnal tides ranging up to 2.6 m. About 800 people live in the village in the western part of Spiekeroog (Flemming & Davis, 1994; Röper et al., 2012; Röper at el., 2013).

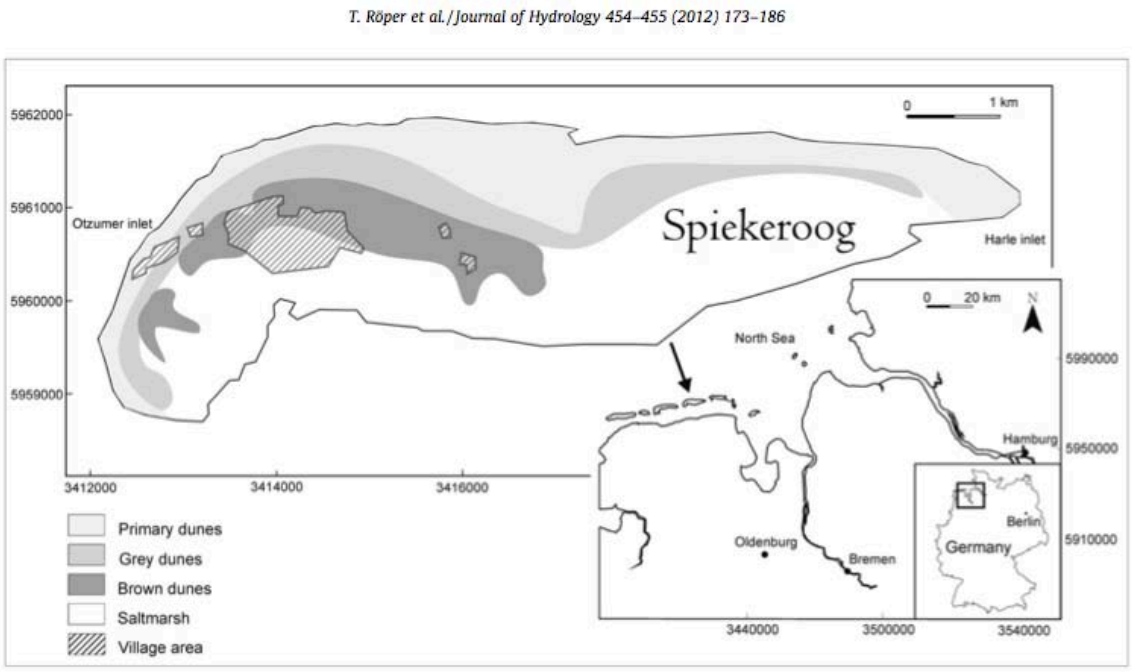

Figure 02: Location map of study area after Röper et al., 2012.

2.2 Hydrology

The tidal inlets separating Spiekeroog from the neighbouring Islands Langeroog and Wangerooge are strongly influenced by high ocean currents and therefore high sediment loads. The northern part of Spiekeroog is mainly wave influenced, contains of very fine sediments and shore-oblique sand bars, is mesotidal characterized and highly influenced by the open ocean (Flemming & Davis, 1994; Röper et al., 2013).

Due to different sand and deeper located clay sediments, an aquifer developed underneath Spiekeroog protected against tidal flooding. In the southern part, salt marshes regularly flooded show lower salinities due to freshwater influence. But also the northern beach area has a freshwater-saltwater interface only covering a few meters. This freshwater lens and some other disconnected once, which could not yet been confirmed by sampling, could develop because Spiekeroog mainly contains of fine sediment and dunes and therefore nearly no surface water runoff exists leading to high recharge rates (Röper et al., 2012; 2013).

2.3 Sampling

In Mai 2014, an incubation experiment and a transect sampling analysis testing nutrient input and groundwater influence on microalgae were conducted at Spiekeroog, Lower Saxony, Germany (53° 46′ N, 7° 42′ O).

For the incubation experiment, twenty-four sediment cores were used taking sediment and water samples at the northern beach side of Spiekeroog. While sampling, the water level was about a few centimetres at lowering tide. Sediment cores were made out of hard plastic material with a length of 20 cm and a diameter of 1.89 cm (about 33.5 cm^3). They were open to both sides and closed with rubber stopper. All cores were filled by putting each core into the sediment and closing them with rubber stoppers at both sides. By that, one half was filled with water and the other half with sediment from the first 5 cm of shore sediment. Afterwards, all cores were transported to a near by laboratory from the National Park Wadden Sea after sampling was conducted and the incubation started within a few hours.

The experimental design included three nutrient treatments (N, P, N + P) plus two controls, one at the start and one at the end were only silicate was added. All treatments included three replicates and were incubated for 24 hours with nutrient input either into the water column or the sediment core (41.73 µmol/l P (K_2HPO_4); 1 mmol/l g N ($NaNO_3$) and 505 µ mol/l Si (Na_2SiO_3)). For all treatments similar light conditions (between 0 W/m^2 during night and maximum 1530 W/m^2 during the day) and temperature conditions (approx. 12°C) were set up.

After 24h the water column was filtered using glass fibre filters (Whatman GFF) and sediment cores were sampled taking each cm of sediment layer. Chlorophyll *a* (Chl *a*) concentration of each filter and each cm of sediment was measured after storage at -20°C and extraction with acetone (dark and cold 24h) photometrically (Wetzel & Likens, 2003).

The second sampling took again place at the northern beach of Spiekeroog. Three transects, were sampled at low tide with only shallow water levels. The first transect contained of 10 sampling stations, the second transect, located 50m east from the first transect, 5 stations and transect three - again 50 m east from the second transect - contained of 3 stations. The distance between each station was about 15 m and covered a length of about 150 m from high tide water level to the surf at low tide. All together 3 transects with 18 sampling stations were analysed, each station was analysed as a single point without replicates. For this experiment, the same sediment cores were utilized as in the incubation experiment taking the first 3 cm of the beach sediment to capture the relevant benthic algal biomass. Pore water (5 cm depth) and surface water for dissolved nutrient analysis were also taken and filtered in situ with 0.2 µm polyester membrane filter into pre-cleaned Zinsser Vails. In a near by laboratory water samples were filtered as well (Whatman GFF glass fibre filters) to analyse particulate organic nutrients and Chl *a* afterwards. These filters from the water column and the sediment samples of each station were stored at - 20°C until further analysis. Particulate organic phosphorus (POP) was measured after muffling the filters at 550°C for 24 hours by molybdate reaction after sulfuric acid digestion (Wetzel and Likens 2003). Particulate organic carbon (POC) and nitrogen (PON) concentrations were measured using a CN Elemental Analyzer (Thermo Flash EA 1112). Chlorophyll *a* concentrations were measured after extraction with acetone for 24h at 4°C in the dark, photometrically (Wetzel and Likens 2003).

For analysing nutrient contents and composition of the benthic microalgae community, a separation technique from Kahlert and Hillebrand was utilized (Kahlert & Hillebrand, 2002). This method has less impact on the algal nutrient content compared to other methods using ultrasonation like Sundbäck & Snoeijs (1991). In this method 0.2 µm filtered seawater was added to the sediment samples. After stirring and a 20 min ultrasonic bath, the overlaying suspension was decanted after most grains settled down. This was done three times and the overall suspension of each sample was filtered through glass fibre filters (Whatman GFF). All of them were stored at -20°C until further analysis of particulate nutrients and chlorophyll *a* analysis as described above.

Additionally, pigment and fatty acid samples were taken. While writing this thesis the samples were still in the phase of analysis using high performance liquid chromatography (*HPLC)* for measuring algal pigment concentrations and a GC for fatty acid composition and could therefore not be included in the results.

2.4 Statistical Analysis

All data were conducted with R 3.0.3 GUI 1.63 Snow Leopard and with help of R Studio 0.98.983 (Rstudio, 2014). Homogeneity of variances and normal distribution were tested with Bartlett test and Shapiro test for incubation data and as a result Chlorophyll *a* data were log transformed. Significances were tested with one-way and two-way ANOVA using nutrient addition, depth and sediment or water type as factors. Effects were considered significant if $p < 0.05$. TukeyHSD test was conducted to detect significant differences between depth and nutrient. Chlorophyll *a* concentration from the transect experiment were analysed with one sample.

For identification of significant differences between stations and transects calculated standardisation of the data was done using data of particulate phosphate, particulate carbon and two chlorophyll *a* concentrations from two different set of sediment cores but from the same stations. Both chlorophyll *a* concentrations were measured photometrically.

To compare between the different samplings sites, POP, POC and Chlorophyll *a* concentrations were standardized with regard to the mean of each parameter for each transect. Log transformation was done to show the deviation of every measured parameter at every station from the transect mean:

$$X\ stand = ln \frac{X_n \left[\frac{\mu g}{l}\right]}{\bar{X} \left[\frac{\mu g}{l}\right]}$$

X_n = Concentration of POP, POC or Chl *a*

$\bar{X}$ = Arithmetic mean of each transect (POP, POC, Chl *a*)

$X\ stand$ = Standardised concentration of POP, POC, Chl *a*

Using three concentrations of three parallel independent sampled scores increased comparability of stations and transects. A positive value indicated a concentration of the respective parameter at a particular station being higher than the mean and a negative value signifies concentrations below mean (Figure 09 and 10). In addition one-way and two-way ANOVA was conducted. Effects were considered significant if $p < 0.05$. TukeyHSD test was conducted to detect significant differences between transects and stations and between water column and sediment of the transect experiment.

3 Results

3.1 Biomass response to nutrient supply

Nutrient enrichment to the sediment layer and enrichment in the water column lead to no significant increase in chlorophyll *a* concentration in each cm^3 compared to each control treatment (TukeyHSD, $p > 0.7$ for all) as the start chlorophyll *a* concentrations were much higher (mean concentration in the sediment layer 152.77 µg/l and 102.42 µg/l in the water column). A tendency of decreasing biomass after nutrient enrichment compared to the controls could be detected especially in the first cm of depth (Figure 03 and 04).

