

A novel time-series station in the Wadden Sea (NW Germany): First results on continuous nutrient and methane measurements

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Abstract

In autumn 2002 a time-series station was installed in the tidal inlet between the Islands of Langeoog and Spiekeroog (Southern North Sea, NW Germany) to continuously measure physical, chemical, and meteorological parameters, even during extreme weather conditions (gale-force storms, drifting ice). Inside the pole of the station sensor tubes are installed in direction of the prevailing tidal currents. The tubes are equipped with hydrographic sensors (pressure, temperature, conductivity) and allow retrieval of water for nutrient analysis by automated instruments located inside the pole. Dissolved methane and the nutrients ammonia, nitrite, nitrate, phosphate, and silicate are measured at the station.

Nutrient patterns obtained during spring and summer 2006 reflect the development of nutrient concentrations during the annual spring phytoplankton bloom. Methane measurements showed a tidal dependence with maxima at low tide, which emphasizes the tidal flat sediments as the dominating source for methane in the open coastal water column.

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1. Introduction

The Wadden Sea is a highly dynamic environment due to physical and biological forcing. In addition to eutrophication, human activities (e.g. dike building, land reclamation) and freshwater contribution influence this coastal system (e.g. Flemming and Davis, 1994; Flemming and Nyandwi, 1994; Dellwig et al., 2000; Hinrichs et al., 2002; Colijn and van Beusekom, 2004). While the

Wadden Sea of the Southern North Sea is mainly controlled by physical forcing in autumn and winter, biological processes dominate the system during spring and summer (e.g. Lunau et al., 2006; Dellwig et al., *in press*). Biomass formation in tidal flat areas is dominated by phytoplankton and microphytobenthos production (Reid et al., 1990), with production rates depending on nutrient availability and light regime (Colijn, 1982). Seasonal as well as tidal changes in aggregate composition and concentration affect the light attenuation coefficient. These changes depend on tidal current velocities, shear rates, and aggregate formation processes

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(Behrends and Liebezeit, 1999; Grossart et al., 2004; Lunau et al., 2006; Dellwig et al., in press). Wadden Sea data for dissolved nutrients are predominantly available at an annual or seasonal resolution (e.g. DeJonge and Postma, 1974; Helder, 1974; van Bennekom et al., 1974; Martens, 1989; van Beusekom and de Jonge, 2002). Nutrient time-series on a tidal resolution are essentially lacking. According to Langner-van Voorst and Höpner (1996), Villbrandt et al. (1999), Billerbeck et al. (2006a, b), and recent pore water measurements (M. Beck, pers. comm.), tidal flat sediments presumably are an important source for dissolved nutrients and dissolved inorganic and organic carbon, and may contribute to the budget of the open water column. Despite of rather small bacterial numbers and low organic matter contents (Bergamaschi et al., 1997; Llobet-Brossa et al., 1998; Rusch et al., 2003) the sandy sediments dominating the investigated area are characterized by high organic carbon mineralization rates (Cammen, 1991; D'Andrea et al., 2002; Huettel et al., 2003).

In coastal zones values of dissolved methane may be orders of magnitudes higher than in open ocean waters (e.g. Scranton and McShane, 1991; Bugna et al., 1996). Methane is generated within the tidal flat sediments by archaea (e.g., *Methanomicrobiales* and *Methanosarcinales*, spp.: Wilms et al., 2006) and is transported by diffusion and advection (Hovland et al., 1993) into the open water column. While methane data for European rivers, estuaries, and the North Sea are available (Scranton and McShane, 1991; Rehder et al., 1998; Upstill-Goddard et al., 2000; Middelburg et al., 2002), information for the Wadden Sea is still scarce.

In spring 2001 a research group was established to investigate biogeochemical processes in the Wadden Sea of Spiekeroog Island (NW Germany). One major aim of this project is to evaluate, whether the Wadden Sea system presently is in a steady state or whether it is subject to a net loss or gain of material and compounds. Modelling, which forms an integral part of the research group, also relies on continuous data sets to tune model parameters and to verify model results. Especially the online availability of nutrient data allows monitoring the biological state of the tidal flat system. The time-series station provides the unique opportunity to obtain data sets over extended time periods at high temporal resolution.

2. Geographical settings

Fig. 1 shows the study area in the Southern North Sea and the position of the time-series station between Langeoog and Spiekeroog Islands in the main tidal inlet

(Otzumer Balje) of the backbarrier area of Spiekeroog Island. The water depth (below mean sea level) is 13.5 m at position 53°45'01.00" N and 007°40'16.30" E. The backbarrier tidal flat area is characterized by semidiurnal tides under mesotidal conditions (tidal range 2.2–2.8 m) and encompasses an area of about 74 km² (Walther, 1972). During low tide, the area of dry-falling tidal flat sediments amounts to 46 km² during spring tide and 30 km² during neap tide. The tidal flat sediments are dominated by sands in the western part while in the eastern part mixed and muddy deposits prevail. The permeable sandy sediments may significantly influence the geochemical budgets of the Wadden Sea water column owing to draining pore waters during ebb tide (e.g. Dellwig et al., 2007).

