Abstract

Methane and nitrous oxide belongs to the greenhouse gases with a 30 respective 300 times stronger greenhouse gas affect comparing to carbon dioxide. Their concentration is increasing in the atmosphere and is why the numbers of investigations have increased rapidly during the last years. Estuaries have shown to be a great source for both gases which is the reason for this investigation in Himmerfjärden (Sweden) during the winter season 2013. In February were in situ concentrations measured in the water together with core incubations and in April was air-sea gas exchanges measured with a Greenhouse gas analyzer. The ice in the water column in February seemed trap the gas which increased the concentration at the surface, nitrous oxide shows a less affect which could be due to the overall lower concentrations. The depth profiles of both gases shows in most cases a supersaturation throughout the water column in both February and April. The highest surface saturations for methane is in H6 (259%) and the lowest in H2 (103%), both occurs in February. Nitrous oxide saturations are also highest in February with the top in H4 (496%) and B1 (132%). The trend is a bit irregular with higher gas concentrations in H6 and H2 in April for methane and H6, H2 and B1 for nitrous oxide. The increased gas concentrations can be explained by a higher microbial activity during warmer seasons which enhances the sediment flux into water. The stations with decreasing gas concentrations have a lot to do with the incredible high saturations in February. The suggestion has been river in-puts but isn´t a valid explanation due to the decreasing nutrient concentration from January to April in all station.

The sediment fluxes of methane were between 1,73- (H6) and 0,013 (B1) mmol $m^{-2}d^{-1}$ in February. This is conformably with other investigations and is supported by the high oxygen uptake in H6 (-0,125 µmol $m^{-2}d^{-1}$) and a low in B1 (-0,012 µmol $m^{-2}d^{-1}$). This suggest that H6, closest to the sewage treatment in Himmerfjärden, has a high nutrient input and therefore a high sediment accumulation rate leading to a higher degradation of organic matter by microorganism, resulting in a higher production of both methane and nitrous oxide.

The air-sea gas exchanges of methane, determined by a wind speed model goes from 0,480 to 0,248 mmol $m^{-2}d^{-1}$ in February and in April 0,439 to 0,083 mmol $m^{2-}d^{-1}$. Nitrous oxide goes from 0,188 to 0,03 in February and 0,108 to 0,03 in April. The wind speed and surface nM is the main factors but temperature as well has a minor role. A chamber approach has been done as well but only on methane in April and showed a 50% lower flux. Air-sea gas exchanges are complex with a dynamic system with winds, surface concentrations, internal energy and both eddy and diffusion movements in the water.

Keywords: methane, nitrous oxide, estuary, water column, sediment flux, air-sea gas exchanges

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1 The aim

The aim of this project is to investigate the movement and production of both CH_4 and N_2O from the sediment, through the water column and finally the atmosphere at Himmerfjärden in Sweden. Himmerfjärden is an estuary which is a well-known source of these greenhouse gases but still needs a lot of investigations to get an accurate conclusion of the global input of greenhouse gases from estuaries into the atmosphere. The treatment plant facility situated in Himmerfjärden is another factor influencing the environment and therefore the gas production as well.

2 Introduction

CH_4 and N_2O belong to the atmospheric trace gases and influence the present climate. Therefore are the sinks and sources of both anthropogenic and natural origin and as well the formation pathways essential keys to understand, not only the variability of the past climate, but also to be able to predict the future development (*Bange, 2006).* Coastal areas (continental shelves, estuaries, deltas, fjords) have the potential to release high amounts of both N_2O and CH_4 due to high nutrient input from rivers and further high biological activity (*Bange, 2006).* Shelves and estuaries only represents 15 and 0,4% of the global oceans but still contribute 68 and 10% to the total CH_4 emissions respectively into the atmosphere (*Abril and Iversen, 2002*). For N_2O, European coastal waters may contribute up to 26% of the total global emission from ocean (*Bange, 2006)*.

2.1 The sewage treatment plant in Himmerfjärden

The sewage treatment plant treats water from Botkyrka, Salem and Nykvarn communes, the major part of Södertälje, parts of Huddinge and southwest of Stockholm. Al together the Himmerfjärden facility treats water from more than 270 000 people (*see Syvab webpage*). A control program has been developed by the counties agency in Stockholm and the department of system ecology at Stockholm University has since 1976 regularly been taken samples in Himmerfjärden. This makes the water of Himmerfjärden to one of the most well-researched areas in Sweden.

In 2011, 15 ton of phosphorous was released from the sewage plant in Himmerfjärden, which represents 40% of the total P input, only exceeded by the land run-off. The release of nitrogen was accounted to 325 ton in the same year and is the major source of N in the water of Himmerfjärden. These data can be seen in table 1 are directly taken from Syvabs environmental accounting.

Table 1 **Amount of nutrient infusion from surrounding drainage area 2011 in Himmerfjärden**

Total input in %	Water %	PO_4-P %	Tot-P %	NH_4-N %	NO_3-N %	Tot-N %
Himmerfjärd facility	7	33	37	58	39	38
Mälaren	25	7	7	1	4	8
Trosaån	21	13	15	11	15	17
land run-off	33	47	41	13	34	31
Precipitation	14	-	-	17	18	6

2.2 Background methane

CH_4 has been known for a long time to be an important greenhouse gas with a capacity for a 30 times stronger greenhouse gas effect than CO_2 in a 100 year timescale (*Schmale et al, 2010*). Aquatic systems represent the major source of atmospheric CH_4 but could have been even higher due to the enormous amounts of CH_4 produced annually in the seas, if it weren´t for the aerobic methane oxidation (AMO) (*Schmale, 2012*). Estuaries like Himmerfjärden are a well-known source for CH_4 due to the high sedimentation rate of organic matter caused by the high terrestrial and riverine run-off. This leads to a high primary production in the water column because of the release of phosphorous and nitrogen from the sewage treatment plant facility in Himmerfjärden and therefore the high amount of organic matter in put at the seafloor (*Thang et al, 2013).* Another reason for enhanced sedimentation rates in estuaries is due to the mixing of salt-and freshwater. This causes a rapid precipitation of the humic substances carried by rivers (*Schlesinger, W, 1997)*. The cations in the water replaces the H^+ on the exchange sites in the humic substances which causes the material to sink to the bottom (*Schlesinger, W, 1997)*.

CH_4 is mainly formed during the degradation process of organic matter by microbial methanogenesis. This process requires an anoxic environment and CH_4 is produced in sediments, inside suspended particles and on zooplankton innards during grazing (*Bange, 2006).* CH_4 is not very energy favorable as an electron acceptor and is only produced when the other electron acceptors (O_2, NO^-_3, Mn^{4+}, Fe^{3+}, SO^{2-}_4) are depleted, thus methanogenesis only stands for 2-5% of the organic mineralization in ocean sediments (*Deborde et al, 2010*). Generally CH_4 is produced further down in the sediments but slowly diffuses upwards to the sulfate (SO^{2-}_4)-zone where it's oxidized to CO_2 (*Schulz and Zabel, 2006)*. However, due to the environment in estuaries, CH_4 can occur at shallow depth in the sediment (*Thang et al, 2013).* CH_4 is oxidized both under oxic and anoxic environments in the water column and sediments but during shifts from oxic to anoxic conditions the production of CH_4 increases radically in both of the environments (*Bange, 2006).* The oxidation processes represents a major sink of CH_4 in marine sediments and the flux to the atmosphere depends on the relative rates between the production and oxidation in marine sediments and water column (*Deborde et al, 2010*

Seasonally variations in wind speeds, temperatures and amount available organic matter are other factors controlling the emissions of CH_4 in estuaries (*Bange et al. 1998, Abril and Iversen, 2002*). Estuaries have a brackish water system with a lower salinity than the oceans and are generally super-saturated with CH_4. One explanation is the connection between less amount of CH_4 with increasing salinity (*Abril and Iversen, 2002).* The higher salinity the more sulfate (SO^{2-}_4) in the sediment which inhabits the methanogenesis because SO^{2-}_4 acts as a stronger electron acceptor in the organic matter degradation process (*Schulz and Zabel, 2006).* The aerobic CH_4 oxidation in the water column also inhabits with increased salinity with the highest efficiency around and under 6‰ (*Abril and Iversen, 2002).* It has been thought that the aerobic CH_4 oxidation rates is a bit higher right above the sediments, the explanation has been that methanotrophs are more efficient in handling the salinity effect

close to sediment surfaces than in the water column (*Abril and Iversen, 2002).* When Abril and Iversen, 2002, compared the CH_4 uptake by sediments and the finally emission flux to the atmosphere in the Randers Fjord in Denmark, they found out that the CH_4 oxidation rates were twice as high in the sediment surface compared with the atmospheric flux in summer. In winter time the situation was the opposite and Abril and Iversen could see a connection with high concentrations of CH_4 in the water stimulated uptake by sediments and vice versa. This is followed by the wind control factor; low wind systems resulting in a decreased flux and the CH_4 transported by rivers builds up in the water and sediment uptake increases, high wind speed systems with increased atmospheric CH_4 flux results in a decreased concentration in the waters which inhabits the sediment uptake (*Abril and Iversen, 2006).* In Randers fjord in Denmark, Abril and Iversen found flux into the atmosphere between 355, 126 and 40 µmol $m^{-2}d^{-1}$ in 2002 and represents fresh-, brackish- and saline water respectively.

2.3 Background nitrous oxide

N_2O is increases in an annual rate 0,3% in the atmosphere and each molecule contributes 300 times more to the greenhouse gas effect comparing to every CO_2 molecule with a mean residence time of 120 years(*Schlesinger W, 1997, Andrew P, 2011)*. The only major sink, so far, seems to be through ozone destruction (*Schlesinger, 1997).* N_2O is mainly produced in oceanic systems as a byproduct in the nitrification; $NH^+_4 \rightarrow NH_2OH \rightarrow NO^-_2 \rightarrow NO^-_3$ and as an intermediate one in the dentrification; $NO^-_3 \rightarrow NO^-_2 \rightarrow N_2O \rightarrow N_2$. These two microbial processes seems to be strongly correlated with O_2 and occurs in the water column, in the sediment and inside suspended particles (*Bange, 2006)*. In the dentrification both nitrite (NO^-_2) and nitrate (NO^-_3) are used instead of O_2 as a terminal acceptor during the degradation of organic matter in anoxic or near anoxic conditions (*Rönner,U., 1983).* Dentrification has also been found close to the oxic-anoxic interface but not on in presence of O_2 *(Dalsgaard et al, 2013).* The nitrification occurs in the upper parts of the sediments and dentrification further down in the anoxic zone. The NO^-_3 from the nitrification, which has managed to diffuse down, is used up through the dentrification. Dentrification also seems to be the biggest sink of nitrogen in both sediment and water (*Dalsgaard, et al., 2013). Dalsgaard et al (2013)* saw in their sediment incubations from the Baltic Sea, that N_2O was a significant product in the dentrification and was about 44% of the total N_2-N_2O gas product. They could also see a connection between the sulfide concentrations and produced N_2O; N_2O production went from undetectable in the lowest sulfide concentration to 75-83% of the total N-gas production when the sulfide concentration increased. Sulfide, as it has been found out, is often an electron donor in the dentrification during anoxic environments. Sulfide is also known to inhabit the reduction of N_2O to N_2 in the dentrification which suggests that the highest N_2O production will occur in the zone with highest sulfide concentrations (*Dalsgaard et al, 2013).* If the gas diffuses downwards will it likely be consumed by the dentrification process. If N_2O diffuses upwards and escapes the dentrification zone and reaches the oxic waters, it may contribute to the supersaturation conditions of N_2O in the Baltic Sea (*Dalsgaard et al, 2013).* Bange et al, (2006) found