In the first cm of sediment the chlorophyll *a* concentrations were higher compared to the samples from cm 2-5. These higher concentrations were independent from location of nutrient addition (ANOVA, $p < 0.001$ Sediment; ANOVA, Water $p < 0.001$; TukeyHSD, $p < 0.0001$ for both in comparison to second to fifth centimetre; Figure 03 and 04).

Between the second to the fifth cubic-centimetres of sediment no significant differences were detected when nutrients were added to the water or to the sediment (TukeyHSD, $p = 0.99$).

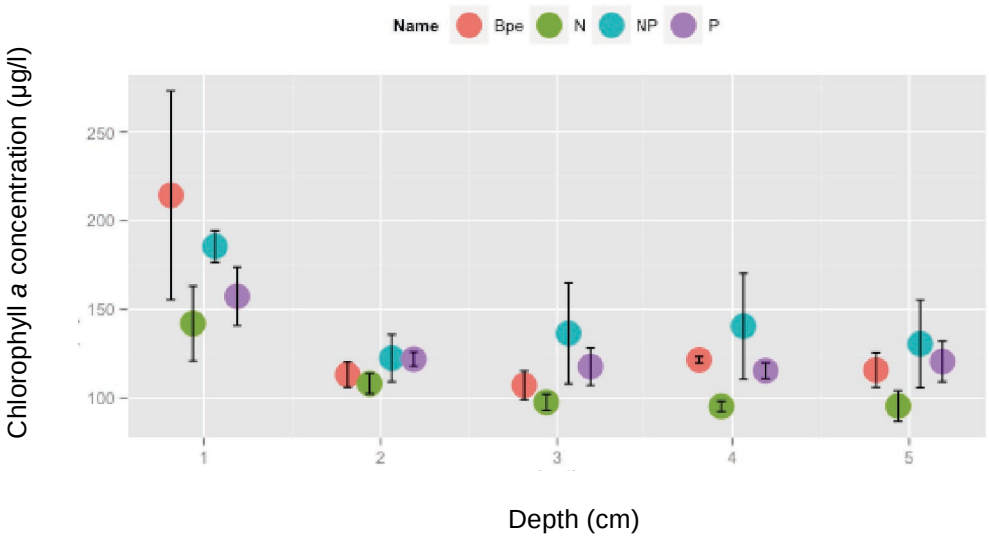

Figure 03: Chlorophyll *a* concentration in µg/l; nutrients (Nitrogen (N), Phosphate (P) and Nitrogen plus Phosphate (NP), Bpe represents the control treatment) were added to the sediment column and Chlorophyll *a* was measured in each cm^3 of sediment indicated by depth (1 – 5 cm) (n=60).

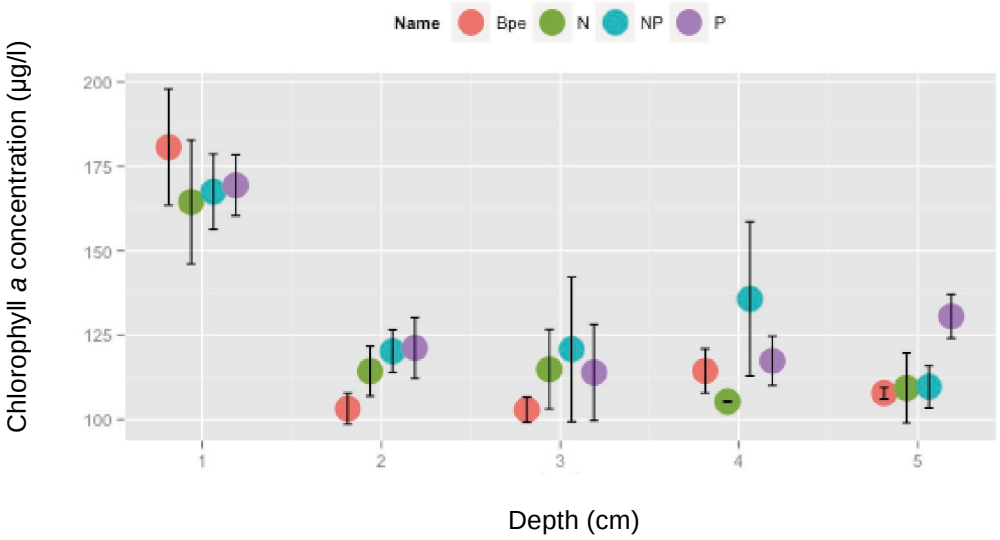

Figure 04: Chlorophyll *a* concentration µg/l when nutrient (N, N+P, P and Bpe as control) added to the water column and measured in each cm^3 of sediment indicated by depth (1 – 5 cm) (n=60).

A significant effect could also be detected for the type of nutrient addition to the sediment (ANOVA, $p< 0.05$). Enrichments of nitrogen plus phosphate in the sediment layer showed a significantly higher chlorophyll *a* concentration compared to addition of nitrogen alone (TukeyHSD, NP-N $p< 0.01$; Figure 05). However, sediment treatments enriched with nitrogen, phosphate or nitrogen plus phosphate showed no significant effect in chlorophyll *a* concentration compared to the control treatment (TukeyHSD, $p= 0.99$, Figure 05). A tendency of a slight effect in biomass by nitrogen plus phosphate addition was detected (Figure 05).

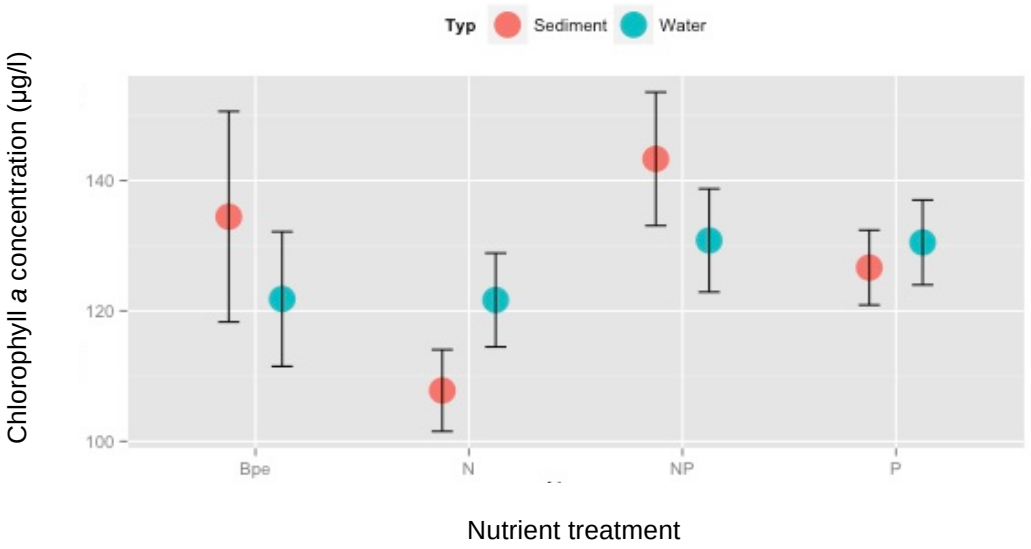

Figure 05: Mean and standard deviation of chlorophyll *a* concentration in µg/l; four nutrient treatments (N, P and NP, Bpe as control treatment) were analysed measuring chlorophyll *a* concentration only in the sediment (5 cm^3). Nutrients were added to the sediment (Sediment) and to the water column (Water), mean start chlorophyll *a* concentration in the sediment was 152.77 µg/l; (n=24).

Between factor “Location of nutrient addition” measured in chlorophyll *a* concentrations in the sediment and the water column, no significant differences were detected (ANOVA, p= 0.99, Figure 05; ANOVA, p< 0.2 figure 06). No significant effect in type of nutrient addition could be detected in the water column as the mean start concentration was 102.42 µg/l chlorophyll *a* in the water column. However, a tendency of a nitrogen effect as well as nitrogen plus phosphate compared to the control treatment can be noticed despite of the high standard error coming from one high replicate with 146.25 µg/l compared to the other two with 31.18 µg/l and 23.18 µg/l (ANOVA, p< 0.4; Figure 06).

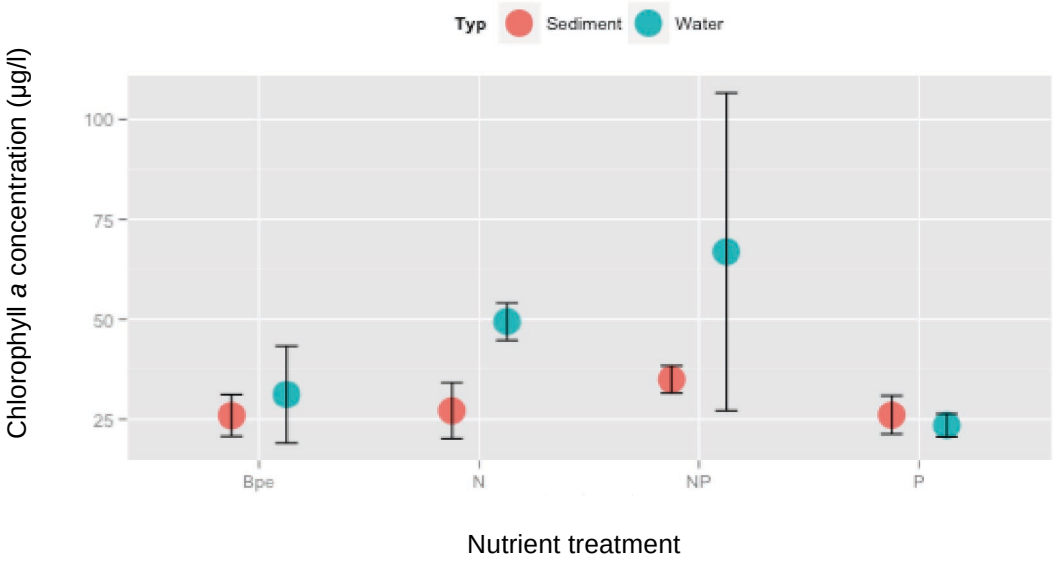

Figure 06: Mean and standard deviation of chlorophyll *a* concentration in µg/l; nutrients (N, P and NP, Bpe as control treatment) were added to the water column (Water) and the sediment layer (Sediment). Chlorophyll *a* concentration was measured in the water column. Mean start chlorophyll *a* concentration was 102.42 µg/l in the water column; (n=24).