3. Materials and methods

3.1. Time-series station

The time-series station (Figs. 2 and 3) consists of a 35.5 m long steel-pole with a diameter of 1.6 m. About 15 m of the pole are grounded in the sediment to resist tidal currents, wind, and floating ice sheets. The water column covers 13.5 m of the pole at mean sea level and the remaining 7 m are above the water line. This station is designed for operation throughout the year, even during heavy storms and ice winters.

On top of the pole a platform houses two containers, one for the electrical system, containing storage batteries, fuse boxes, battery charging equipment, and a PLC (Programmable Logic Controller), with the latter controlling the electrical equipment. The second container houses a station computer for data storage, power management, and sensor control. A wind generator, solar panels, and a gas generator (in case of insufficient wind and sun) are located on an upper platform for electric power supply. The whole station has a self-sufficient electrical system and does not require any connection to onshore electricity networks.

Ladders provide access to the station, the platforms, and the inner pole. The submerged part of the pole contains ten flanges and sensor tube openings, ranging from 0.5 m to 11.5 m above sea floor (Fig. 3). These openings serve to install sensor tubes in the prevailing tidal current direction. Five openings are equipped with exchangeable sensor tubes (inner diameter 22 cm) at 1.5 m, 3.5 m, 5.5 m, 7.5 m, and 9.0 m above the seafloor. This set-up enables measurement of several physical parameters (temperature, pressure in the lowermost tube, and conductivity) at different depths to identify possible vertical gradients.

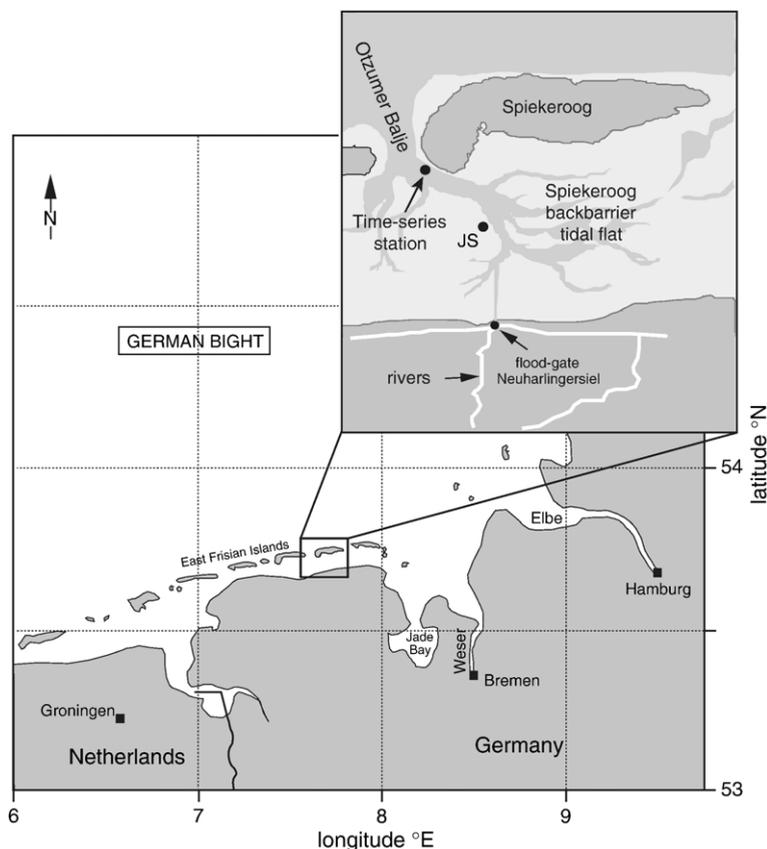


Fig. 1. Map of the study area in the German Bight. The detailed map shows Spiekeroog Island, the backbarrier tidal flats, the position of the time-series station in the tidal inlet (Otzumer Balje), and the pore water sampling site Janssand (JS).

For nutrient measurements, water from the sensor tube 9.0 m above seafloor is used. The sensor for methane measurements is attached at the exterior pole at a fixed position about 0.5 m below low-tide water level.

The entire system described above is controlled by a land-based computer station located at the University of Oldenburg. It is possible to connect to the time-series station via modem and wireless LAN (local area network). Special remote software enables to manage the whole measuring and controlling equipment. Data stored on the time-series station computer are transferred automatically every four hours to the land station. If required, data transmission can be initiated manually.