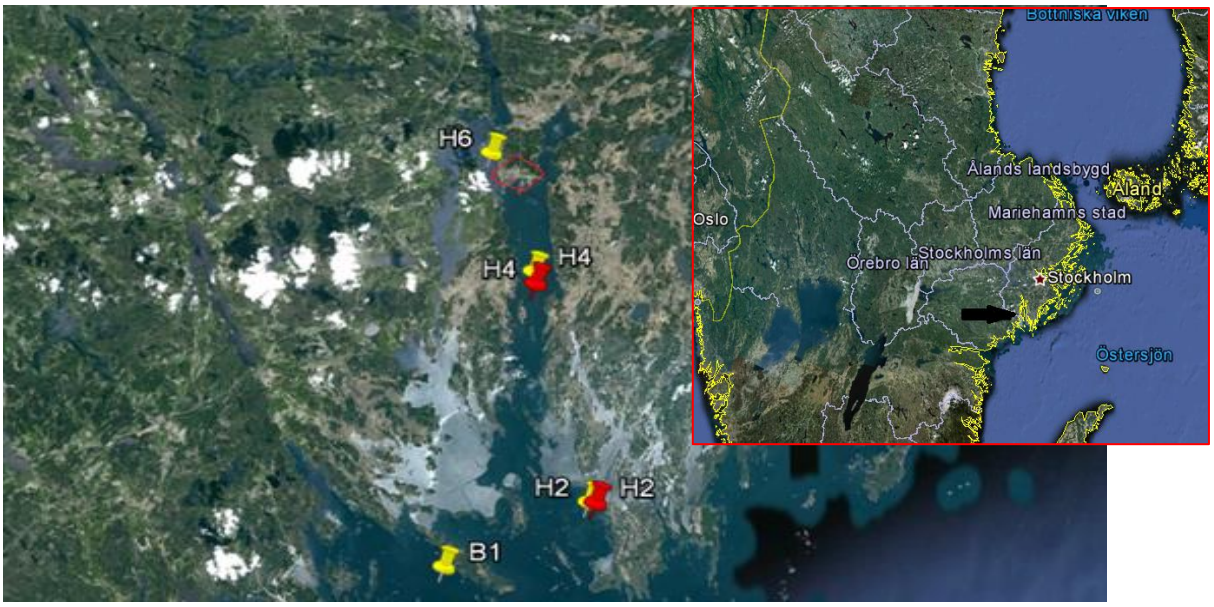
saturation values in the southern Baltic Sea /western River estuary area, between 91% and 312% in March.

During August-September 1977, July 1979 and May-June 1980 were the first measurements made of N_2O in surface waters in the central and northern Baltic Sea. They showed saturation values between 79% and 148% indicating Baltic Sea acting as a source (*Bange W, 2006)*. The trend in the well-oxygenated water was with increased N_2O concentrations, nitrate increased as well together with a decrease of O_2. Generally, since *Goreau et al., 1980,* is has been accepted that the O_2 concentration determines the N_2O production which seems to be highest during low O_2 (1-30% O_2). *Rönner, 1983* suggested that in environments containing high O_2- and NO^-_3 concentrations and nitrifying activity, nitrification is the most likely source of N_2O. In deep waters with less than 2% saturation of O_2, dentrification is the possible source (*Rönner, 1983).* However, in anoxic waters there´s a sharp decrease in the N_2O concentration in the Baltic Sea, which both *Bange W, 2006* and *Rönner, 1987,* explained as a consumption of N_2O by the dentrification process.

A study made of *Seitzinger and Kroeze 1998,* showed a correlation between the N_2O formation and the riverine nitrate input, which in turn were a function of fertilizer use, sewage inputs and atmospheric deposition of nitrogen oxides (NO_y). Because of the strong correlation with nitrogen inputs, the emissions of N_2O will increase in the future due to human activity (*Seitzinger and Kroeze 1998).*

3 Study sites

In this study the stations H6, H4, H2 and B1 in Himmerfjärden was investigated with H6 as the closest station to the treatment plant facility and the following stations with a greater distance in the same order. The H6 station represented a nutrient rich environment with a massive input of organic matter to the seafloor due to high nutrient concentrations in the water column. H6 is strongly influenced from the treatment plant comparing to the other stations. The H4 and H2 represent stations with less influence from the treatment. B1 is ultimately the station with no effect from the treatment plant situated outside the estuary and was the reference station. The yellow arrows are the sampling place in February and the red ones in April. Between the sampling spots in H4 there was approximately 850m and in H2 400m. The other two stations had less than 20m in between and the red circle is the sewage facility plant.



The coordinates for H6: N 59°04,0957 E017°40,5254, H4 (1): N 58°59,4313 E017°43,3835, H4 (2): N 58°58,9579 E017°43,5122, H2 (1): N 58°50,5757 E017°46,9874, H2 (2): N 58°50,5520 E017°47,4230, B1: N 58°48,1470 E017°37,4530. The red circle is the treatment plant. Source: Google Earth, taken in the end of May.

4 Method and calculations

4.1.1 Water column

Water and sediment samples were collected between 5th and 7th of February and 5th of April 2013. In February, CTD (conductivity, temperature, O_2 content and depth) measurements always began the sampling, recording data five times per second. This was followed with water column samples, tree replicates per depth every fifth meter with a 5L Niskin bottle. Every exeteiner had a size of 12 ml and contained 50 µl $ZnCl_2$ in a 50% concentration to prevent a continued microbial activity. This ended with a collection of 15-20 L of bottom water which later on was used to sediment fluxes. The water column samples were placed upside down until the analysis, which started 2 weeks after the sampling and spanned over 2 weeks.

In April the water column samples were taken in the same way but instead of CTD measurements, a saline-, temperature- and O_2 meter was put in the Niskin bottle at every depth. Due to short amount of time, only three depths were taken in B1. Fluxes between water-air were measured with a *Greenhouse gas analyzer (Los Gatos)* in all stations.

Headspaces were done and Helium gas was inserted with one needle and at the same time approximately 3ml of water was taken from the exeteiners and shaken hard afterwards (approximately 10s). To get an accurate volume, the exeteiners were weighted both before and after headspacing and placed upside down again until the analysis. For analyzing the water column- and sediment flux samples, the gas chromatograph SRI 8610C was used. There were two detectors; FID (flame ionization detector) for CH_4 and ECD (electron capture detector) for ECD. The reasons for the different detectors are due to their different sensitivity which in turn depends on the amount of gas available. N_2O is in a ppb amount whereas CH_4 is in ppm and therefore the detector needs to be more sensitive when measuring N_2O so that the small concentrations can be detected.

4.1.2 Calculations of gas concentrations in the water

The calibration curves made from the GC solves the concentration in the water. From the calibration curve this general equation is used:

$$y = kx + m \qquad Eq.1$$

y = peak area from GC
k = value from calibration
x = unknown amount
m = 0

So the ultimate equation to get the concentration in ppm (CH_4) and ppb (N_2O) is:

$$x = y/k \qquad Eq.2$$

The ppm and ppb needs to be converted to moles, which is why the general gas law is used:

$$pV = nRT \qquad Eq.3$$

p = 101,325 kPa
T = 298, 15 K
R = 8,314462 J•K^{-1}•mol^{-1}
V = volume
n = mol

The volume is achieved through the ppm which is multiplied to 10^{-6} to get µl/l and this is later on multiplied with the volume in the headspace. The gas law is altered and the concentration changes to mol:

$$n = RT/pV \qquad Eq.4$$

The moles is transformed to nmol and by dividing this with the amount of water left in the exeteiner, the nM is calculated in the samples.

4.1.3 Bunsen solubility for CH_4 and N_2O in water column

The Bunsen solubility coefficient (β) makes it possible to accurate measure gases in water and seawater in equilibrium with the atmosphere. The Bunsen solubility for CH_4 was calculated from one single equation as a function of temperature and salinity with constant values taken from the paper of *Denis A. Wiesenburg and Norman L. Guinasso, 1979.*

$$\ln C^* = \ln f_G + A_1 + A_2(100/T) + A_3 \ln(T/100) + A_4(T/100) + S‰[B_1 + B_2(T/100) + B_3(T/100)^2] \quad Eq.5$$

The A and B are constants, ln f_G is the concentration in the atmosphere, S is the salinity in ‰, C* is the equilibrium solubility in nmol/l and T the temperature in kelvin. It has been assumed that this gas behaves as an ideal gas.

The equations for N_2O solubility was taken from *R.F Weiss and B.A Price, 1980.* These data has been corrected due to standard conditions, one mole of N_2O occupies ~0, 7% less volume than one mole of ideal gas. The equilibrium concentration of the substrate is calculated as in eq.6.

$$C^* = x`F \quad Eq.6$$

where x´ is the dry mole fraction in air and F is expressed as mol l^{-1} atm^{-1}. The calculation of F is seen in eq. 7.

$$\ln F = A_1+A_2(100/T)+A_3 \ln(T/100)+A_4(T/100)^2+S[B_1+B_2(T/100)+B_3(T/100)^2] \quad \text{Eq.7}$$

The data for water temperatures and salinity is visible together with saturation values for respective gas and the constants can be seen in appendix 10.1.1 and 10.1.2.

4.1.4 Saturation values in water column

Saturation values, *sat,* were calculated as the ratio between the dissolved gas in water, C_w, and the concentration of the dry mole fraction in air, C_a. This is expressed in eq.8 and it taken from *Bange W, et al, 1998*.

$$Sat = C_w/C_a*100 \quad \text{Eq.7}$$

$$C_a = \beta/x \text{ and } C_w = \beta/x`$$

x is the concentration of the gas in the air and x` is the measured concentration in the headspace of the sample and β is the Bunsen solubility described in section 4.1.3.

4.1.5 Air-sea gas exchanges of CH_4 and N_2O

The gases in the atmosphere always interact with the surface water and the net rate direction is always towards equilibrium conditions (*Pilson, M.E.Q, 2013).* Both air and water is constantly in motion by turbulent eddies which prevent inhomogeneity. The eddy motion stops very close to the surface and another process is taking over; diffusion. Very reactive gases reacts so fast at the water surface that the diffusion acts as a barrier and limits the exchange (*Pilson, M.E.Q, 2013).* The gas transfer velocity (k) depends on the turbulent energy exchange between the air and surface water and has been tricky to achieve (*Cole, 2010).* The k value vary with both temperature and gas which ultimately is related to the Schmidt number; the ratio between the kinematic viscosity of water and the diffusion coefficient of the gas (*Cole, 2010).* The diffusion coefficient is the same as the molar flux which depends on the molecular diffusion (mass transport) and the concentration gradient (*Incropera, F. P. et al., 1990).*

The sea-air gas exchange has been calculated through two approaches; with the chamber used in April (*see Cole, 2010)* and with a wind speed model (*Wanninkhof, 1992)* with the equation:

$$F = k\,(C_{sur}-C_{eq}) \quad \text{Eq.8}$$

where F is the flux in mmol m^{-2} d^{-1}, k is the gas transfer velocity in m d^{-1}, C_{sur} and C_{eq} the actual surface water and air equilibrium concentrations. The Schmidt number is calculated from Sc_{CH4} = 1897,8-114,28t+3,2902t^2+0,039061t^3 which has been used by both *Cole, 2010* and *Wanninkhof, 1992* and where t is the temperature in C°. The Schmidt number for N_2O is calculated from Sc_{N2O} = 2301,1-151,1t+4,7364t^2-0,059431t^3 (*Wanninkhof, 1992).*

The floating chamber were put in the water for 30 minutes and connected with a Greenhouse gas analyzer (Los Gatos) which in situ measured the CH_4 (CO_2 as well but isn´t included in this report) concentration every 10 sec. The values creating an r^2-value less than

0,7 were sloped whilst the remaining values gave an average ppm/day from each station. The wind speed was taken as a single measurement and surface water temperatures and salinity were taken along with the water column samples. Converting mass and concentration to partial pressure (*see calculations from Cole, 2010)* and dividing the area, the flux was achieved.

The wind speed model calculated the C_{eq} through converting ppm to nM and multiplied both with the standard atmosphere pressure and the mol atm^{-1} in the water, the nM in the water (C_{sur}) is then subtracted with C_{eq} and converted to mmol m^{-3}. The k-value equation is taken from *Wanninkhof, 1992:*

$$k = 0{,}31 * u^2 (Sc/660)^{-0{,}5} \qquad Eq.9$$

where u is the wind speed, Sc the Schmidt number, 660 is the Schmidt number of CO_2 in seawater at 20°C, 0,31 an experimental value depending on wind speed environment and $n^{-0{,}5}$ which is assumed to be appropriate when the sea is less calm. The k-value is then multiplied with the C_{sur}-C_{eq} value described above.