3.2 Microphytobenthos distribution patterns

Biomass of phytoplankton and microphytobenthos within the sediment and within the water column was measured in chlorophyll *a* concentrations. As only one sample per treatment was measured only tendencies can be described.

Highest concentration of chlorophyll *a* could be measured at stations within the tideway (I-05: 65.7 µg/l; I-06: 87.6 µg/l). Lowest concentrations were detected in all transects close to the high tide and low tide shoreline (I-02: 18.3 µg/l; I-11: 11.6 µg/l).

Concentrations of chlorophyll *a* in the water column showed tendencies of higher concentration close to the high tide and low tide shoreline (I-02: 34.0 µg/l; I-11: 36.2 µg/l) compared to stations within the tideway like I-06 with 7.4 µg/l or III-05 with 12.3 µg/l. One exception was transect I station 5 with highest concentration of chlorophyll *a* in the water of 59.7 µg/l.

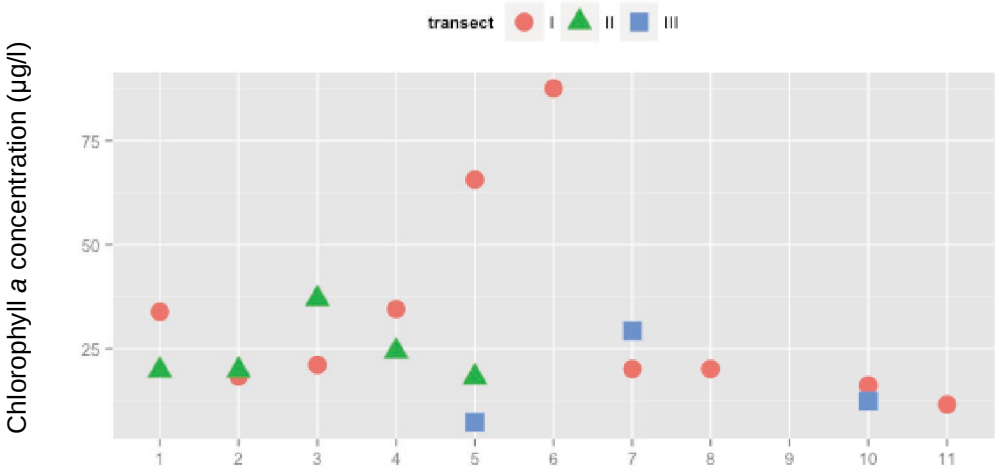

Figure 07: Chlorophyll *a* concentration in µg/l per station (1 to 11) and for all three transects (I, II and III) of the first 3 cm of beach sediment, one sample per station (n=18).

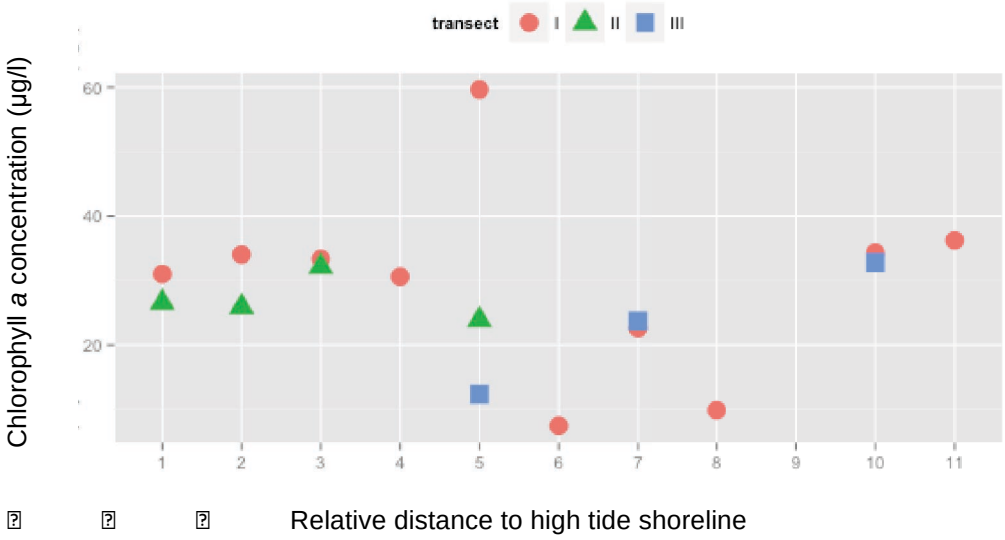

Figure 08: Chlorophyll *a* concentration in µg/l per station (1 to 11) and all three transects (I, II and III) of the water column right above sediment, one sample per station (n=18).

For identification if significant differences between stations do exist, the standardisation of the data was used and calculated as described in chapter 2.6 statistical analyses. Figure 09 and 10 show results of calculated standardised data for each station.

Significant differences using these standardised data between stations could be detected of the sediment and as well of the water column. In the sediment differences were highly significant (ANOVA, $p < 0.001$). Especially station number 6, transect I was

significantly different compared to all other stations at each transect particularly to stations close to the shorelines (TukeyHSD, p< 0.01 for all; Figure 09).

The standardisation data showed that high tide and low tide shoreline stations differed not significantly in sediment but stations from both shoreline areas were significantly different to stations within the tideway, especially station 6, transect I (TukeyHSD, 06:I-03:I *p*< 0.001; 11:I-06:I *p*< 0.001; 10:III-06:I *p*< 0.01; Figure 09).

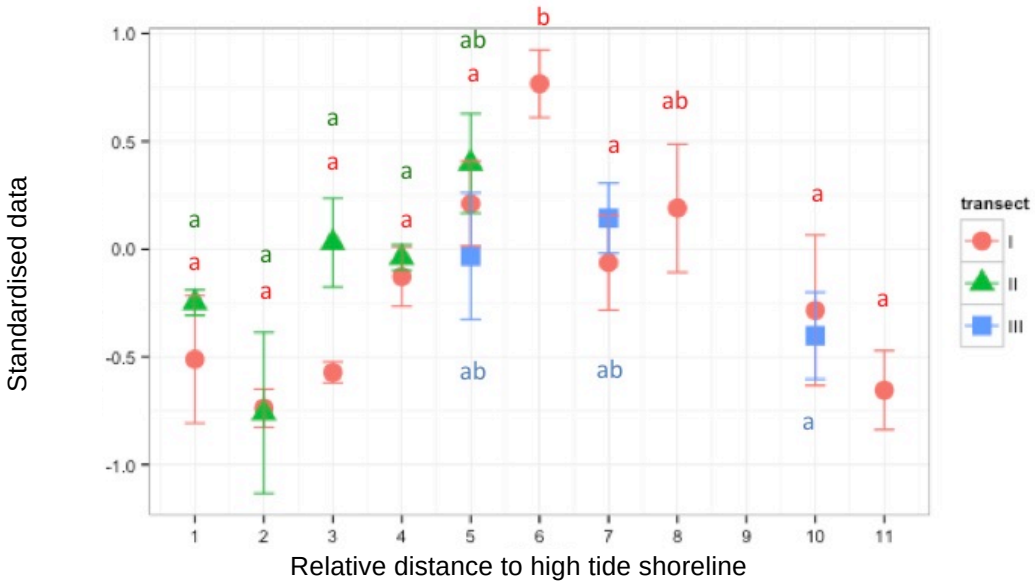

Figure 09: Standardised POP, POC and Chlorophyll *a* data of the sediment for all stations in the three transects. Arithmetic mean and standard error of the standardised values were calculated for each station. Means with different letters are significantly different (TukeyHSD, p< 0.05; (n=54). Stations with a positive ratio signify a higher biomass, POP and POC concentrations compared to the transect mean. Stations with a negative value signify lower concentrations than transect mean.

As well in the water column highly significant differences between stations were detected with the help of the standardised data (ANOVA, p< 0.001). Main differences were shown at transect I, station 05, 06, 08 and 11, which differ most significantly with all other stations at each transect (TukeyHSD, 11:I-06:I *p*< 0.001; 08:I-05:I p< 0.001; 11:I-07:I p< 0.001). Shorelines and sediment bank differ as well like tideway to shorelines and high tide to low tide shoreline (Figure 10).

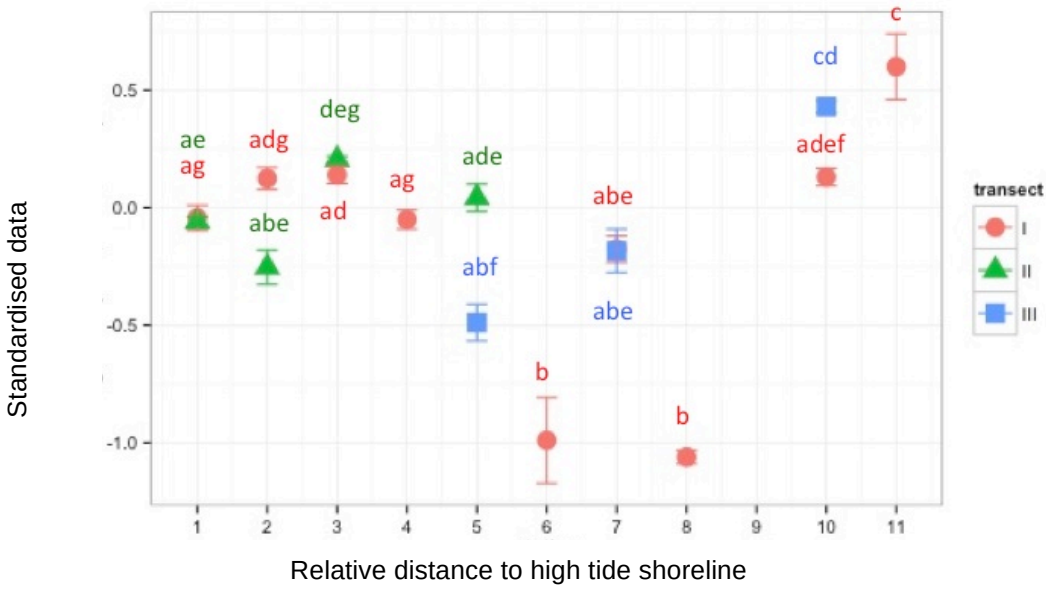

Figure 10: Standardized POP, POC and Chlorophyll *a* data of the water column for all stations in the three transects. Arithmetic mean and standard error of the standardized values were calculated for each station. Means with different letters are significantly different (TukeyHSD, p< 0.05; (n=54). Stations with a positive ratio signify a higher biomass, POP and POC concentrations compared to the transect mean. Stations with a negative value signify lower concentrations than transect mean.