3.2. Nutrient analyses

Fig. 4 shows a sketch of the hardware set-up of the nutrient analysers. The belt filter and the analysers are mounted to the uppermost ladder at the inside of the pole. While the filter system is unmovable fixed, the nutrient analysers and a container (20 L) with imidazole buffer solution for nitrate measurements are situated on

swivel-mounted racks. All racks are attached by hinge joints to a stainless steel pipe. This concept allows maintenance of the analysers without dismounting. De-ionized (DI) water is stored in three fibre reinforced polyethylene (PE) bags (total volume 150 L).

At the 9.0 m sensor tube a water-inlet device is installed, consisting of a ball valve, a self-closing corrosion-free magnetic valve (Bürkert, Fluid Control System Type 0121, Germany), and a sediment trap. A water volume of approx. 7 L min^{-1} is transported by a membrane pump (Johnson, Aqua Jet, WPS 2.4, 24V, Germany) to the belt filter (Metrohm, Series 01.12, Germany). If the water flow falls below an alarm threshold, the entire system is stopped to prevent damage. The cellulose filter belt (length 100 m; Schleicher & Schuell, No. 1574, Germany) has a pore size of 7 to $12 \mu\text{m}$. Prior to analysis the entire tubing from the inlet via the belt filter towards the outlet is rinsed for three minutes, followed by a five minute rinse of the nutrient analysers with filtered water. After nutrient analysis the analysers are cleaned with 75 mL DI-water from the PE bags. The supply of DI-water lasts



Fig. 2. Photograph of the time-series station.

for about two weeks when measurements are performed once every hour.

Controlling and monitoring of nutrient analyses, including pump, valve, and flow meter, is assured via Soft-PLC software (-4H-Jena, Germany). The Soft-PLC is subdivided into four main sub-programmes: 'wait for start', 'operate', 'stop water', and 'error water'.

Continuous nutrient measurements for ammonia, nitrite, nitrate, phosphate, and silicate are performed by Systea μ Mac1000 analysers (Systea, Italy). These analysers are based on a loop-flow reactor (LFR) and loop flow analysis (LFA) technology. The filtered sample is pumped into the analysers and the required reagents are added automatically by negative pressure. Determination of nutrients is performed by conventional photometry.

Three analysers are installed on the station for ammonia and phosphate, nitrite and nitrite+nitrate, and silicate. Analysers for two parameters operate in sequential mode. After each measurement a wash cycle with DI-water is performed automatically. If concentrations exceed the calibration range by a given percentage (Table 1, 'Full range'), the analysers automatically dilute the sample and repeat the measurement (dilution factor approx. 10). An overview of determination methods, calibration ranges, cuvette lengths, and wave lengths is

given in Table 1. Reagents used for nutrient measurements have a shelf life of about two to three weeks, depending on the ambient temperature inside the pole. Approximately 330 to 500 analyses of each parameter are performed in-between maintenance intervals. Despite of the temperature-depending durability of reagents, no interference of measurements with temperature or humidity of the inner pole was recognized. Calibration and reproducibility measurements are performed with solutions containing $11.1 \mu\text{mol L}^{-1}$ ammonia, $2.1 \mu\text{mol L}^{-1}$ phosphate, $60 \mu\text{mol L}^{-1}$ nitrite+nitrate ($6.5 \mu\text{mol L}^{-1}$ as nitrite), and $50 \mu\text{mol L}^{-1}$ silicate (see Table 1).