The floating chamber approach was only made on the CH_4 in April and N_2O was calculated with the wind speed model both in February and April. In table 2 and 3 is the wind speed, salinity and temperature seen for both samplings.

Table 2 **February**

Station	Date	Arriving time	Average wind 3h(m/s)	Temp. C°	Kelvin	permil	hPa
H6	2013-02-06	11:30	4,7	0,15	273,3	4,61	1020
H4	2013-02-05	13:30	7,3	0,51	273,66	5,7	1020
H2	2013-02-05	10:30	9,7	0,15	273,3	6,16	1020
B1	2013-02-07	10:20	7,4	0,27	273,42	6,23	1020

*The wind speed has been achieved from SMHI (Swedish Meteorological and Hydrological Institute) from the wind station 8744, Landsort A.

Table 3 **April**

Station	Date	Arriving time	wind(m/s)	Temp. C°	Kelvin	permil	hPa
H6	2013-05-04	12:06	6	2,7	275,85	4,8	1020
H4	2013-05-04	13:03	5	2,2	275,35	5,5	1020
H2	2013-05-04	13:03	6	1,9	275,05	5,8	1020
B1	2013-05-04	16:03	4	1,5	274,65	5,9	1020

*The wind speed is a single measurement taken on the boat.

4.2.1 Sediment

Sediment samples were collected at all stations except for H4 and only in February. In H2 five kajak cores were collected; four of them for sediment fluxes and one for methane concentrations. At station H6 was five kajak cores collected; two for sulfate reduction rates, one for porosity and organic matter, one for pore water and one for methane concentrations. The flux cores were collected by a multicorer (MUC) from J.U.M Umelt-und Meeres-technik Kiel GmBh Company which made it possible to take four cores at the same time. Only one cast was successful retrieved at station H6, whereas at station B1 giant waves made it impossible to use the MUC. Instead at B1, 6 kajak cores were collected; three for

fluxes, one for porosity, one for sulfate reduction rates and one for methane concentrations. The values from the two porosity cores were assumed to be the same for all station and used in the flux calculations from H2 as well. The porosity was determined by the difference in the wet weight against the dry weight after 80°C in oven over night.

4.2.2 Methane concentration in sediments

All of the methane cores were immediately taken care off on the boat. Every cm 2, 5> ml sediment was taken from pre-drilled holes and into 20 ml bottles containing 5ml of a supersaturated salt solution, afterwards the samples were shaken hard. The samples were determined in the same gas chromatograph as for the water column samples but without the ECD detector. They were weighted before and after to get the analyzed gas amount but also the empty ones to get the accurate amount of sediment in every bottle. The amount sediment was multiplied with the porosity to get the pore volume, further was the mmol concentration calculated as described in section 4.1.2. Instead of dividing the amount of water is the mmol multiplied with the pore volume to get mM.

4.2.3 Sediment fluxes in core incubations

The kajak cores taken from H2 were stored in the original cores whilst the cores from B1 and H6 were subsampled into smaller ones. The water above the cores was replaced with the bottom water taken with the Niskin bottle. The water and sediment were given six hours to settle down before the incubation started. One sample from each core was taken in the beginning and in the end; in total did the incubations last for 10, 5 h for all cores. Every water column length and the diameter of the sediment surface are seen in table 4.

Table 4

	B1		**H6**		**H2**	
	Diameter (cm)	Water column length (cm)	Diameter (cm)	Water column length (cm)	Diameter (cm)	Water column length (cm)
Rep. 1	3,6	14	5,6	16,5	5	31
Rep. 2		15		16,5		32
Rep. 3		14		13		30
Rep. 4				12		30

The calculations were the same as for the nM calculations described in section 4.1.2. The only thing different is that the nmol is divided by the water amount in ml instead of L→ nmol/ml. The total volume of the water column is calculated and multiplied with the nmol/ml in the 12ml exeteiners, which gives the total nmol in respective core. To get the flux in the incubations, the start amount simply is subtracted from the end amount. The flux is now given in nmol cm h^{-1} but multiplied with 24 turns it to nmol day^{-1}. To convert it to m^2 the area from the cores is divided by a factor of 10000. If one is divided by this number, we get the number we need to multiply the nmol day^{-1} to get the ultimate flux → *nmol* $m^{-2}day^{-1}$. Table 5 shows how the factor, which was multiplied to get the flux, was calculated.

Table 5	**B1**	**H6**	**H2**
Area (cm^2)	10,1787	24,6301	19,6350
m^2 (Area/10^4)	0,0010	0,0025	0,0020
Factor ($1/m^2$)	**982,44**	**406,01**	**509,30**

4.2.4 Sediment fluxes with Fick's law

The flux is driven by the difference in the partial pressure of the gas between the water and air. The concentration, which is proportional to the partial pressure, is therefore the main factor to the flux amount. The Fick´s law makes it possible to calculate the exchange of different gases through mediums. Diffusion processes in sediments take place in the pore water volume (porosity, ϕ) and thus surveys as an important limiting factor in the sediment fluxes (*Schulz and Zabel, 2006).* The sediment diffusivity (D_s) which is a function of both porosity (ϕ) and the diffusivity in free water (D) were calculated by the equation:

$$D_s = D/(1+3(1-\phi)) \quad Eq.10$$

The D value (cm^2s^{-1}) is taken from the compendium by *Ramsing, N and Gundersen, J.* with O_2 coefficients but needed to be corrected for CH_4 and N_2O coefficients (0, 8495 and 1, 0049 are multiplied with the O_2 coefficients respectively). The equation is taken from a manual for profiles, given by Volker Brüchert. The change in concentration per depth (k) is taken from the CH_4 core and the porosity from the sliced porosity cores. The k-value from the top cm are then multiplied with D_s and ultimately multiplied with 86400 and 10000 to get the flux in mmol m^{-2} d^{-1}.

The reason for calculating the fluxes in two different ways were to see if there were a difference and to give a clue weather our values are correct or not.

4.2.5 Oxygen consumption

The oxygen consumption was measured in the same time as the core incubations. It was made by a *PC based fiber optic oxygen meter FireSting O2* from the company *PyroScience* which measured the concentration in *µmol/l*. Similar to the core incubations it stopped after 10,5h and was calculated in the same way; the final concentration was subtracted with the start concentration and multiplied with the volume (L) of water in the core, further this was divided by the hours and multiplied with 24 to get the flux per day. This flux was then multiplied with the surface area (transformed from cm^2 to m^2 by multiplying with factor 10000) and expressed as µmol $m^{-2}d^{-1}$. Table 5 contains water column- and diameter length.

4.5 Organic matter

From station H6 was the organic matter and nitrogen content in the core determined by measuring the stable isotopes ^{13}C and ^{15}N. For this were a mass spectrometer thermo delta V Advantage, which was linked to an elemental analyzer NC 2500 and a thermo conversion elemental analyzer, used. The samples, one every cm the first ten cm and then every second, were freeze dried in a ScanVac Scan Speed Maxi Vac beta instrument for three days and crossed into a fine powder. Then two samples were taken from every depth; the first

samples were weighted (approximately 5mg) and put into tin capsules and sealed immediately, the second samples were put into silver capsules and treated with 2 mole HCl and put in 60 degrees overnight. This process got rid of the C in the carbonates which reacted with the HCl and leaved as CO_2. The samples in the tin samples were for nitrogen measurements and are done separately to make sure that the HCl not changed the nitrogen content.

5 Results

5.1.1 CTD profiles

The CTD provides profiles of the salinity, O_2 content and temperature are seen in diagram 1 to 4 which also includes the calculated saturation values of both CH_4 and N_2O.