C:N, C:P and N:P ratios were measured and calculated on a molar basis of POP, POC and PON for sediment of the first 3 cm and samples taken from the water column right above the sediment surface. To detect differences of nutrient availability between sediment and water column of each transect averaged values for transect I, II and III of C:N, C:P and N:P molar ratios were calculated (Figure 11).

The C:P ratio showed no significant difference between sediment and water column (ANOVA, *p*=0.12). However, the ratio tended to be higher in the sediment compared to the water column and increased with distance to high tide shoreline (mean C:P ratio in sediment transect I = 267, II =343.5 III = 301.4; in water column transect I = 215.1, II = 207.4, III = 197.2; Figure 11A). Also slightly higher but not significant N:P mean ratios in the sediment (I = 18.7, II = 24.4, III = 18.4) compared to the water column (ANOVA, p= 0.12; I = 13.4, II = 16.3, III = 14.9) were detected (Figure 11B). Transect I, station 10 showed with 4.6 the lowest N:P ratio. Generally higher ratios of the sediment could be detected within the tideway with 35.2 at station I-06 or 35.5 at station I-07 compared to shore line stations like transect I station 02 with a ratio of 8.6 or transect I station 10 with an N:P molar ratio of 4.6.

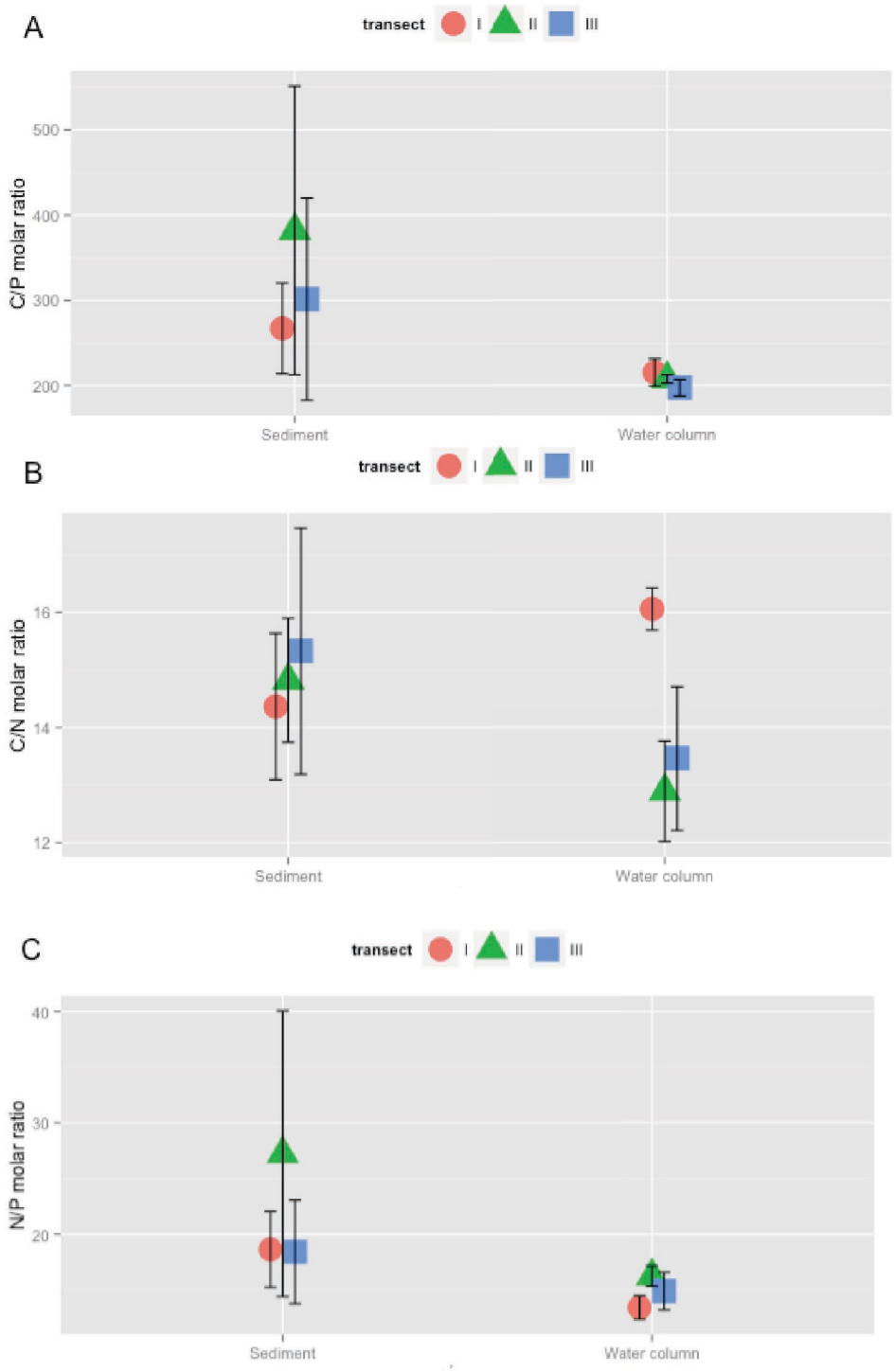

Figure 11: Mean and standard deviation of A= C:P, B= C:N and C= N:P molar ratio for each transect (I, II and III) shown for sediment layer (Sediment) and water column (Water column) in each panel (n=35 for each ratio).

C:N molar ratios were as well as the C:P and N:P molar ratio not significantly different between sediment and water column (ANOVA, *p*= 0.88; Figure 11). A higher mean C:N molar ratio showed in the water column of transect I could indicate a lower N-availability (sediment I = 14.4, II =14.7, III = 15.3; in water I = 16.1, II = 12.9, III = 13.5). But overall nutrient repletion (C:N ratio >10) can be noticed. Although representing a

very small and therefore limited amount of samples from the Wadden Sea, 13 out of 22 from sediment were below the Redfield ratio of 16 and 12 samples out of 16 from the water column were below the Redfield ratio of 16 (Figure 12A and 12B).

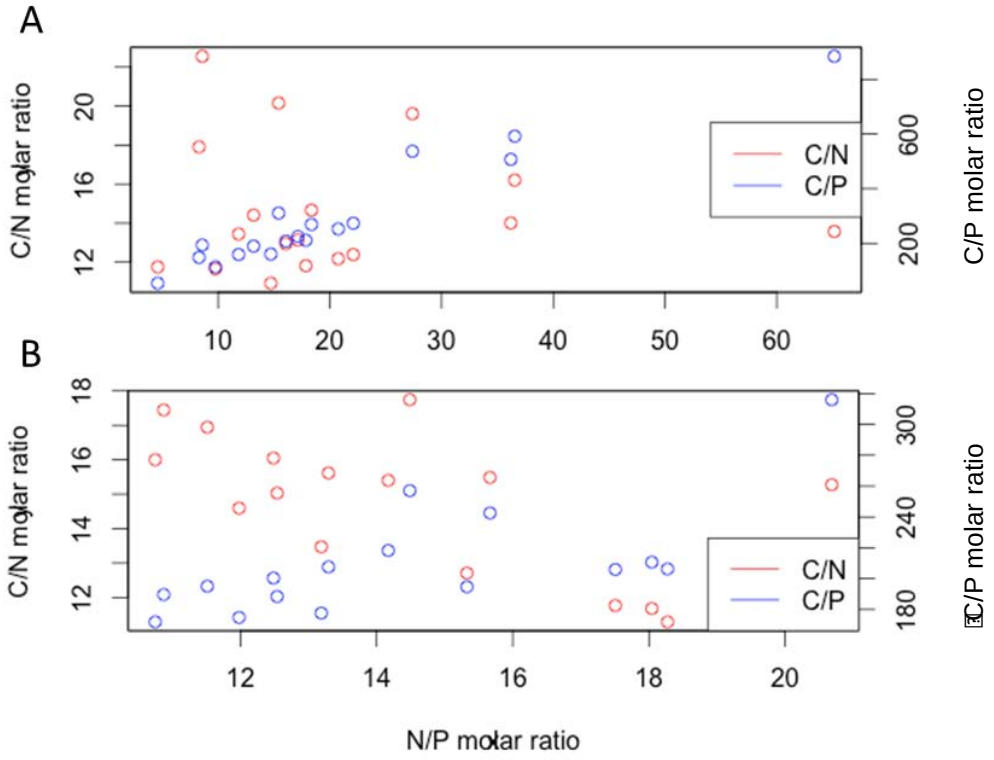

Figure 12: Stoichiometry of particulate nutrients C, N and P in A: sediment samples and B: water samples from all transect experiments at Spiekeroog. The diagram presents C:N (red) and C:P (blue) molar ratios depending on N:P ratios. The graph allows a determination of nutrient availability of benthic microalgae. High C:N in combination with low N:P ratios indicate N-limitation (upper left quadrant), whereas high C:P in combination with high N:P ratios (upper right quadrant) indicate P-limitation. Note different x-axis scaling.