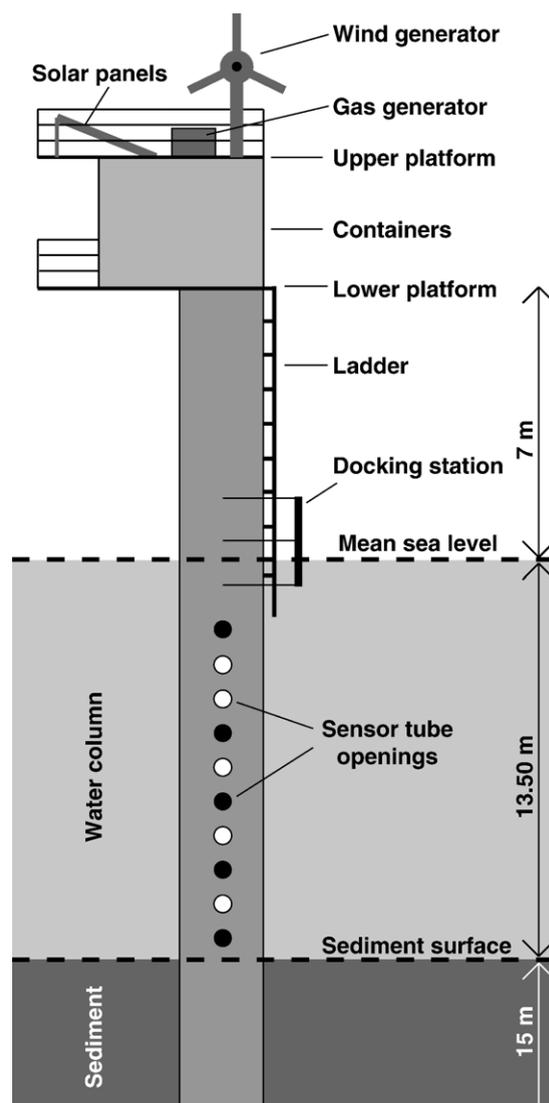


Fig. 3. Sketch of the time-series station. White sensor tube openings are equipped with sensor tubes, black ones are not.

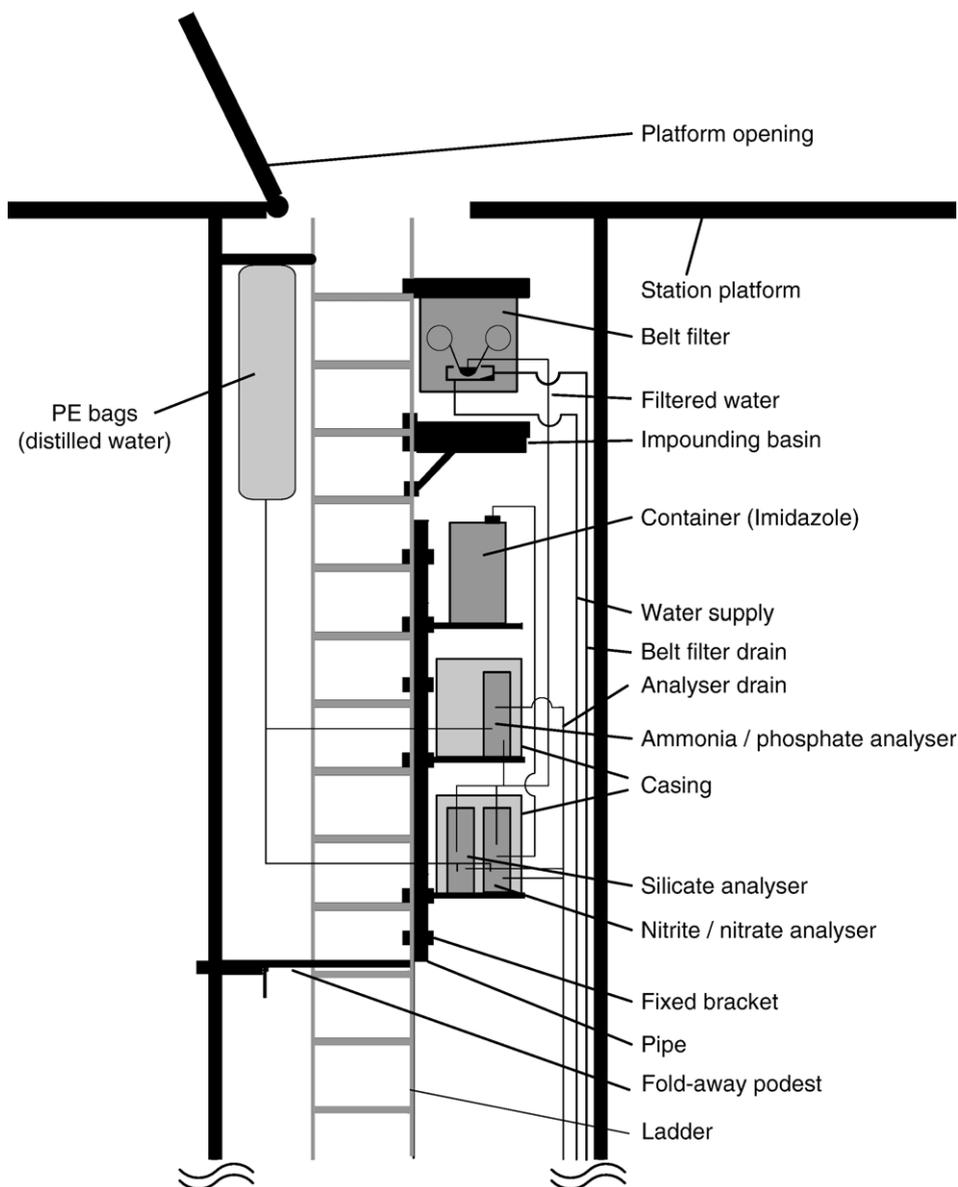


Fig. 4. Sketch of nutrient measurement hardware arrangement located in the upper part of the pole.