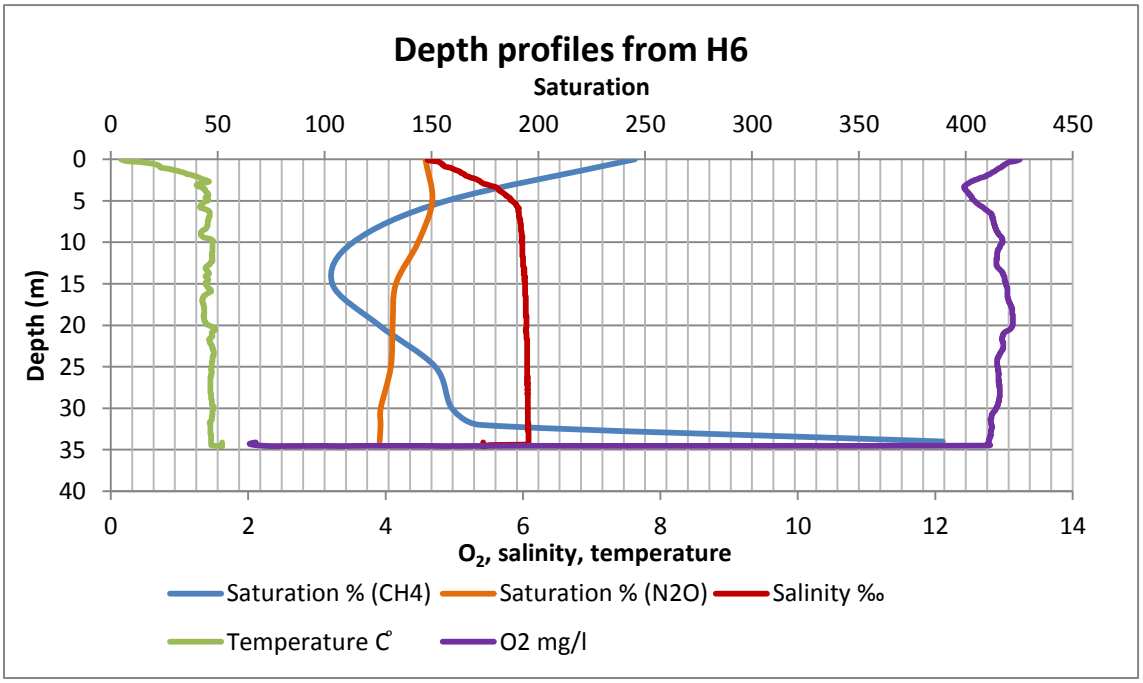


Diagram 1

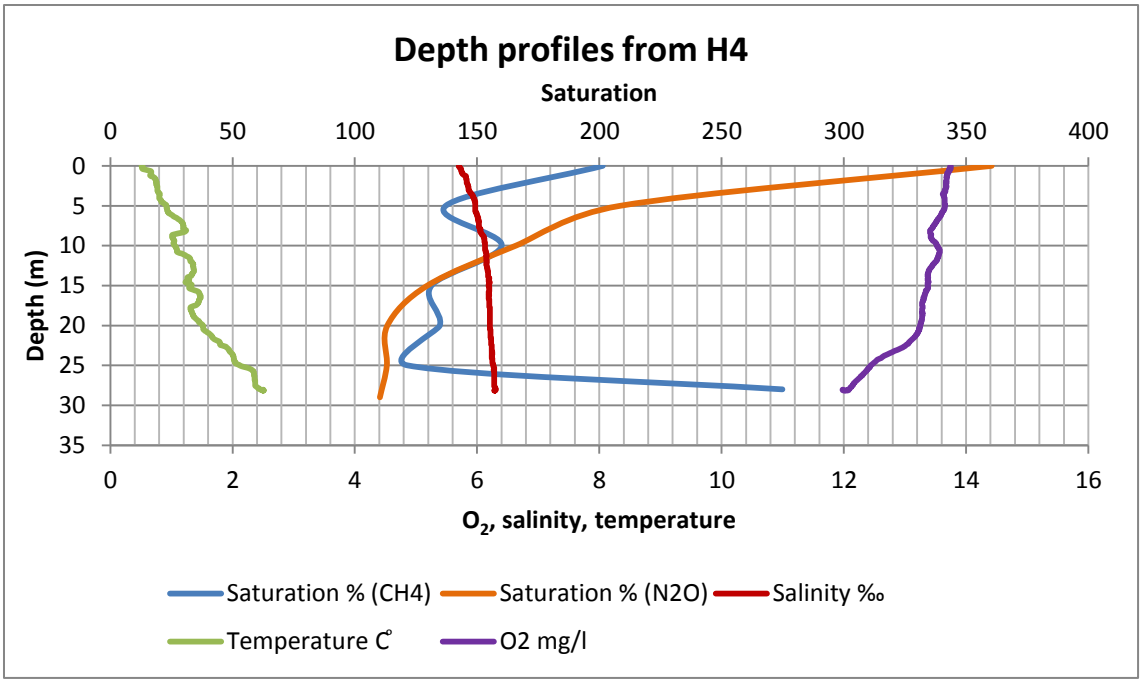


Diagram 2

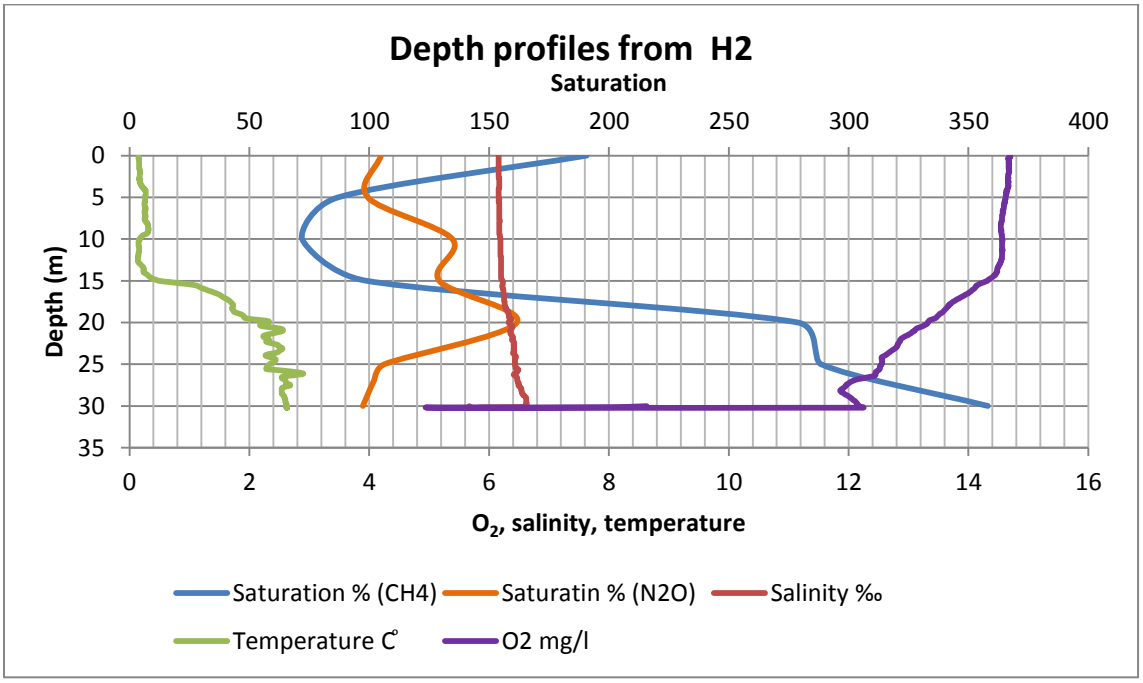


Diagram 3

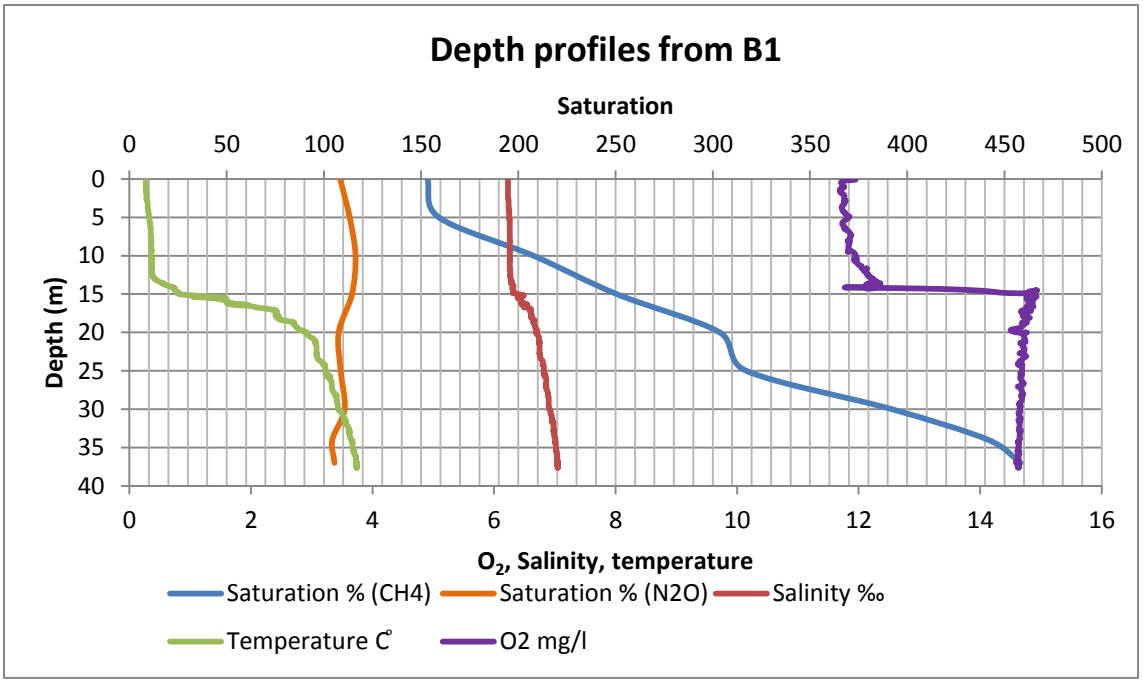


Diagram 4

5.1.2 Gas concentrations in the water column in February

The gas concentration of CH_4 is seen in table 5 and diagram 6 and the results of N_2O in table 6 and diagram 7. According to the measured data of NOAA from Mauna Lau´s laboratory station, the global average of CH_4 in the air is of about 1, 84 ppm (from December 2012). The six taken air samples in February resulted in an average of 2, 06 ppm analyzed by the GC, but in April during the flux measurements, the Los Gatos instrument measured an air average of 1, 88 ppm. This together with another investigation from Roskildefjorden (Denmark), in December 2012 which also resulted in average ppm value about 1, 87 from the Los Gatos but 2,11 ppm in the GC, made it clear that the GC overestimates the CH_4 concentrations. The choice has been to correct the data and take away 0,18 ppm (the difference between 2, 06 and 1, 88 ppm) from the methane results shown in the diagrams.

Exactly the same were done with the N_2O measurements. The GC in February showed an air value of 340, 31 ppb whereas the global value, taken from the *combined HATS N_2O file* from the webpage of NOAA, showed a value of 325 ppb. The difference of 15, 31 ppb between the GC and NOAA values has been subtracted from the results in table 6.

Table 5 ***nM and saturation values of CH_4***

H6					**H4**				
Depth (m)	Average nM	SD ±	SD %	Saturation %	Depth (m)	Average nM	SD ±	SD %	Saturation %
0	65,75	3,94	5,99	259,0	0	53,10	2,57	4,85	210,6
5	41,50	1,91	4,60	162,2	5	36,53	1,24	3,41	141,0
10	29,15	0,47	1,62	114,4	10	42,63	2,54	5,96	165,4
15	26,83	1,64	6,10	104,3	15	34,31	1,76	5,12	134,0
20	32,74	2,61	7,98	127,7	20	35,08	2,13	6,06	137,8
25	40,47	2,18	5,39	156,4	25	31,59	1,71	5,42	123,4

30	42,59	2,16	5,08	165,4	29	74,34	2,51	3,38	291,0
35	46,31	1,06	2,28	179,3					
37	107,27	1,25	1,16	416,0					
H2					**B1**				
Depth (m)	Average nM	SD ±	SD %	Saturation %	Depth (m)	Average nM	SD ±	SD %	Saturation %
0	26,50	4,42	16,69	103,2	0	41,19	0,62	1,50	158,0
5	22,17	5,03	22,67	97,3	5	42,37	2,92	6,89	164,4
10	17,69	0,94	5,34	69,1	10	55,62	1,80	3,23	217,6
15	25,22	4,00	15,87	89,4	15	67,73	0,91	1,34	264,4
20	74,65	4,73	6,34	295,2	20	82,91	1,00	1,21	322,9
25	78,50	3,91	4,97	305,9	25	87,27	2,65	3,03	322,9
30	98,44	50,15	50,94	382,4	30	110,10	4,13	3,75	337,2
32	106,84	3,63	3,40	419,9	35	121,75	1,36	1,11	419,1
					38	128,76	4,69	3,64	473,4

Table 5. Average nM, standard deviations and saturation values of CH_4 from all stations

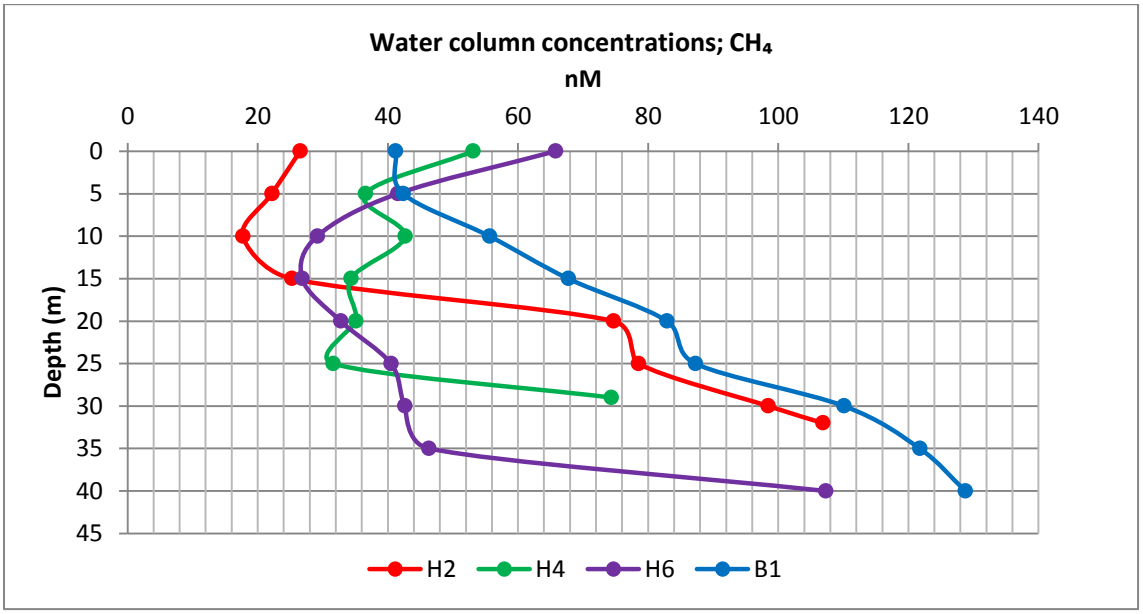


Diagram 6

Table 6 ***nM concentrations and saturation values of N_2O***

H6					**H4**				6
Depth (m)	Average nM	SD ±	SD %	Sat. %	Depth (m)	Average nM	SD ±	SD %	Sat. %
0	8,86	0,51	5,72	201,7	0	21,66	1,24	5,74	496,5
5	9,12	0,46	4,99	206,2	5	12,80	0,82	6,43	285,3
10	8,68	0,13	1,48	196,9	10	10,07	0,87	8,61	225,9
15	8,13	0,39	4,74	182,3	15	7,78	0,58	7,40	175,6
20	7,98	0,34	4,25	180,1	20	6,73	0,44	6,50	152,9
25	8,01	0,38	4,75	178,9	25	6,74	0,33	4,84	152,5
30	7,68	0,26	3,33	172,4	29	6,56	0,27	4,18	148,6
35	7,69	0,41	5,30	172,3					
37	7,65	0,10	1,32	171,6					
H2					**B1**				