Additionally dissolved nutrients were measured and described with single concentrations of nitrate and phosphate in pore water and the water column (Figure 13 and 14). High dissolved phosphate concentration in the pore water of the first 5 cm of sediment could be detected within the tideway at all transects during low tide (I-06: 455.6 µg/l; II-05: 245.5 µg/l) and lower concentration in pore water close to the high tide shore line (I-01: 24.1 µ g/l; II-01: 20.1 µg/l). In the water column slightly lower dissolved phosphate concentration within the tideway (9.8 µg/l transect I station 05) and on top of the sediment bank like station 8 of transect I with 10.48 µg/l could be detected compared to stations at the high tide or low tide shore-line (I-01 = 16.9; I-11 = 22.7 µg/l; Figure 13).

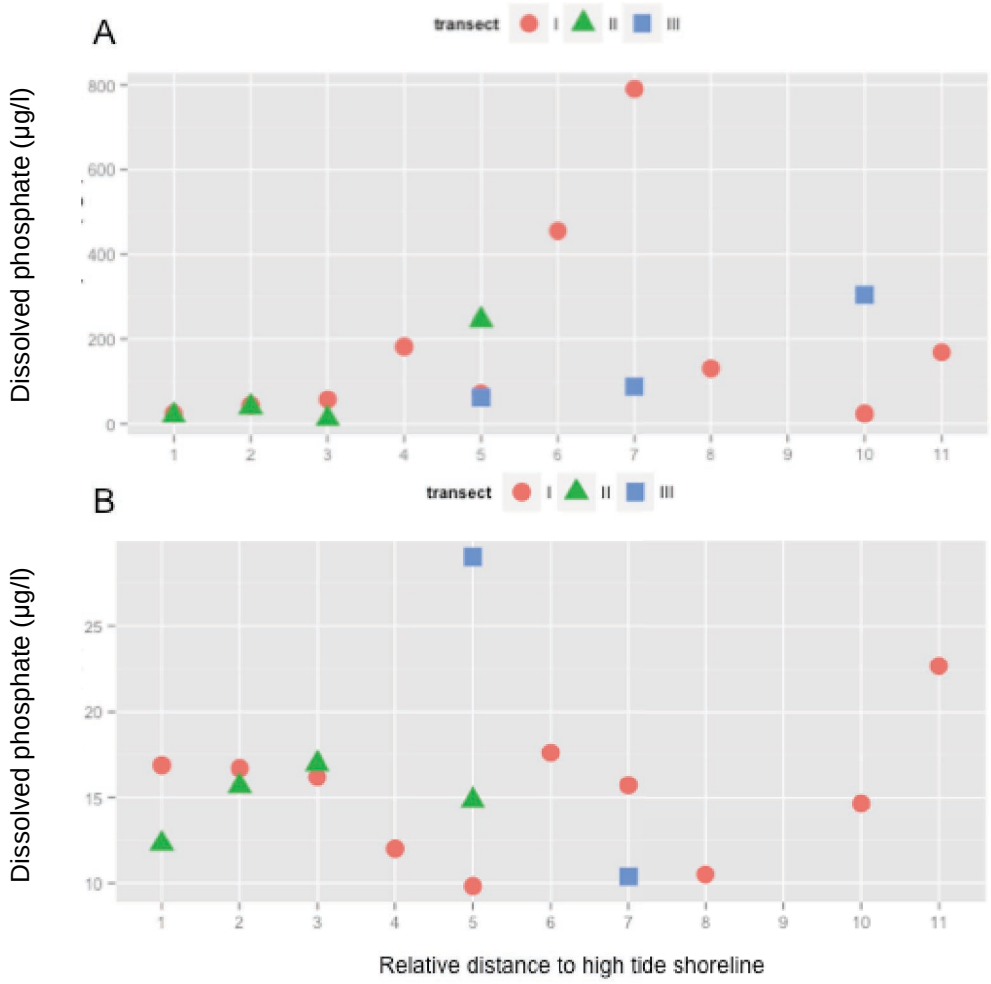

Figure 13: Dissolved phosphate concentration in µg/l per station in A: pore water and in B: water above sediment surface per station (1-11) and transect (I, II and III); one sample per station (extreme outliers not included (III-10)). Note different y-axis scaling; A: n=17; B: n=16.

Dissolved nitrate concentrations of pore water were distributed contrary to the phosphate concentration with higher enrichment rates at high tide level stations (I-02: 868.4 µg/l; I-01: 515.1 µg/l) and lower concentrations at low tide stations or within the tideway (I-07: 39.5 µg/l; III-05: 18.7 µg/l). In the water column dissolved nitrate concentrations were more equally distributed over all stations and transects compared to the pore water (Figure 14B).

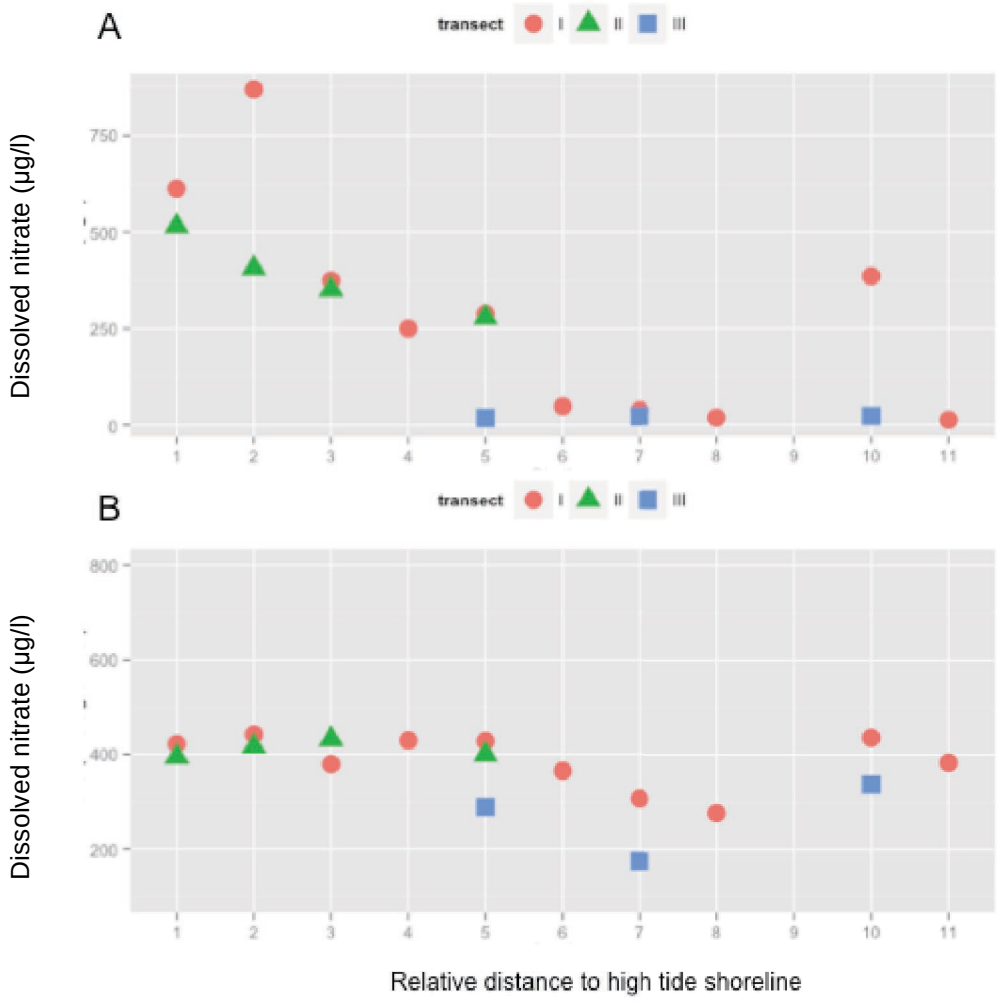

Figure 14: Dissolved nitrate concentration in µg/l in A: pore water and in B: water above sediment per station (1-11) and transect (I, II and III); one sample per station; A: n=17, B: n=17.

4 Discussion

4.1 Biomass response to nutrient supply

One laboratory experiment and one field-sampling analysis were designed to test how microphytobenthos is altering the nutrient flow from sediment to water column, which nutrient is most limiting in the investigated marine environment and if groundwater inflow may affect the nutrient transport, growth rates and as well distribution of benthic algae communities.

The primary production of coastal marine environments like the Wadden Sea is mainly nitrogen limited (Beusekom & Jonge, 2002; Collijn & Cadeé 2003; Slomp & Capellen, 2004). In our incubation experiment nitrogen enrichment alone via the water column showed a slight but no significant effect on the pelagic biomass growth. Enrichment of nitrate plus phosphate over the sediment showed as well only a slight tendency of increasing response in pelagic biomass (Figure 6). However, compared to the control treatment no significant effect in the water column was detected. In contrast to the water column the biomass of microphytobenthos in the first centimetre sediment showed generally higher chlorophyll *a* concentrations in the control treatment and when nutrients were added via the sediment or the overlaying water (Figure 05). In addition the first centimetre of sediment significantly differed compared to deeper layers independent from nutrient addition (Figure 03 and 04). A sink of biomass and a nutrient flux directed into the sediment can be an explanation for higher chlorophyll *a* concentrations in the first cubic centimetre of sediment. Reduced light conditions below the surface decrease the productivity rates in deeper sediment layers (Nilsson et al., 1991). Such a productivity of benthic microalgae can increase the control of nutrient flux to the water column and decrease the availability of nutrients for the water column and therefore for phytoplankton growth (Nilsson et al., 1991; Blumenshine et al., 1997; Pasternak et al., 2009). The lack in response by phytoplankton chlorophyll *a* could be an indication of such a reduced release of nutrients (Carlton & Wetzel, 1988; Nilsson et al., 1991; Sundbäck et al., 1991).