3.3. Methane measurement

For the measurement of dissolved methane (CH_4) in surface water, a sensor (Capsum Technologies, Germany) is installed at the exterior pole at 10.5 m above the seafloor. The measuring principle of the sensor is based on the adsorption of hydrocarbon molecules (mainly CH_4) on a tin dioxide semiconductor detector, which results in resistance variation as reported by Garcia and Masson (2004) and Marinaro et al. (2004). During operation, hydrocarbon molecules diffuse through a silicone membrane into the detector chamber. The

detection limit of the sensor is $0.02 \mu\text{mol L}^{-1}$. As the measurement is diffusion-controlled, the sensor has been modified by adding a pump (Rule, 360 GPh, 23 L h^{-1} , USA), which ensures a constant flow of water to the membrane surface and reduces equilibration time. Furthermore, the constant jet of water protects the membrane from fouling.

For data verification methane was determined in water samples by gas chromatographic headspace analysis as described by Niewöhner et al. (1998). Sampling was done with a FreeFlow sampler (Hydro-Bios, Germany) at the time-series station. The water was

Table 1
Measuring principles and parameters of nutrient determination

Parameter	Reference	Cuvette length (mm)	λ (nm)	Calibration range ($\mu\text{mol L}^{-1}$)	SD*	Full range** (%)	Remarks
Ammonia	Patton and Crouch (1977)	50	660	0.01–11.1	0.4	350	Trisodium citrate and disodium EDTA are added to prevent precipitation of Ca and Mg hydroxides or carbonates.
Phosphate	Murphy and Riley (1962)	50	660	0.01–2.1	0.1	500	
Nitrite	Shinn (1941) Bendschneider and Robinson (1952)	15	530	0.01–6.5	0.3	266	
Nitrite+nitrate	Morris and Riley (1963) Strickland and Parsons (1968)	15	530	0.17–60	1.85	184	Internal copper-coated cadmium granule column (operation time \sim 1000 samples) to reduce nitrate to nitrite
Silicate	Chow and Robinson (1953)	15	850	0.38–50	1.01	208	

* Standard deviation of calibration solution measurements.

** % excess of maximum calibration concentration measured without dilution.

immediately transferred into serum flasks, crimped, and frozen upside down in dry ice. The results (Fig. 5) generally show a reasonable agreement between both techniques with a mean sensor deviation of +11%, most likely caused by the inaccuracy of sensor calibration.

4. Results and discussion

4.1. Nutrients

Concentrations of silicate, phosphate, nitrate, nitrite, and ammonia measured from April to July 2006 at our time-series station are shown Fig. 6. In Table 2 mean values of ship-based measurements from previous years are shown for comparison.

Decreasing concentrations of silicate in April (from about $20 \mu\text{mol L}^{-1}$ to minimum values of on average $0.26 \mu\text{mol L}^{-1}$) reflected the development of the spring diatom bloom (Fig. 6a). The subsequent breakdown of this algal bloom in late April to early May led to a moderate increase in silicate of up to $5 \mu\text{mol L}^{-1}$, due to decomposition of diatom frustules within the water column of the backbarrier area. Such processes may be accelerated by high shear stress due to tidal forces. Maximum concentrations were observed at low tide (Fig. 6f), which suggests the tidal flats to be an essential source for dissolved silicate. Pore water measurements from a sand flat site (Janssand (JS), Fig. 1) between March and June 2006 revealed an average concentration of $60 \mu\text{mol L}^{-1}$ in the upper 10 cm of the sediment (M.

Beck, pers. comm.). In contrast, during high tide silicate remained extremely low, caused by the influx of silicate-low North Sea water. Additionally to the above mentioned mineralization processes a distinctly lower consumption of dissolved silicate by diatoms after breakdown of the spring bloom must be taken into account. Thus, the pore water discharging at low tide will impact silicate water column signals. Due to the lack of silicate mineralization rates as well as pore water fluxes, we cannot assess the importance of these two processes at this point of time.

The minor decrease in silicate in early May might be due to a further, less pronounced onset of diatom growth, followed by another breakdown at the end of May. The

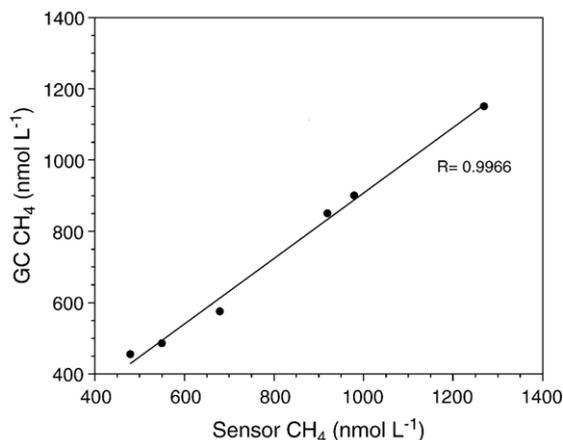


Fig. 5. Methane measurements of sensor vs. GC.