Depth (m)	Average nM	SD ±	SD %	Sat. %	Depth (m)	Average nM	SD ±	SD %	Sat. %
0	6,30	0,22	3,57	141,9	0	5,93	0,13	2,14	132,0
5	6,21	0,23	0,00	135,2	5	6,15	0,30	4,81	137,8
10	5,88	0,36	6,20	132,8	10	6,25	0,29	4,66	141,4
15	6,26	0,17	2,64	178,9	15	6,17	0,10	1,66	139,4
20	5,75	0,34	5,96	131,9	20	5,80	0,19	3,31	130,5
25	5,71	0,51	9,00	128,7	25	5,88	0,30	5,18	131,4
30	5,67	0,18	3,16	127,7	30	6,08	0,31	5,13	133,9
32	5,48	0,02	0,31	123,2	35	5,60	0,28	4,91	126,0
					40	5,79	0,30	5,10	127,8

Table 6. Average nM and standard deviations of N2O from all stations

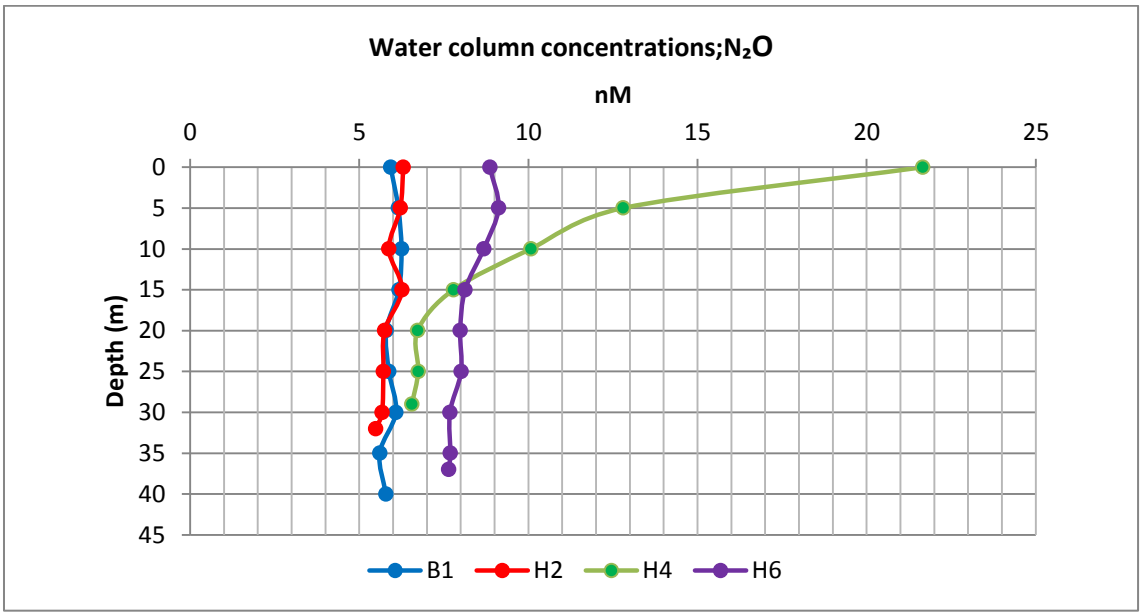


Diagram 7

5.1.3 Temperature and salinity profiles from April

This time the temperature and salinity were measured with a salinity and temperature probe from every sampling depth. Unfortunately was the probe measuring oxygen content broken during sampling and are lacking in the data. This is visible in table 7.

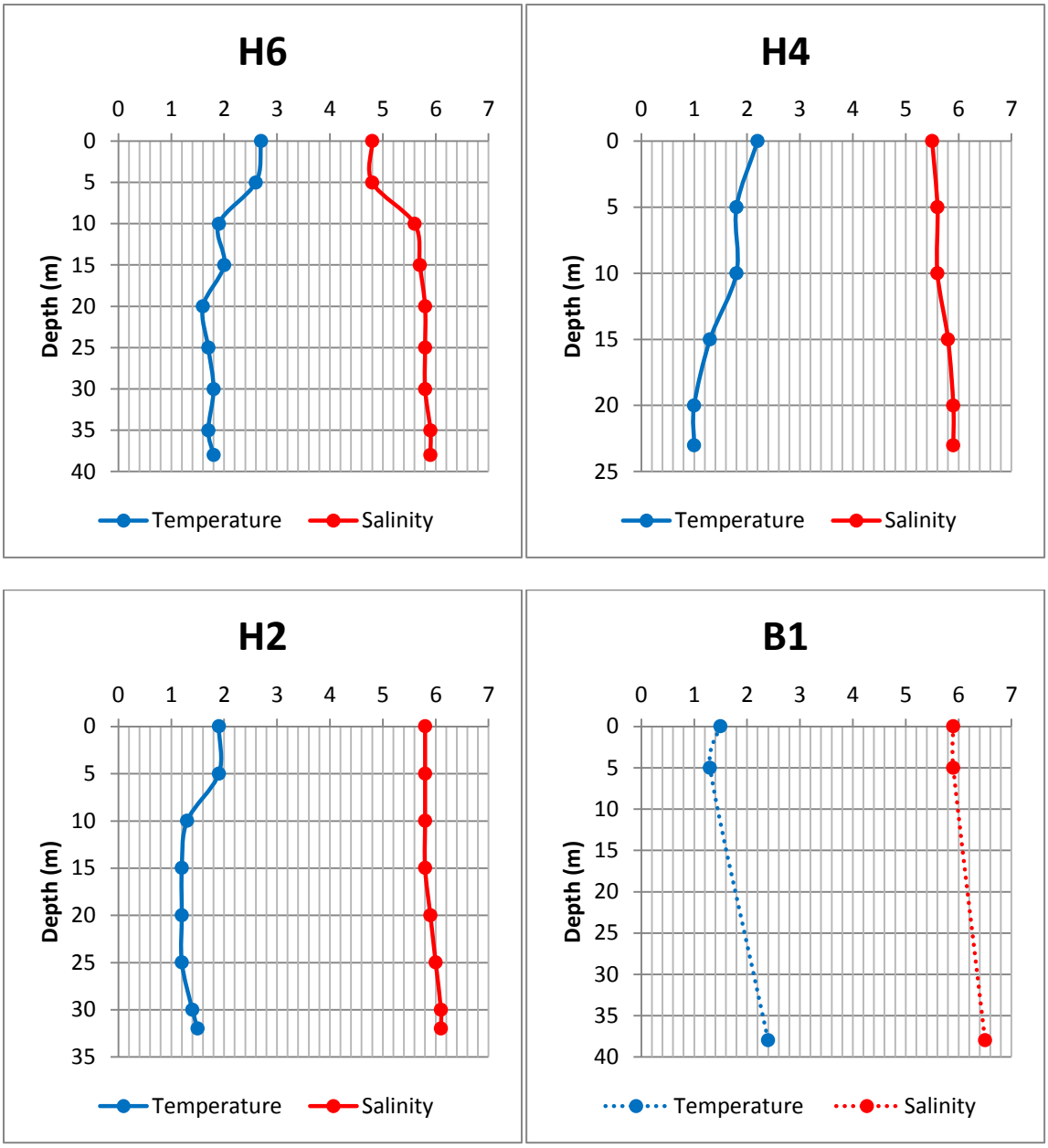


Table 7. The temperature is measured in C° and salinity in

5.1.4 Gas concentrations in the water column in April

On the 5th of April, water column samples were taken from H6, H4 and H2 in triplicates as in the earlier sampling. On B1 only the depth from 0, 5 and 38 m was taken due to lack of time. The gas concentration is shown first in table 8 and 9 which is followed by diagram over the nM profiles from respective station. Air samples weren´t taken this time and only the value measured from the Los Gatos was achieved (1, 88 ppm) for the CH_4 but unfortunately nothing for N_2O, the global value of the dry mole fraction of N_2O in air from NOAA were taken instead. Like discussed in section 5.1.2, the GC overestimates the concentrations but because the air samples are lacking it is impossible to know by how much and the choice has been to not correct the samples.

The later on mentioned ammonium, nitrate and nitrite concentrations in the water column in the discussion, is all taken from the webpage *www2.ecology.su.se* which can be found on a link in Syvabs webpage. The concentration can be seen in appendix and are an average between 0-10m and 20-30 m and expressed in mg m^{-3}.

Table 8 ***nM and saturation values of CH_4***

H6					**H4**				
Depth(m)	Average nM	SD ±	SD %	Sat.%	Depth(m)	Average nM	SD ±	SD %	Sat.%
0	65,70	8,09	12,32	249,4	0	52,80	7,93	15,02	200,9
5	56,34	0,29	0,51	216,9	5	45,16	3,30	7,31	177,0
10	41,70	2,38	5,71	162,7	10	48,74	1,00	2,05	192,3
15	40,18	3,67	9,14	160,4	15	50,05	0,52	1,03	196,4
20	36,32	2,05	5,65	140,9	20	46,05	1,81	3,93	179,7
25	32,48	1,65	5,09	125,5	23	44,17	1,92	4,35	180,4
30	28,45	1,85	6,50	110,6					
35	46,03	2,23	4,84	173,9					
38	409,27	25,28	6,18	1592,7					
H2					**B1**				
Depth(m)	Average nM	SD ±	SD %	Sat.%	Depth(m)	Average nM	SD ±	SD %	Sat.%
0	45,78	7,07	15,44	176,2	0	31,40	1,28	4,08	121,0
5	43,60	2,26	5,19	171,6	5	33,00	0,59	1,78	126,9
10	42,19	2,93	6,94	165,7	38	31,83	1,94	6,09	121,3
15	46,10	2,50	5,43	170,0					
20	48,91	1,21	2,47	192,6					
25	74,73	1,70	2,27	293,4					
30	144,54	2,17	1,50	564,9					
32	167,91	5,26	3,13	662,5					

Table 8. Average nM, standard deviations and saturation values of CH_4 from all stations

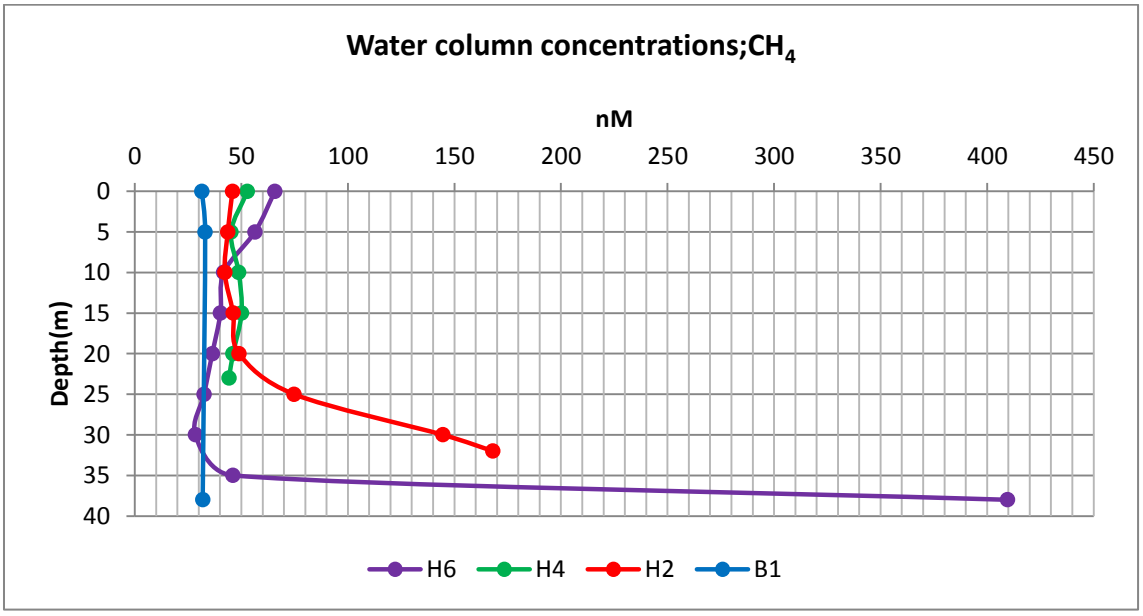


Diagram 8

Table 9 ***nM and saturation values of N_2O***

H6					**H4**				
Depth(m)	Average nM	SD ±	SD %	Sat. %	Depth(m)	Average nM	SD ±	SD %	Sat. %
0	8,23	0,21	2,60	181,4	0	11,40	0,60	5,24	251,2
5	9,07	0,14	1,59	202,3	5	10,72	0,21	1,95	243,0
10	9,37	0,39	4,13	211,9	10	10,91	0,39	3,57	248,9
15	8,85	0,46	5,24	204,9	15	9,24	0,23	2,44	209,7
20	9,03	0,25	2,77	203,1	20	7,93	0,15	1,86	178,7
25	9,24	0,35	3,75	207,1	23	7,45	0,56	7,47	175,9
30	9,28	0,73	7,86	209,3					
35	9,41	0,46	4,92	206,3					
38	9,39	0,25	2,61	211,9					
H2					**B1**				
Depth(m)	Average nM	SD ±	SD %	Sat. %	Depth(m)	Average nM	SD ±	SD %	Sat. %
0	7,23	0,16	2,18	160,3	0	6,45	0,11	1,72	145,2
5	7,37	0,23	3,18	167,2	5	6,70	0,16	2,33	150,5
10	7,46	0,15	1,97	168,9	38	7,65	0,20	2,57	170,5
15	7,95	0,96	12,14	168,0					
20	7,36	0,09	1,16	166,8					
25	6,82	0,12	1,70	154,2					
30	7,04	0,40	5,74	158,4					
32	6,86	0,40	5,81	155,7					