The benthic chlorophyll *a* concentration in the sediment tended to increase in response to nitrogen plus phosphate addition to the sediment compared to any nutrient alone. However, compared to the control no significant effect was detected (Figure 5). Despite that, these results signify that the combination of phosphate and nitrate can play a role for benthic microalgae growth. Previous studies like from Sundbäck & Granéli (1988) or Nilsson et al. (1991) in shallow lakes and in sediments in 15m depths were able to illustrate a fast reproduction of benthic microalgae due to higher P-supply in the top

layer of sediment. The nitrogen availability and also fixation is often depending on and regulated by the availability of phosphorous. A co-limitation of the benthic community was therefore often discussed and could also be supported in this experiment (Deresmus, 1982; Smith, 1984, Vitousek & Howarth, 1991; Hillebrand & Kahlert, 2002; Vadeboncour et al., 2003, Pasternak et al., 2009). An additional indicator for a co-limitation is the lack of response in the sediment treatment to any nutrient alone (nitrate or phosphate) and a constant light availability and temperature during the experiment reducing light limitation as one of the key limitation factor for benthic and pelagic biomass growth (Hansson, 1992; Tillmann et al., 2000; Wyatt et al., 2010).

Such fixation and turnover processes like nitrification or denitrification, which are significant loss pathways can give an explanation for the measured negative effect in the sediment when adding $NaNO_3$ compared to the control treatment (Figure 05) (Sundbäck & Granéli, 1988; Carlton & Wetzel, 1988; Smith, 1984). Under in situ conditions sandy sediment and high disturbances in the Wadden Sea increase oxygen supply within the sediment. But during our incubation experiment no disturbances for 24 hours could have decreased the oxygen supply and therefore increased conditions for denitrification (Scheffer & Schachtschabel).

Generally, the benthic chlorophyll *a* concentration after 24 hours of incubation was considerable higher than the pelagic one, however, it slightly increased during the experiment compared to the control (Figure 6). Despite no significant difference in location of nutrient addition, a somewhat higher competition can be noticed between benthic and pelagic microalgae when adding phosphate and nitrogen to the water column. However, because benthic microalgae biomass was considerably higher throughout the experiment an advantage in use of nutrients from the sediment and as well from the water column can be seen resulting in a more competitive position, which could even increase with a longer time period of the experiment. Affects like shading by the pelagic system can then have less chance to come into effect (Pasternak et al., 2009).

Overall, the decrease in chlorophyll *a* concentration during the incubation experiment and no significant effect to the control treatments is signalizing a weakness of the results explained. Sediment cores were maybe too small for a 24 h incubation experiment, leading to a possible oxygen limitation within the cores and therefore lower production rates of benthic and pelagic microalgae. No natural disturbances during the experiment could have additionally decreased oxygen supply within the core. Bigger sediment cores or for instance mesocosm experiments with an increasing water column compared to the sediment are a better possibility to show different effects in

biomass and trophic interactions between benthic and pelagic microalgae communities (Blumenshine et al., 1997; Pasternak et al., 2009).

4.2 Microphytobenthos distribution patterns

The Wadden Sea is a high-energy system with high disturbances due to wave action and tidal movement leading to quite heterogeneous conditions of these coastal waters and sediments (Cloern, 1991; Beusekom & De Jonge, 1995; Cadeé & Hegeman, 2002; Waska & Kim, 2010). Such constant mixed conditions can be underlined in our second analysis where the calculated standardised data showed no significant difference between sediment at high tide stations and at low tide stations. Depending on the disturbances and conditions of the sediment like roughness or low concentration of microphytobenthos stabilizing the upper sediment layers, sediment can easily be resuspended (Beusekom & De Jonge, 1995; Scholes et al., 2005). Therefore a combination of nutrient diffusing sediment and well mixing heterogeneous water column conditions shows that such physical processes play a primary role in controlling nutrient availability, nutrient distribution and therefore growth rates of benthic and pelagic algae (Smith, 1984; Pasternak et al., 2009).

As discussed in the incubation experiment, nitrate is a limiting factor in the North Sea and a relevant factor for pelagic algae growth and productivity. In our field analysis of three transects we could again detect slightly higher chlorophyll *a* in the water column at the high and low tide level stations, which could be an evidence for a higher pelagic productivity. In addition a slightly higher measured NO_3 concentration in the water column could stimulate phytoplankton growth (Figure 06; Pearl, 1997; Slomp & Capellen, 2004). Molar ratios of C:P and N:P in the water column are tending to be lower compared to ratios in the sediment (Figure 11A, 11C). Slightly higher C:N ratio indicate nutrient repletion of the analysed overlaying water (Figure 11B). However, many factors can interfere with C:N:P ratios in the pelagic system and increase or decrease nutrient concentrations. What is known is that grazing reduces C:P and N:P ratios but not C:N ratios (Hillebrand & Kahlert, 2001). Because we did not analyse the taxonomic composition, also grazing communities could be a reason for higher biomass measured in the water column of the shoreline stations maybe influencing the nutrient supply. Resuspension due to high turbidity bringing benthic microalgae from the upper sediment layers into the overlaying water column was as well discussed as a reason for higher variability in chlorophyll *a* concentration in the water column limiting phytoplankton growth due to increasing grazing pressure (Beusekomp & Jonge, 1995; Maclintyre & Cullen, 1996; Waska & Kim, 2010).

Nevertheless, moderate dissolved nitrate concentrations, dissolved phosphate leaking

into the water column and additionally low light limitation measured in our experiment are indicators for suitable conditions for phytoplankton growth (Smith, 1984; Tillmann et al., 2000; Vadeboncour et al., 2003, Pasternak et al., 2009). In the Wadden Sea light limitation plays a major role for phytoplankton growth in comparison to nutrient limitation, which plays only a minor role since nutrient concentrations in the Wadden Sea and in the Atlantic are generally higher than for instance in the Baltic region (Grizzetti et al., 2012; Tillmann et al., 2000). And since sampling took place at lowering tide and only a few centimetres of water column were left, we assumed similar light availabilities in the water and in the first 3 cm of sediment at all transect stations.

More suitable conditions for phytoplankton growth at the shorelines like tidal movement and also sandy sediments supporting the oxygen supply can lead to an increase in phosphate release from the sediment, which can be taken up by phytoplankton. Lower dissolved phosphate concentrations in the overlaying water column at high and low tide shoreline could underline such an effect (Nilsson et al., 1991; Sundbäck et al., 2003; Grunwald et al., 2010).

The nutrient availability for microphytobentos in the sediment differs to patterns measured in the water column. Molar ratios of C:P and N:P in the sediment tend to be higher compared to the water indicating P limitation (Hillebrand & Sommer, 1999, C:P > 258, N:P > 22). This could mainly be detected at station within the tideway (transect I station 06, 07 and 08 as well as transect II station 02), which significantly differ to shoreline station (Figure 09). A possible limitation by particulate phosphate could be explained by aerobic conditions making POP strongly immobile and therefore not fully available in the sediment for benthic microalgae. Also Grunwald et al. (2010) emphasised that sediment of tidal flats are a significant sink in the phosphorus cycle. Compared to quite low detected particulate phosphate concentrations at the northern beach side of Spiekeroog, higher dissolved phosphate concentration (2.5 to 8.3 µM) in pore water could be observed within the tideway at all transects during low tide to somewhat lower concentration close to the shore line at high tide (0.1 to 0.6 µM Sundbäck et al., 2003). Similar concentrations of dissolved phosphate in pore water at low tide and extremely low at high tide were as well documented by Grunwald et al. (2010) at the tidal inlet of the back barrier area of Spiekeroog Island.

A possible explanation for higher dissolved phosphate concentrations within the tideway is a high amount of organic matter produced during spring-bloom and therefore higher concentrations are incorporated into the upper sediment layers. As a result of the consequently resulting increase in microbial activity a large quantity of dissolved phosphate is released and leads to a rise in pore water concentrations (Grunwald et

al., 2010). As our sampling took place in April, such an increase in microbial activity can be a reason for the rise in dissolved phosphate in tideway stations.

Such an availability of dissolved phosphate within the tideway area can be a positive factor for higher productivity rates of benthic algae. Higher chlorophyll *a* concentrations, significant differences within the sediment compared to shoreline sediment and the positive response to nitrate and phosphate addition of microphytobenthos during the incubation experiment give evidence of higher productivity rates of benthic microalgae within protected areas like this tideway at the northern beach side of Spiekeroog (Figure 05, 07 and 09). Dale & Miller (2007) also mentioned tideways as an additional shelter like tide pool areas with more constant conditions compared to the shorelines. Even Beusekomp & Jonge (1995) could detect that ebb periods and less wave action are positively affecting biomass on the sediment surface. Such suitable conditions for benthic microalgae putting them into a more competitive position compared to phytoplankton can result in higher alteration rates in nutrient flow to the overlaying water column. A much lower nutrient availability in dissolve and particulate nutrients in the water at stations within the tideway could underline an effect like that (Figure 10, 13B, 14B).

Another reason and point of discussion for nutrient distribution is the groundwater-lens below Spiekeroog. Higher dissolved phosphate concentration in the tideway could as well be due to leaking groundwater. But recent data from the University of Oldenburg showed that only at some areas in 2 m depth slightly lower pore water salinities were measured (Reckhardt, unpublished data). Robinson et al. (2007) were able to detect that groundwater discharge and its recirculation is mainly depending on the tidal fluctuation and the inland hydraulic gradient. Depth is than just a minor indicator for groundwater discharge measurement (Burnett et al., 2006). Moreover, nutrient concentrations within the groundwater are decreased due to sandy dunes having a high filtering efficiency of substances and as well of nutrients (Scheffer & Schachtschabel, 2002). A high phosphate influence coming from leaking groundwater should therefore only play a minor role.

An influence of groundwater or freshwater inflow in coastal waters can generally increase the variability in nutrient composition and distribution in such an already very dynamic system depending on its catchment. Nevertheless, in such a small-scale experiment it is quite difficult to make reliable assumptions about limitations and turnover rates of nutrients. Many physical and biological factors are influencing the nutrient availability and therefore variations and fluctuations can be quite high, especially in such a highly dynamic ecosystem leading to deviations also in C:N:P

ratios (Broecker & Henderson, 1998; Geider & La Roche, 2002; Cadeé & Hegeman, 2002).