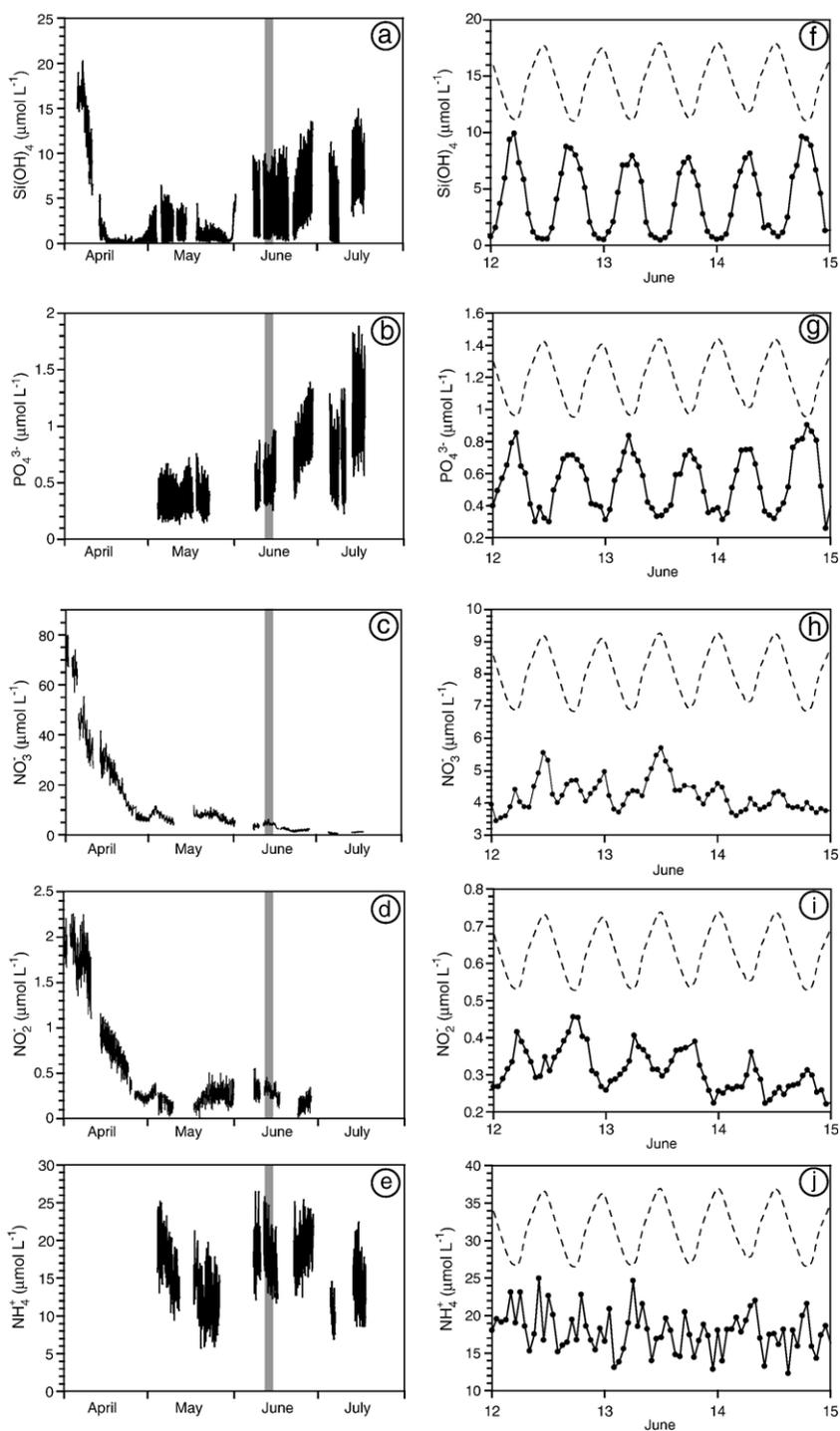


Fig. 6. Nutrient concentrations at the time-series station from April to July 2006 (a–e). The grey bar indicates the time period shown in f–j, where the tidal resolution of the individual parameter is shown. The dots mark the hourly measurements and the tidal gauge is given by the dashed line.

subsequent increase in distinct amplitudes with higher values at low tide point towards recycling processes within the Wadden Sea system.