**Table 9. Average nM, standard deviations and saturation values of N2O from all stations*

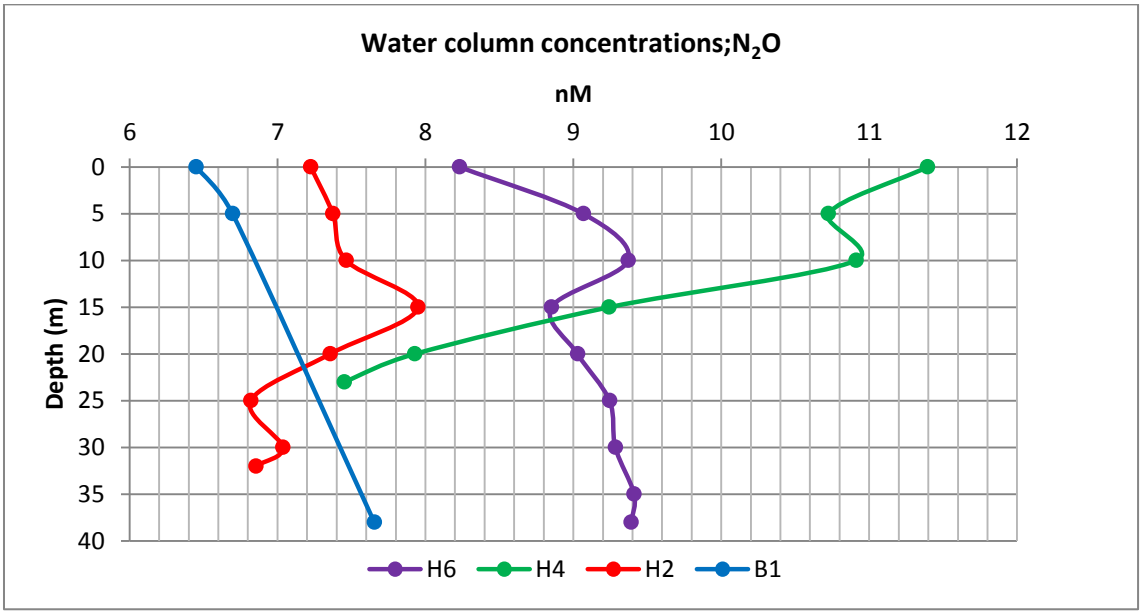


Diagram 9

5.1.5 Air-sea gas exchanges of CH_4 and N_2O

In all of the flux calculations the air values 1,88 ppm (CH_4) and 325 ppb (N_2O) have been used even though the different values measured from the GC didn´t affect the flux in a particular big way. The fluxes from the two different approaches showed a difference of about 50% with the higher value from the wind speed model. Therefore it would have been impossible to compare the result and therefore were the CH_4 in April also calculated with the wind speed model. The calculations can be seen in table 10, 11 and 12.

Table 10 **CH_4 flux in February**

Station	C_{sur} (nM)	C_{eq}(nM)	C_{aq} -C_{eq}(mmol m^{-3})	C°$_{sur}$	Schmidt nr	k-value	F (mmol m^{2}-d^{-1})
H6	65,74	4,285	0,061	0,15	1881	3,91	**0,248**
H4	52,84	4,320	0,049	0,51	1840	9,54	**0,480**
H2	45,82	4,338	0,041	0,15	1881	16,67	**0,378**
B1	31,42	4,460	0,027	0,27	1867	9,73	**0,369**
			N_2O flux in February				
	C_{sur} (nM)	C_{eq}(nM)	C_{aq} -C_{eq}(mmol m^{-3})	C°$_{sur}$	Schmidt nr	k-value	F (mmol m^{2}-d^{-1})
H6	8,86	0,806	0,008	0,15	2279	3,69	**0,030**
H4	21,66	0,790	0,021	0,51	2225	9,00	**0,188**
H2	6,30	0,797	0,006	0,15	2279	15,70	**0,086**
B1	5,93	0,793	0,005	0,27	2261	9,17	**0,047**

Table 11 **CH_4 flux in April**

Station	C_{sur}(nM)	C_{eq}(nM)	C_{aq} -C_{eq}(mmol m^{-3})	C°$_{sur}$	Schmidt nr	k-value	F (mmol m^{2}-d^{-1})
H6	65,75	4,661	0,061	2,7	1614	6,88	**0,439**
H4	53,10	4,569	0,049	2,2	1663	4,71	**0,237**
H2	26,50	4,609	0,022	1,9	1693	6,72	**0,289**
B1	41,19	4,588	0,037	1,5	1734	2,95	**0,083**
			N_2O flux in April				
	C_{sur} (nM)	C_{eq}(nM)	C_{aq} -C_{eq}(mmol m^{-3})	C°$_{sur}$	Schmidt nr	k-value	F (mmol m2-$d^{-1)}$
H6	8,23	0,739	0,007	2,7	1926	4,01	**0,030**
H4	11,40	0,748	0,011	2,2	1991	9,51	**0,101**
H2	7,23	0,753	0,006	1,9	2031	16,63	**0,108**
B1	6,45	0,763	0,006	1,5	2085	9,55	**0,054**

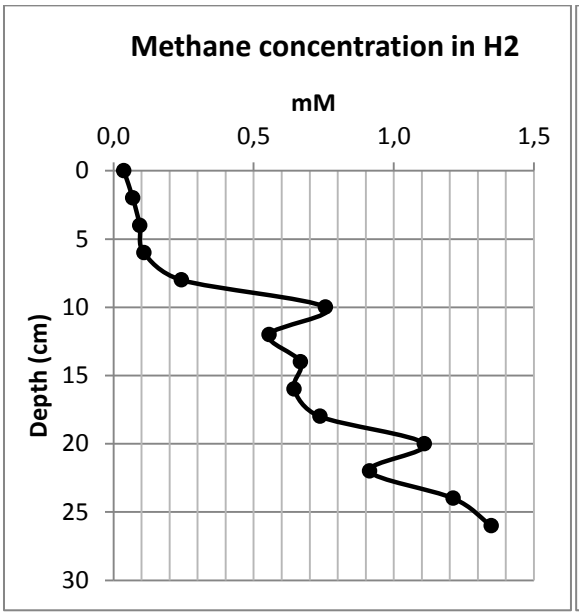
Table 12 **Chamber fluxes of CH_4**

Station	nM	mol/atm	ppm	Pa/d	Volume (cm^3)	m^2	mol/d	**mmol m^{-2} d^{-1}**
H6	65,7	2,26E-03	1,88	4,44	7518,50	0,07	1,46E-05	**0,199**
H4	52,8	2,29E-03	1,88	3,05	7518,50	0,07	1,00E-05	**0,137**
H2	45,8	2,30E-03	1,87	2,89	7518,50	0,07	9,50E-06	**0,130**
B1	31,4	2,33E-03	1,90	1,12	7518,50	0,07	3,68E-06	**0,050**

*Chamber calculations. The nM is the CH_4 concentration in the surface waters.

5.2.1 Methane concentration and porosity in February sediments

The CH_4 concentrations from H6, H2 and B1 are seen in diagram 10, 11 and 12. N_2O were not measured due to lack of calibration gas at the time. The porosity values from H6 and B1 are chosen to be together with methane concentrations because of their essential role in the calculation of the concentrations (diagram 13 and 14).



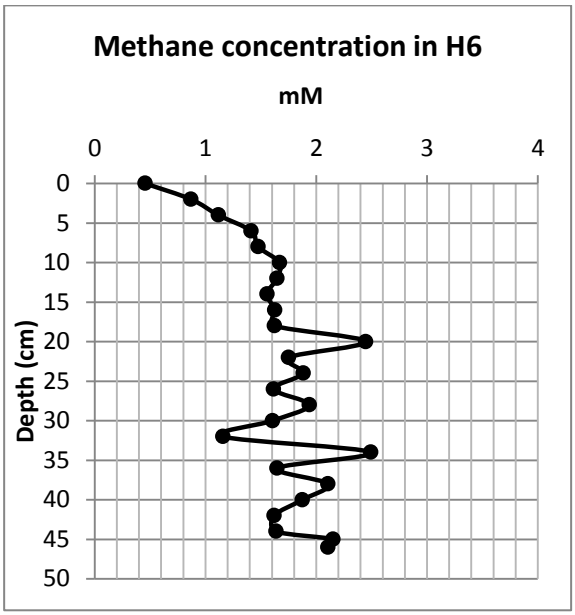


Diagram 10 (H2) and diagram 11 (H6)

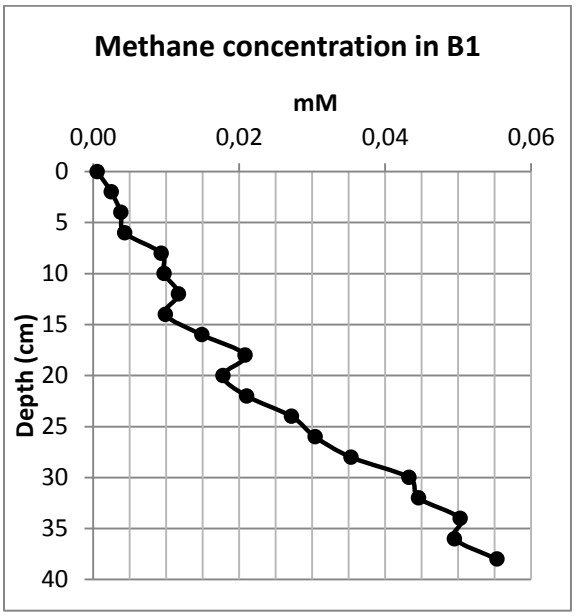


Diagram 12

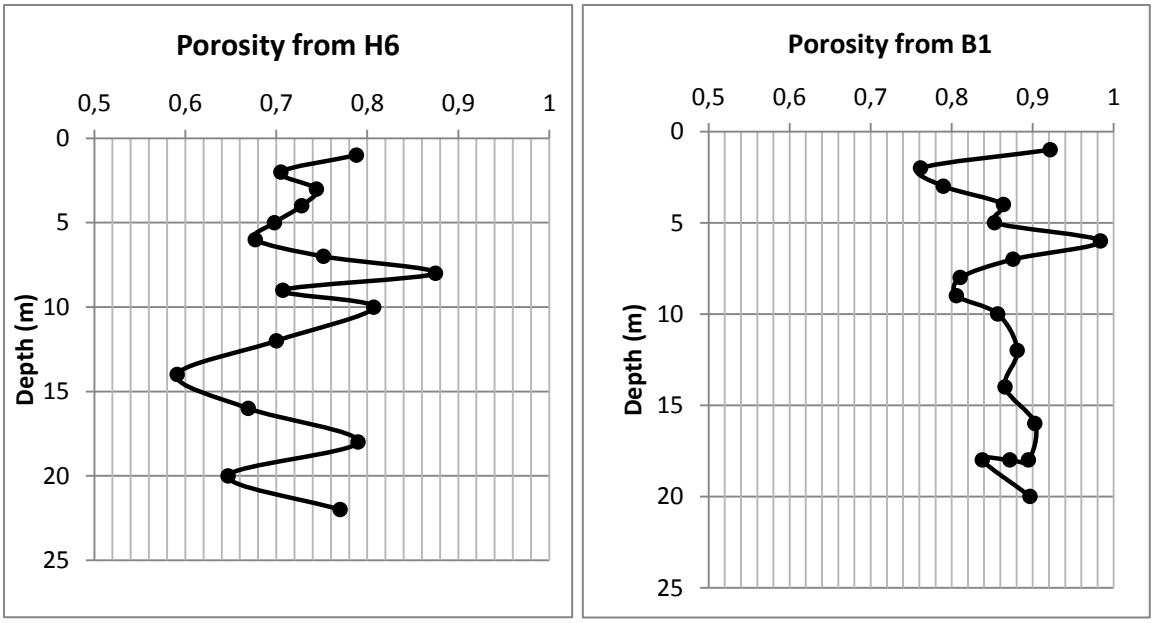


Diagram 13 and 14

5.2.2 Sediment fluxes in core incubations in February

The fluxes from the core incubations are seen in the table 13 and are calculated as described in the section 4.2.3.