5 Conclusion

In the marine environment of the Wadden Sea we were able to detect that nitrogen and phosphate are important factors for growth rates and development of benthic and pelagic microalgae. Phosphate is known in freshwater studies as the main limiting factor. Our experiments can in addition support studies analysing co-limitation of nitrogen plus phosphate affecting growth rates and composition of marine microalgae (Deresmus, 1982; Smith, 1984, Vitousek & Howarth, 1991; Vadeboncour et al., 2003, Pasternak et al., 2009). Our results suggest likewise that even in a well-mixed environment benthic microalgae can become dominant if phosphorous is available and when protected areas like tideways with less current do exist leading to an increase in nutrient alteration by microphytopbenthos growth.

What is not exactly known yet, is the amount and the location of leaking groundwater at the northern beach side of Spiekeroog. Despite a high variability and a small-scale experiment including higher uncertainties, it was possible to detect significant differences between stations of all three transects. Main differences were detected between shorelines (high tide and low tide shoreline) with strong mixing conditions and the tideway with somewhat more constant conditions.

These significant differences are on the one hand influenced by tidal movement and wave action leading to the mentioned strong mixing conditions. On the other hand, nutrient availability is constantly changing due to natural and anthropogenic sources influencing the trophic interaction of benthic and pelagic communities. That groundwater could additionally affect the community structure could not be surely confirmed so far. For further studies this could be an interesting aspect to discuss, which is already planned by the University of Oldenburg to understand among others influences of groundwater biogeochemistry on benthic community structure and diversity.

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Appendices

Appendix A

Incubation experiment raw data including three replicates for each nutrient and sediment or water column treatment (Control, N, P and N+P)

Sample	Location of nutrient addition	Nutrient	Chlorophyll-*a* [µg/l]	Chlorophyll-*a* [µg/l]	Chlorophyll-*a* [µg/l]
			Replicate 1	Replicate 2	Replicate 3
Start					
0-1cm			336,14	248,95	228,87
1-2cm			123,33	122,75	126,19
2-3cm			103,82	111,28	159,46
3-4cm			114,72	122,75	126,19
4-5cm			115,30	128,49	123,33
Water column			87,34	117,83	102,10
Control					
0-1cm	Sed	Si	275.03	157.57	
1-2cm	Sed	Si	108.29	122.62	
2-3cm	Sed	Si	117.46	101.42	
3-4cm	Sed	Si	125.48	122.04	
4-5cm	Sed	Si	127.77	108.29	
Water column	Sed	Si	32.25	21.78	
Control					
0-1cm	Water	Si	199.97	165.59	
1-2cm	Water	Si	100.84	110.01	
2-3cm	Water	Si	101.42	108.87	
3-4cm	Water	Si	123.19	110.01	
4-5cm	Water	Si	111.73	108.29	
Water column	Water	Si	44.38	20.12	
N					
0-1cm	Sed	N	185.64	130.64	116.31
1-2cm	Sed	N	121.47	101.99	107.72
2-3cm	Sed	N	108.87	96.26	94.54
3-4cm	Sed	N	103.14	96.26	93.40
4-5cm	Sed	N	114.02	84.80	94.54
Water column	Sed	N	42.17	20.67	21.78
N					
0-1cm	Water	N	132.93	170.75	195.96
1-2cm	Water	N	110.58	107.72	131.21

2-3cm	Water	N	103.14	107.72	140.38
3-4cm	Water	N	107.72	107.72	107.15
4-5cm	Water	N	107.15	96.26	131.21
Water column	Water	N	56.78	41.35	53.20
P					
0-1cm	Sed	P	181.06	170.17	127.20
1-2cm	Sed	P	130.64	116.89	124.91
2-3cm	Sed	P	120.33	101.42	138.09
3-4cm	Sed	P	126.63	112.88	113.45
4-5cm	Sed	P	145.54	114.02	108.87
Water column	Sed	P	31.97	NA	22.33
P					
0-1cm	Water	P	181.63	179.34	153.56
1-2cm	Water	P	132.93	131.78	105.43
2-3cm	Water	P	125.48	134.65	88.24
3-4cm	Water	P	113.45	134.08	111.16
4-5cm	Water	P	120.90	143.24	134.08
Water column	Water	P	23.15	30.04	20.40
N+P					
0-1cm	Sed	N+P	199.40	150.12	193.09
1-2cm	Sed	N+P	106.57	110.01	150.69
2-3cm	Sed	N+P	120.33	107.15	194.24
3-4cm	Sed	N+P	NA	101.99	172.47
4-5cm	Sed	N+P	NA	102.56	114.02
Water column	Sed	N+P	29.22	39.14	39.69
N+P					
0-1cm	Water	N+P	174.18	186.22	148.40
1-2cm	Water	N+P	133.50	122.04	111.73
2-3cm	Water	N+P	165.59	104.85	98.55
3-4cm	Water	N+P	181.06	103.71	128.92
4-5cm	Water	N+P	124.34	106.57	104.85
Water column	Water	N+P	32.25	148.29	24.26

Appendix B

Transect experiment raw data including chlorophyll *a* data, particulate nutrients, C:N:P ratios and dissolved nutrients for each transect and for sediment and water column.

		Chlorophyll *a*							Particulate Nutrients				
Type	Name	*Chl a [µg/l]*	*Chl a standardized*	*Chl a Mean [µg/l]*	*SD Chl a*	*Chl a extract C/N samples*	*Chl a extract P samples*	*Chl a Pig samples [µg/l]*	*PON [µg/l]*	*PON [mol/l]*	*POC [mg/l]*	*POC [mol/l]*	*POC standardized*
Sediment	I-01- 01	33,88746237	1,217715892	49,80292061	29,0889017		76,29146702	72,15378425	23,72141372	1254,716179	8,95797E-05	12,5463591	0,001044571	0,390988251
Sediment	I-02- 02	18,33524534	0,658860772	35,64971188	26,563596		57,52622715	59,13780748	16,94386694	969,138425	6,91911E-05	18,7412342	0,001560341	0,58404214
Sediment	I-03- 03	21,11827365	0,758866425	52,75943594	45,4130022		101,5497704	80,64246475	10,16632017	1596,206536	0,000113962	27,5927092	0,002297291	0,859884933
Sediment	I-04- 04	34,54229256	1,241246634	75,16418186	61,3644658		148,0042234	102,7699703	16,94386694	2994,531904	0,000213793	28,047339	0,002335141	0,874052779
Sediment	I-05- 05	65,64672662	2,358956873	125,8971814	100,955298		261,9829416	140,6623923	27,11018711	3859,362835	0,000275537	39,1187981	0,003256911	1,21907801
Sediment	I-06- 06	87,58353801	3,147236726	238,4851416	200,674894		398,6733482	424,0214433	40,66528067	11228,90434	0,000801681	134,909205	0,011232141	4,204240762
Sediment	I-07- 07	20,13602836	0,723570313	64,67161347	55,1471845		99,36433777	123,8525659	16,94386694	5752,504023	0,000410697	79,9344592	0,006655101	2,491036187
Sediment	I-08- 08	20,13602836	0,723570313	112,9273685	107,709336		227,9250151	181,5821352	37,27650728	9387,853114	0,000670241	99,7216813	0,008302531	3,10767495
Sediment	I-10- 10	16,20704722	0,582385861	39,84161184	33,1246536		61,47672866	74,47954468	27,11018711	1802,064189	0,000128657	18,1674243	0,001512571	0,566160225
Sediment	I-11- 11	11,62323588	0,417670668	64,88986324	57,088069		105,08809	122,6027716	20,33264033	2196,264298	0,000156801	22,9355589	0,001909551	0,714751907
Sediment	II-01- 11	19,80861327	0,711804942	48,03889879	33,7319511		77,26836995	77,21862026	33,88773389	2206,031358	0,000157498	24,8501546	0,002068951	0,774417377
Sediment	II-02- 12	19,80861327	0,711804942	94,23107019	131,148296		58,30422103	288,4771097	50,83160083	1066,325062	7,61296E-05	12,4140008	0,001033551	0,386863507
Sediment	II-03- 13	36,99790577	1,329486916	63,77721385	47,7618176		74,8000748	125,8809206	16,94386694	1738,209952	0,000124098	26,6913025	0,002222241	0,831793961
Sediment	II-04- 14	24,3924246	0,876520135	86,21377692	107,474741		NA	210,3146359	40,66528067	2249,269652	0,000160585	27,8004617	0,002314581	0,866359224
Sediment	II-05- 15	18,17153779	0,652978087	110,9285497	115,652061		249,2585274	163,4703621	27,11018711	4653,310661	0,000332221	58,5109005	0,004871441	1,823403471
Sediment	III-01- 4	7,366839645	0,264720846	43,1315382	36,6474665		81,29809454	67,33165552	33,88773389	4963,52866	0,000354368	83,4518124	0,006949795	2,600649163
Sediment	III-02- 4	29,30365103	1,053000699	120,1748072	109,487995		246,2796601	177,3314687	20,33264033	3902,299313	0,000278602	43,3239445	0,003607021	1,350125022
Sediment	III-03- 4	12,44177362	0,447084096	66,05115861	61,0594436		110,3376972	126,8643653	16,94386694	2789,650379	0,000199165	32,1571834	0,002677311	1,002129849
Sediment	5m-5	NA	NA	NA	NA		437,6626893	665,7706773	169,4386694	11093,91211	0,000792043	199,881105	0,016641151	6,228991491
Sediment	10m-6	NA	NA	NA	NA		6183,423402	1721,096506	410,041581	NA	NA	NA	NA	NA
Sediment	10m-5	NA	NA	NA	NA		NA	NA	362,5987526	80233,69953	0,005728237	908,331505	0,075624971	28,30677337
Water colu	I-01- 21	31,00882029	1,114274443	35,70782509	NA		NA	NA	NA	438,5526106	3,13102E-05	6,6723968	0,000555521	0,207935029
Water colu	I-02- 22	34,04079383	1,223225722	39,27315943	NA		NA	NA	NA	618,0139724	4,41227E-05	8,2071542	0,000683321	0,255763515
Water colu	I-03- 23	33,35170893	1,198464068	38,65647133	NA		NA	NA	NA	560,217537	3,99964E-05	7,7101604	0,000641931	0,240275568
Water colu	I-04- 24	30,59536935	1,09941745	34,91429095	NA		NA	NA	NA	396,9015554	2,83366E-05	5,9380768	0,000494381	0,185049003
Water colu	I-05- 25	59,67475193	2,144359261	64,14072953	NA		NA	NA	NA	NA	NA	NA	NA	NA
Water colu	I-06- 26	7,442116869	0,267425866	10,18358007	NA		NA	NA	NA	227,4609869	1,62394E-05	2,979316	0,000248051	0,092845865
Water colu	I-07- 27	22,60198456	0,812182261	27,34171256	NA		NA	NA	NA	355,4864476	2,53797E-05	4,8775608	0,000406091	0,152001786
Water colu	I-08- 28	9,853914002	0,354091656	11,5484516	NA		NA	NA	NA	171,0277167	1,22104E-05	2,204464	0,000183541	0,068698777
Water colu	I-10- 30	34,31642778	1,233130384	40,65680378	NA		NA	NA	NA	463,7920763	3,31122E-05	6,7390658	0,000561071	0,210012764
Water colu	I-11- 31	36,24586549	1,302463016	47,21284949	NA		NA	NA	NA	964,0500881	6,88278E-05	12,066239	0,001004611	0,376025786
Water colu	II-01- 31	26,57111356	0,954809389	31,30405436	NA		NA	NA	NA	529,7788978	3,78232E-05	5,3050202	0,000441681	0,165322909
Water colu	II-02- 32	25,90959206	0,931038201	29,97437073	NA		NA	NA	NA	346,7912786	2,4759E-05	3,7788036	0,000314611	0,117760683
Water colu	II-03- 33	32,15729511	1,155543867	38,85776978	NA		NA	NA	NA	673,6323237	4,80936E-05	6,7959666	0,000565811	0,211785807
Water colu	II-05- 35	23,88827637	0,858404015	29,66870837	NA		NA	NA	NA	478,5883551	3,41685E-05	6,3203479	0,000526211	0,19696404
Water colu	III-01- 4	12,33461963	0,443233612	15,74801563	NA		NA	NA	NA	391,7729482	2,79704E-05	4,5263109	0,000376851	0,141055611
Water colu	III-02- 4	23,7045204	0,851800907	29,45478706	NA		NA	NA	NA	373,8196567	2,66886E-05	5,0060312	0,000416791	0,15600537
Water colu	III-03- 4	32,80044101	1,178654744	42,58532101	NA		NA	NA	NA	1146,343816	8,18425E-05	11,098062	0,000923991	0,345854278
Seawater	C/N	NA	NA	NA	NA		NA	NA	NA	NA	NA	NA	5,81764841	0,000484361	NA
Seawater	P	NA	NA	NA	NA		NA	NA	NA	NA	NA	NA	NA	NA	NA
Seawater	C/N 26,(	NA	NA	NA	NA		NA	NA	NA	NA	NA	NA	5,30124344	0,000441371	NA
Seawater	P 26,05.	NA	NA	NA	NA		NA	NA	NA	NA	NA	NA	NA	NA	NA
Seawater	11.06.	NA	NA	NA	NA		NA	NA	NA	0,1555	NA	NA	7,4256	NA	NA
Mean		27,82870996	NA	NA	NA		NA	NA	NA	NA	NA	NA	NA	NA	NA