Phosphate showed a general increase during the time interval, with a tidal signal similar to that of silicate (Fig. 6b and g). This behaviour was most likely caused by

Table 2

Mean concentrations of ship-based measurements in the tidal inlet at time-series station position

Month	Year, day	Silicate ($\mu\text{mol L}^{-1}$)	Phosphate ($\mu\text{mol L}^{-1}$)	Nitrite ($\mu\text{mol L}^{-1}$)	Nitrate ($\mu\text{mol L}^{-1}$)	<i>n</i>
April	2000, 19–20	13.6 (7.4/32.2)	0.5 (0.2/0.8)	1.0 (0.5/1.8)	30 (24.6/34.9)	48
	2003, 23–26	2.9 (0.1/9.1)	0.2 (0.02/1.0)	0.5 (0.3/1.0)	10.0 (6.9/13.4)	82
	2005, 27	1.7 (0.6/2.9)	0.4 (0.1/0.8)	0.4 (0.3/0.5)	5.1 (3.9/9.2)	25
May	2000, 17	8.6 (1.2/16.1)	0.5 (0.1/1.1)	0.5 (0.1/1.8)	2.0 (0.4/5.0)	21
July	2005, 20–22	2.9 (0.6/9.3)	0.5 (0.0/1.1)	0.05 (0.0/0.2)	0.7 (0.0/2.4)	55

Values in brackets show concentration ranges (min/max). The numbers of analysed samples are given by 'n'. Nutrient measurements are performed according to Liebbezeit et al. (1996).

release of phosphate from the tidal flat sediments as well as re-mineralization processes within the water column. During winter phosphate is scavenged by ferric oxyhydroxides within the sediments. More pronounced reducing conditions during warmer periods lead to reduction of iron compounds and release of phosphate (Gunnars and Blomqvist, 1997). A further source during low tide is the decomposition of particulate phosphate imported from the North Sea, as described by DeJonge and Postma (1974). Because of technical problems, April data were not available. However, time-series station data combined with ship-based measurements of previous years (2000, 2003, and 2005) showed a mean value in April of about $0.4 \mu\text{mol L}^{-1}$, which supports the trend of increasing concentrations from spring to summer.

Nitrite and nitrate showed a general decrease from April to July (Fig. 6c and d) due to consumption by phytoplankton, where nitrate is used for biomass formation. In contrast to nitrite, which showed the typical tidal pattern with maxima at low tide, nitrate revealed an indifferent behaviour (Fig. 6h and i). In April maximum concentrations occurred during high tide (not shown), which is supported by elevated North Sea values. Raabe et al. (1997) reported concentrations of about $10 \mu\text{mol L}^{-1}$ for the German Bight. However, in July the pattern changes to high nitrate values (on a generally low level) at low tide (not shown), possibly caused by re-mineralization processes within the upper sediment layer of the tidal flats. The pattern of nitrate in June (Fig. 6h) showed no distinct tidal dependence, which may be caused by enhanced bacterial ammonia oxidation during high and low tide. In contrast, tidal behaviour of nitrite (Fig. 6i) reflected the release of nitrite enriched pore waters during low tide.

Ammonia (Fig. 6e) in general revealed almost no coupling to other nutrient patterns. Fig. 6j shows a tendency towards lower values occurring during high tide and low tide in parallel to higher nitrate concentrations, probably caused by bacterial ammonia oxidation. Ammonia may have two different sources. Enhanced bacterial activity after algal bloom breakdown within the

water column may lead to ammonification of proteins and amino acids (Herbert, 1999) and corresponding increases in ammonia concentration. Bacteria cell counts (J. Stone, unpubl. data) of up to 6×10^6 cells mL^{-1} in May 2006 support the assumption of high bacterial activity, when compared to cell counts with a maximum 2×10^6 cells mL^{-1} in January 2005. The second source is the pore water, which is enriched in ammonia (up to $100 \mu\text{mol L}^{-1}$ in the upper 10 cm of the sediment, M. Beck, pers. comm.), when compared to the Wadden Sea water column. Both, microbial production within the water column and the pore water signal seem to impact the water column signal, thus obscuring tidal variation (Fig. 6j).

4.2. Methane

Fig. 7a shows surface concentrations of dissolved methane from September to November 2005. The concentration ranges between 0.12 and $0.54 \mu\text{mol L}^{-1}$ (mean $0.29 \mu\text{mol L}^{-1}$). Such values correspond well to concentrations reported for estuaries and rivers of the German Bight (Scranton and McShane, 1991; Upstill-Goddard et al., 2000; Middelburg et al., 2002).

The concentration pattern shows a tidal dependence with maxima at low tide (Fig. 7b), which indicates the Wadden Sea to be a source for methane. Pore water draining from tidal flats seems to be the main source for dissolved methane in this system. Pore water methane concentrations of up to $180 \mu\text{mol L}^{-1}$ at 4.0 m and $90 \mu\text{mol L}^{-1}$ at 1.0 m sediment depth and additional measurements of tidal creek waters with concentrations up to $3.7 \mu\text{mol L}^{-1}$ support this assumption.