Table 13 ***Core incubations***

Station	**mmol $m^{2-}d^{-1}$**	SD ±	SD %
H6	**1,73**	2,96	170,88
H2	**1,99**	2,80	140,28
B1	**0,10**	0,10	92,22

5.2.3 Sediment fluxes with Fick´s law in February

The results from the Fick´s law calculations are seen in table 14 and described in section 4.2.4.

Table 14 ***Fick´s law fluxes in H6***

Depth cm	L gas taken	L sed.	Poro-sity	Pore volume	Volume in hs	mmol	K-value	R^2	K*Ds	Flux mmol m^{2-} d^{-1}
0	5,94E-03	4,21E-03	0,64	2,68E-03	2,99E-05	1,22E-03	4,23E-04	0,98	2,04E-09	**1,763**
2	5,99E-03	4,26E-03	0,64	2,71E-03	5,76E-05	2,36E-03				
4	5,90E-03	4,11E-03	0,64	2,61E-03	7,14E-05	2,92E-03				
6	5,91E-03	4,29E-03	0,64	2,73E-03	9,43E-05	3,85E-03				

*hs means headspace, the salinity (5, 42 ‰) and temperature (1, 62°C) is taken from CTD measurements. Sed. is sediment.

Table 15 ***Fick´s law fluxes in H2***

Depth cm	L gas taken	L sed.	Poro-sity	Pore volume	Volume in hs	mmol	K-value	R^2	K*Ds	Flux mmol m^{2-} d^{-1}
0	5,94E-03	4,54E-03	0,64	2,88E-03	2,59E-06	1,06E-04	4,52E-05	0,99	2,26E-10	**0,195**
2	5,91E-03	2,82E-03	0,64	1,79E-03	3,02E-06	1,23E-04				
4	5,89E-03	4,82E-03	0,64	3,06E-03	7,02E-06	2,87E-04				

* hs means headspace, the salinity (5, 67 ‰) and temperature (2, 61°C) is taken from CTD measurements

Table 16 ***Fick´s law fluxes in B1***

Depth cm	L gas taken	L sediment	Poro-sity	Pore volume	Total volume in hs	mmol	K-value	R^2	K*Ds	Flux mmol m^{2-} d^{-1}
0	5,79E-03	4,17E-03	0,64	2,65E-03	3,71E-08	1,52E-06	2,5274E-06	0,99612	1,45E-11	**0,013**
2	5,91E-03	4,81E-03	0,64	3,06E-03	1,86E-07	7,59E-06				
4	5,90E-03	4,82E-03	0,64	3,07E-03	2,84E-07	1,16E-05				

* hs means headspace, the salinity (7, 05 ‰) and temperature (3, 74°C) is taken from CTD measurements

5.2.4 Oxygen consumption

The oxygen consumption from H6 (diagram 15 and 16) and B1 (diagram 17 and 18) can be seen below. Diagram shows the consumption from 10pm to 00 pm and diagram shows the consumption between 00 am to 08:15 am.

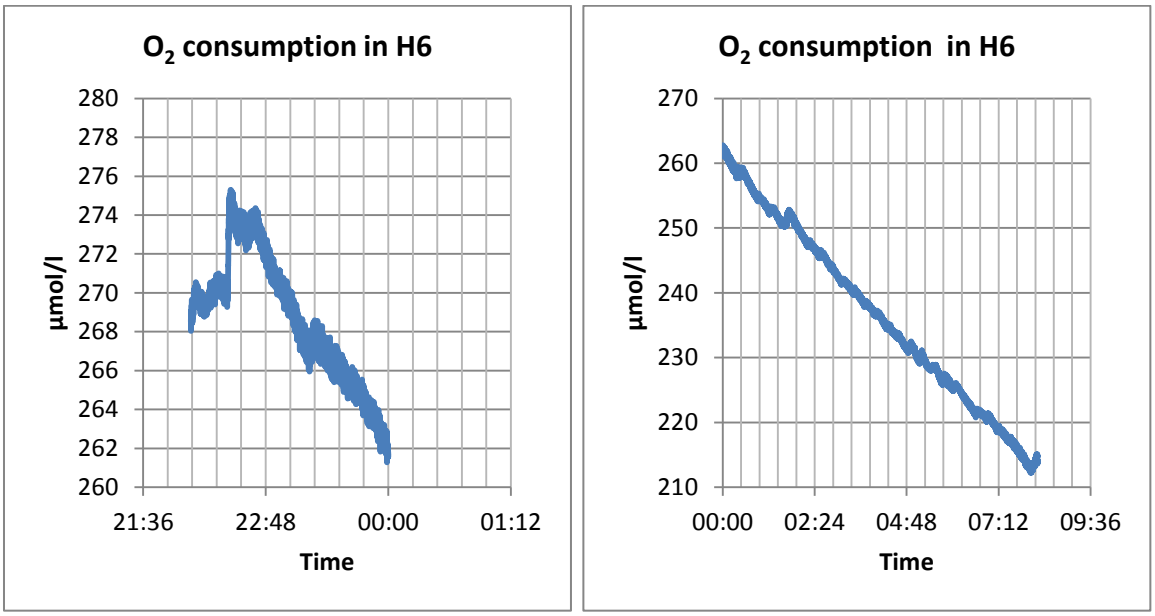
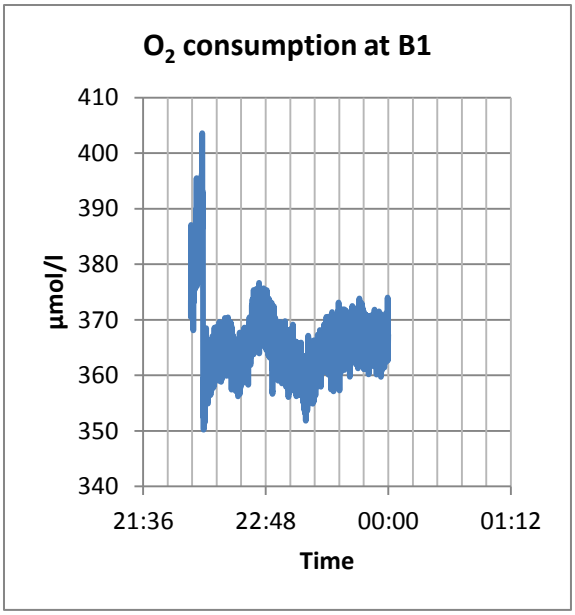


Diagram 15 and 16



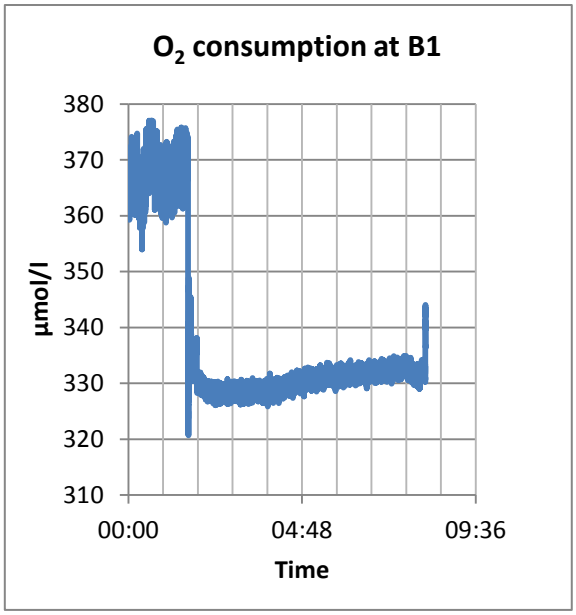


Diagram 17 and 18

In table 17 is the oxygen flux in the sediment.

Table 17		**The O_2 flux in sediments**			
H6					
C_t-C_0	µmol	µmol/h	µmol/d	area m^2	µmol m^{-2} d^{-1}
-55	-22,158	-2,110	-50,644	0,003	**-0,125**
B1					
-37	-5,201	-0,500	-11,890	0,001	**-0,012**

**Table 17. Ct and C0 is the end respective start concentration.*

5.2.6 Organic matter content

This is the organic matter and nitrogen result from the sediment in H6.

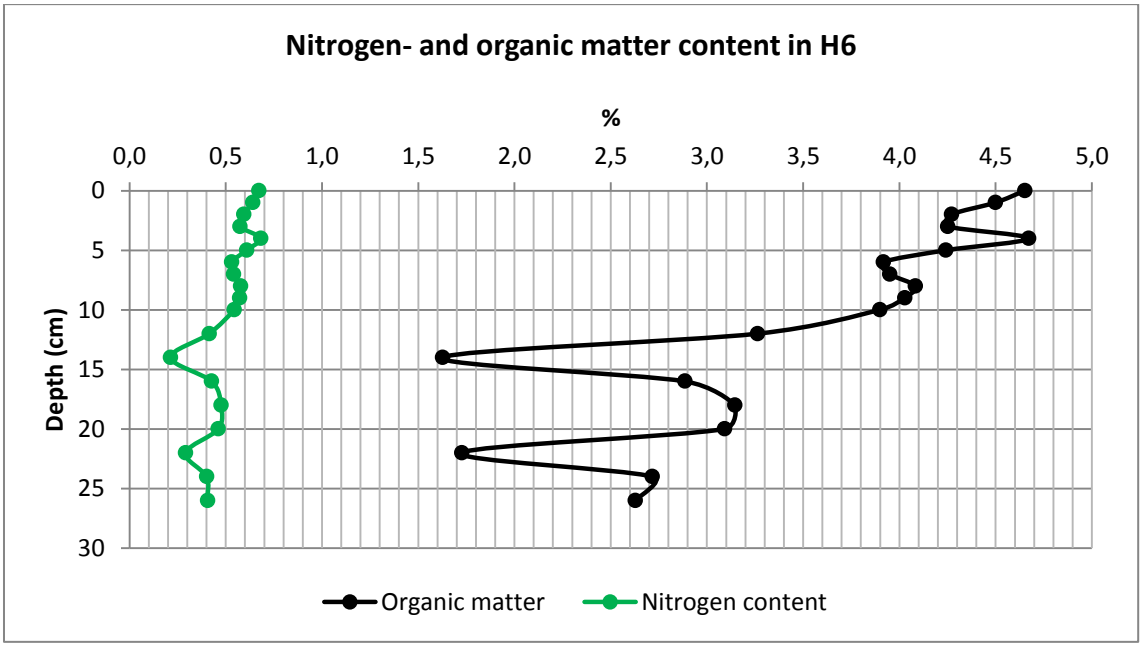


Diagram 19

6 Discussion

6.1.1 Water column methane

Comparing the overall saturations of CH_4 in Himmerfjärden with the result made *by Bange et al. 2006*, which had saturation values of about 113% and 395% in February and July/August in the central Baltic Sea, the results are in the range of what´s normal in estuaries. In February the CH_4 on the stations showed similar trends; the highest concentrations in the bottom, a steadily decrease towards the middle and then an increase at the surface. H2 have a little different trend with a faster decrease in the middle reaching CH_4 undersaturations but with a slightly increase towards the surface to 103%. Looking at the CTD profiles the salinity is, as expected, highest in B1 and lowest at H6. H6 is the station situated deepest in the estuary and is exposed to large amount of river input of freshwater and in this case the Himmerfjärden facility with 1600L s^{-1} of water pumping out, plays a role in the dilution of the salinity.