						Dissolved Nutrients			
C/N	*C/PO4*	*N/PO4*	*POP [µg/l]*	*POP [mol/l]*	*POP standard*	*Nitrat [µg/l]*	*Nitrat [µmol/l]*	*Phosphat [µg/l]*	*Phosphat [µmol/l]*
11,6608142	113,905668	9,76824311	870,9205957	9,1705E-06	0,695912623	612,6443255	9,880579205	24,10925395	0,253861787
22,5511677	193,62503	8,58603119	765,319667	8,05856E-06	0,611531774	868,3823284	14,00505974	43,58060555	0,458888128
20,158672	310,953286	15,4252862	701,6255185	7,38788E-06	0,560636707	375,2936091	6,052644374	57,37712126	0,604160485
10,9224327	160,841403	14,7257857	1378,795929	1,45183E-05	1,101732462	249,8825158	4,030044655	182,2053683	1,918557105
11,820247	211,082071	17,8576701	1465,346521	1,54296E-05	1,170891063	288,7469292	4,656840495	71,73180341	0,755310134
14,0107331	507,171916	36,1988135	2103,258093	2,21466E-05	1,680616884	49,4056026	0,796801585	455,630375	4,797624249
16,2044304	592,172329	36,5438534	1067,313774	1,12385E-05	0,852841387	39,52292601	0,637416172	789,9562647	8,317955825
12,3873944	273,76113	22,0999769	2880,208909	3,03276E-05	2,301442574	18,55075513	0,299182083	129,7722498	1,366455195
11,7565464	54,1800468	4,60850021	2651,307908	2,79174E-05	2,118538304	385,6822221	6,220189405	23,14846165	0,243744989
12,1781519	252,772935	20,756264	717,4389309	7,55439E-06	0,573272479	12,85504821	0,207323102	168,4028783	1,773221842
13,1363307	225,281404	17,1494925	872,1876485	9,18385E-06	0,696925067	515,0590707	8,306747865	20,10067948	0,211652938
13,5762183	884,339747	65,1388869	110,9938221	1,16873E-06	0,088690062	407,1000096	6,565610292	39,67462041	0,417759507
17,9070562	148,701298	8,30406164	1419,257477	1,49443E-05	1,134063426	352,1745216	5,679785334	12,70479106	0,133776888
14,4134234	189,932599	13,17748	1157,333913	1,21863E-05	0,924772343	NA	NA	NA	NA
14,663289	269,256413	18,3626206	1718,212637	1,80922E-05	1,372944755	279,2575532	4,503798139	245,4517826	2,584519139
19,6065824	537,029278	27,3902543	1228,694721	1,29377E-05	0,981793485	18,71	0,3	62,22033339	0,65515777
12,9468487	208,088488	16,0725202	1646,213354	1,73341E-05	1,315413437	22,91519915	0,369570778	87,84802729	0,925008185
13,4426498	159,193416	11,8424134	1597,199199	1,6818E-05	1,276248478	23,25530234	0,37505588	303,7742819	3,198634115
21,0108529	103,157131	4,90970699	15320,70213	0,000161322	12,24206898	NA	NA	NA	NA
NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
13,2021365	1040,09511	78,7823324	6905,219787	7,27097E-05	5,517643792	NA	NA	NA	NA
17,7425739	257,042348	14,4873201	205,25	2,16121E-06	0,164005842	422,4714143	6,813516582	16,86831632	0,177617314
15,4864175	242,591172	15,6647703	267,5	2,81669E-06	0,213746957	442,2488037	7,132481525	16,69252288	0,175766272
16,0495765	200,373006	12,4846288	304,25	3,20365E-06	0,243112193	379,3937876	6,118771058	16,17693104	0,170337275
17,4467531	189,701924	10,8731936	247,5	2,60609E-06	0,197765876	429,6654023	6,929539477	12,00074063	0,12636349
NA	NA	NA	235	2,47447E-06	0,1877777	428,2262456	6,906329107	9,827091289	0,103475743
15,2744756	315,93831	20,6840691	74,5625	7,85118E-07	0,059579467	365,2226384	5,890222198	17,59446027	0,185263349
16,0006014	171,979398	10,7483084	224,25	2,36128E-06	0,179187869	306,6893469	4,946211458	15,70695309	0,165388576
15,0311834	188,463023	12,5381361	92,4875	9,73863E-07	0,073902511	276,8858103	4,465547244	10,49562955	0,110515211
16,9446667	195,09423	11,5136068	273,125	2,87592E-06	0,218241636	436,1243585	7,033707957	14,66167052	0,154382126
14,5958266	174,857214	11,979946	545,625	5,74525E-06	0,435983862	383,2916789	6,181635304	22,67201636	0,238728192
11,6774777	210,679348	18,0415114	199,1	2,09646E-06	0,15909166	394,9859947	6,370238396	12,297066	0,12948369
12,7069937	194,754706	15,3265761	153,4166667	1,61543E-06	0,122588208	417,0256678	6,725688902	15,65764488	0,164869379
11,7648013	205,94688	17,5053428	260,9166667	2,74737E-06	0,208486518	432,6131396	6,97707987	16,94862554	0,178462941
15,4005234	218,228591	14,1702061	229	2,41129E-06	0,182983376	399,7613336	6,447253904	14,82998882	0,156154457
13,4730706	177,668416	13,1869283	201,4375	2,12107E-06	0,160959449	288,7362427	4,656668146	29,01550255	0,305522824
15,6166572	207,598858	13,2934248	190,6666667	2,00766E-06	0,152352971	174,2818839	2,810775986	10,3938623	0,109443638
11,2898695	206,291521	18,2722679	425,375	4,47906E-06	0,339897614	337,6246802	5,445129017	74,86915825	0,788345354
NA	NA	NA	NA	0	NA	NA	NA	NA	NA
NA	NA	NA	104	1,09509E-06	NA	NA	NA	NA	NA
NA	NA	NA	NA	0	NA	NA	NA	NA	NA
NA	NA	NA	74,7	7,86566E-07	NA	NA	NA	NA	NA
NA	NA	NA	59,8	6,29674E-07	NA	NA	NA	NA	NA
NA	NA	NA	NA	NA	NA	NA	NA	NA	NA

Eigenständigkeitserkärung

Hiermit erkläre ich, dass diese Arbeit selbstständig und ohne Benutzung anderer Hilfsmittel als der angegebenen Quellen erstellt worden ist. Diese Arbeit wurde bisher nicht in einem anderen Studiengang als Prüfungsleistung verwendet.

Sandra Rovó Wien, 15. Dezember 2014