The development and spontaneous change in concentration, like in late October 2005 (Fig. 7), was apparently caused by variation of wind speed and direction (data not shown). As described by Scranton and McShane (1991) increasing wind speed ($>10 \text{ m s}^{-1}$) leads to enhanced degassing of methane from the water column, whereas long-term changes are a consequence of changes in the variation of the tidal water level. The larger the amplitude

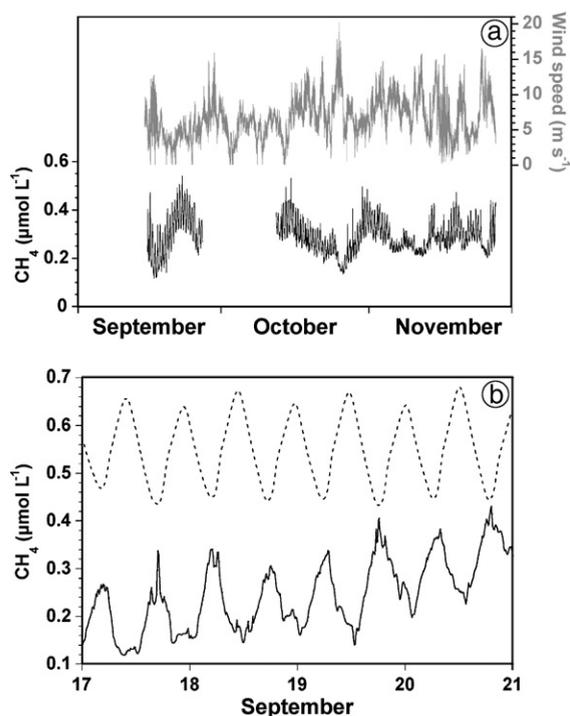


Fig. 7. Methane concentrations at the time-series station from September to November 2005 (a) Methane concentrations (black) and corresponding wind speed data (grey). (b) Tidal pattern from 17th to 21st of September 2005. The dashed line denotes the tidal gauge.

from low tide to high tide, the more pore water is released from the sediments, and vice versa. This effect additionally supports the assumption that tidal flat pore waters form the main source for dissolved methane in the Wadden Sea.

4.3. Maintenance of the instrumentation

Larger data gaps are due to different reasons, like insufficient electrical power supply owing to low production by the wind generator and solar panels, clogging/breakdown of the water supply pump, and severe weather conditions preventing maintenance work. The latter reasons are in most cases responsible for malfunctions and data loss. Continuous measurements in the study area require intensive maintenance efforts, due to pronounced bio-fouling of sensor components and tubes. The sensor tubes have to be cleaned or replaced manually. If necessary, anti-fouling paint has to be applied. Analyser tubings are preferentially made of silicone for inhibition of fouling. Despite of this precaution tubings need to be cleaned and/or exchanged approx. every four months, since bio-films might be a source for ammonia and phosphate as well as a sink for ammonia by nitrifying bacteria.

We will try to reduce these effects by applying new anti-fouling techniques (e.g. electrochemical). Additionally to bio-fouling, high SPM concentrations complicate the operation of a continuous and autonomous time-series station. High SPM concentrations alter the durability of the belt filter. The life-time of a 100 m filter belt varies between three weeks and two months, depending on the SPM load.

The pump of the methane sensor is treated with commercial anti-fouling paint which protects it from fouling for more than two months, but the silicone membrane of the sensor has to be changed every four to six weeks due to abrasion by the water-jet of the pump. However, this abrasion protects the membrane against bio-film formation.

The analysers perform wash cycles with distilled water after each measurement. This largely inhibits fouling inside of the analysers. But on the longer term they are affected by (bio) film formation and residua of analysis solutions. Therefore the analysers have to be periodically removed and cleaned onshore.

5. Summary

It has been demonstrated that a continuous nutrient and methane analysis of surface waters by a time-series station is feasible in a highly dynamic area, the NW German Wadden Sea. The direct measurements do not require sample storage or treatment such as preservation. Hourly sampling frequencies of nutrient measurements allow resolving tidal, diurnal and seasonal variability. Such a time-series station can provide the necessary data for long-term monitoring of processes in coastal waters, e.g. the development of toxic plankton blooms. We have used the data of the time-series station for the planning of ship-based sampling campaigns focussed on questions related to the development and breakdown of plankton blooms. The combination of meteorological and oceanographic parameters with nutrient data (and methane) allows new insights into the dominant driving forces of the bioreactor Wadden Sea. The impact of events like heavy storms, ice winters or other extreme weather conditions can be evaluated.

Besides the online availability these data may help to verify mathematical models describing the complex Wadden Sea system, and to perform balance calculations for specific compounds like nutrients. In summary, the operation of the station helps to answer one of the key questions whether the Wadden Sea system is in a steady state regarding import/export from or to the German Bight and to the North Sea.

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