The O_2 level in the top meters doesn´t differs much except for the last 2-3 meters in the bottom in H6 and H2 where there´s a sharp drop of the O_2. The O_2 concentration in B1 remains unchanged through the water column except through the thermohaline stratification which occurs in the depth of 15m. Another important factor is whether ice covered the surface or not. During the sampling H6, H4 and H2 were covered with ice (the sampling on H2 was actually a bit from the normal sampling place, close to the fairway due to too thick ice). The ice could be an explanation for the increased concentrations in the top where the CH_4 gas, which has been able to escape the potential methane oxidation (MO), has been trapped.

The high concentrations in the bottom decrease fast to the next depth. The biggest contrast is in H6 were the saturation roughly decreases with 47% in just two meters. The *lowest* drop is in B1 and H2 with a drop of roughly 11, 5 and 9 % respectively within 3-2 meter. This could be due to the AMO and one theory is that they are attracted to places with a lot of CH_4 due to the high availability of electron donors. The problem is that this suggests that B1 with the highest saturation values in the bottom should have had the sharpest drop, but as mention before the situation is the total opposite. The AMO is also known to be inhibited by salinity and could be the explanation to a smaller activity of AMO for B1 (*Abril and Iversen, 2002)*. To think about is also the short water column which is between 23m (H4) and 38m (B1). The shorter water column the shorter residence time for the CH_4 and more gas could be able to escape the AMO and reach the water surface and the atmosphere. This implies that sediment dynamics maybe has a bigger role in the CH_4 emissions than the water column in Himmerfjärden.

The next question; if AMO were attracted to places with large amounts of CH_4, why aren't they in the sediment surface where the trapped CH_4 are situated in February? The only explanation at the moment is that there´re not enough time. The sample stations where all close to the fairway and every time a boat pass the ice cracks and CH_4 can escape until the ice seals again. The CH_4 concentration doesn't necessarily needs to be high all the time

during winter in the top. To get better evidence for AMO activity, measurements of the isotope composition in the CH_4 gas, could have provided us with valuable information. During the MOB the $\delta^{12}C$-CH_4 is preferred and the remaining CH_4 pool in the water goes towards more positive values due to remaining δ^{13}-CH_4 (*Schmale, O., 2012)*.

The gas concentration in April looks a bit different with sharp decreases in bottom waters in H2 and H6 but seem rather unaffected in the middle of the water column and ending with a slight increase at the surface. The gas concentrations from B1 and H4 doesn´t change from bottom to surface very much. Similar to the February measurements, H6 and H2 had the highest saturations in the bottom with 1592,7 and 662,5% respectively. These stations also had the sharpest decrease of CH_4 from the bottom and 2-3 m above (89 and 15% respectively).

Comparing the bottom-and surface values and the total change in gas concentration in April versus February, the results is a bit irregular and without a visible trend;

In H6 it becomes clear that even if there´s an increase of CH_4 of about 283% in bottom waters in April comparing to February, the CH_4 in surface waters still have the same concentration. Looking at the change from bottom to surface waters from respective February and April, February had a decrease of the gas concentration in surface waters of about 39% but in April the decrease is big as 86%. In total has the gas concentration in the water column increased in April.

In H4 in April there actually was an increase of about 20% in surface versus bottom waters, whereas in February there where a decrease of about 30%. This increase in surface waters can´t be explained by enhanced concentrations in bottom water because there´s actually a decrease of about 38% comparing to February. H4 has the shortest water column and therefore it would make more sense if the values were a bit more uniform. A reasonably explanation could be an external input of CH_4, but to point at a CH_4 river input or some bacterial process as sources is hard to say. To remember is that the sampling places differed by 850m and the environment probably changes a bit. In total has the gas concentration decreased in April.

In H2 the surface waters decreased with 75% comparing to the bottom in February but only 36% in April. However, the gas concentration in surface waters increased with 71% in April and bottom saturations with 57 %comparing to February values. In total has the gas concentration increased in April.

In B1 there almost was an unchanged concentration looking at bottom to surface values in April which is a drastically change from February where the surface versus bottom saturations decreased with 67% in the surface. The bottom concentration decreased with 75% in April and in overall has the CH_4 concentration lower in April.

Assuming that the “missing” CH_4 is due to oxidation it´s difficult to draw outlines from these results. According to *Abril and Iversen, 2002,* the AMO should be most efficient in H6 due the high nutrient input from the treatment plant, highest sedimentation rates and lowest salinity which leads to high CH_4 concentrations and then the production slowly decrease towards the Baltic Sea. In February, the environment with surface ice clearly

changed the trends which isn´t the same as the general ones in estuaries with B1 with a large activity of AMO. However, in April the statement from Abril and Iversen seems to agree with the profiles with H6 and H2 as the highest methane oxidation places and with almost no activity in B1. Abril and Iversen also stated a higher activity of AMO towards warmer temperatures (spring and summer). It seems to be the case for H6. In H2 the much higher CH_4 concentration in April could explain the smaller change in gas concentration looking at bottom to surface waters; the bacteria have less time to consume CH_4 in a short water column. H4 had higher bottom values in February which don´t agree with the general statement that the CH_4 concentration should be higher due to increased temperatures, higher nutrient input which leads to more organic matter reaching the bottom and a higher CH_4 production during spring and summer time. As discussed before, a river input could be the explanation but at the same time, a river input should be higher in April and therefore also be seen in the bottom waters in April.

The strangest station is B1 with the highest saturation value of them all in bottom waters and with one of the largest decreases in surface comparing to bottom waters in February. In April the gas concentration seems to be reasonable with in comparison low values from bottom to surface waters. The later on discussed sediment flux in February is low at B1 and doesn't explain the high values at the bottom. B1 is the station situated further out from Himmerfjärden and are not supposed to be affected of the sewage treatment plant or other nutrient inputs and therefore isn´t a river input explanation valid enough. The season is also wrong; rivers transports the river produced CH_4 into the estuary which normally is higher during the spring rivers. This would have effect all stations and cause higher concentrations in April but not for B1 in February. Another thing is that the winter was really cold and in April during the measurements the spring rivers hadn´t started yet. But to be certain isotopes measurements would be a good tool to use and hopefully give more accurate explanations.

6.1.2 Air-sea gas exchanges methane

Comparing the flux result from the wind speed model with the ones from Abril and Iversen 2002, it at least seems like the fluxes are in the right range. In February the fluxes ranged from 0,480 to 0,248 mmol $m^{2-}d^{-1}$ in and in April 0,439 to 0,083 mmol $m^{2-}d^{-1}$. In comparison the fluxes ranged from 0,355, 0,126 and 0,040 mmol $m^{-2}d^{-1}$ in Randers fjord in fresh-brackish and saline water respectively. All stations had a decrease in April except for H6. Because of the small changes of the gas concentration in surface waters between February and April in H6 and H4, clearly there´s other factors affecting the flux on these stations. The wind speed in H6, which seems to be the most important factor in the equation from Wanninkhof, was lower in February than April. In comparison with the other stations H6 had the lowest flux of all in February even though containing the highest surface gas concentration but had at the same time the lowest wind speed resulting in a decreased flux.

The difficulties with the fluxes are that it isn´t enough to just look at the gas concentration in the surface but also the wind speed and temperatures. In the wind speeds model, wind speed is by far the most difficult factor to determine due to the irregularities. The wind

speeds in February of course didn´t affect the flux due to the ice cover and probably enhanced the flux as well. The reason for the calculations was to see how large the flux would be during the ice break.

In the end it feels like ice is the factor explaining the increased fluxes in February due to the higher surface concentrations. The Schmidt numbers also affects the flux and is lower in April and the only factor able to affect this in the calculations is the temperature which increased 2,5°C in April. This is causing a higher piston velocity witch increases the flux. But looking and comparing tables 2, 3, 10 and 11 the changed Schmidt numbers don´t have a particular large affect and the reasons for the lower fluxes in April mostly depends on the decreased wind speed and lower surface concentrations. The higher flux in H6 in April probably has to do with an enhanced wind speed.

Comparing these results with the chamber in April, the chamber values were between 55 and 40% lower. During the measurements the waves was calm so the chamber remained on the surface all the time. It´s good question whether the chamber prevented the wind and therefore the flux but considering the constant movement, the chamber only measures the flux in a couple of seconds at every spot which restrain the chamber from affecting the surface for a long time. The irregularities in wind speed and the dynamic system with winds, concentration in the surface, internal energy and both eddy and diffusion movements in the water makes it difficult to account for all factors with one single equation. The chamber approach needs to be tested a lot more before any statement can be done about the validity in the results.

6.1.3 CH_4 fluxes across the sediment/ water interface

Sediment concentration of CH_4 was measured in H6, H2 and B1 with the highest concentration in H6 and the lowest in B1.

In H6 the CH_4 concentration at the top layer was 0,46 mM with a steadily increase until approximately a 20 cm depth where the concentrations remained between 1,6 and 2 mM. At 20- and 35 cm there was peak concentrations of roughly 2,5 mM.

In H2 the concentration was 0,037 mM in the top cm and steadily increased until the depth of 10 cm (0,756 mM) with the highest concentration at the bottom (1,347 mM).

In B1 had the lowest concentrations and close to zero in the top (0,01 mM) but with a steady increase with the top value at the bottom (0,055 mM).

From earlier investigations made by Thang et al, the sediment accumulations are high in Himmerfjärden with the highest rates close to the sewage treatment, approximately 1,5-3,5 times higher than in the open Baltic Sea. Measurements were made on the C_{org} content but only at station H6 in February. The core top had a C_{org} content of 4,65% and comparing with the investigations Thang et al made in Himmerfjärden 2012; H5, H3 and H2 had 2,8-, 3,2- and 3,8% respectively. When the organic matter input is high, the bacteria amount increases during the degradation due to high availability of organic matter. Oxygen is used during the decomposition and when it´s totally depleted, the anoxic degradation starts. This is a slower process due to the lower energy gain from the electron acceptors such as SO^{2-}_4 and CH_4. Then the C_{org} should increase in an anoxic environment because of the lower decomposition

rates when oxygen is depleted. Looking at table 17, the oxygen uptake in H6 is about 10 times higher (-0,125 µmol $m^{-2}d^{-1}$) than the uptake in B1 (-0,012 µmol $m^{-2}d^{-1}$), another proof of the correlation between high organic input and high bacteria activity. The high C_{org} in February could also be explained by lower temperatures during winter time which slow processes down.

Looking at the sediment fluxes starting with the Fick´s law calculations, H6 had the highest (1,763 mmol $m^{-2}d^{-1}$), then H2 (0,195 mmol $m^{-2}d^{-1}$) and the lowest rate was in B1 (0,013 mmol $m^{-2}d^{-1}$). The flux in H6 is 9 times higher than in B1 which also is supported by the sediment concentrations. The oxygen uptake, which is higher in H6 than B1, also supports that H6 is a station with high degradation rates which leads to oxygen depletion and CH_4 production. The results from the core incubations look a bit different with a flux of 1,73-, 1,99- and 0,10 mmol $m^{-2}d^{-1}$ respectively, which could be compared with the fluxes from Thang et al; 1,02-, 0,69- and 0,3 mmol $m^{-2}d^{-1}$ in station H5, H3 and H2 2012. In this investigation, H6 is closer to the sewage treatment and should have higher CH_4 flux than H5. The flux in H2 is a bit smaller than the fluxes from Thang et al. but considering the season the fluxes in February should be lower than the fluxes from Thang et al. which made their investigations in May and June. Considering the season, place of the station and the comparison with Thang et al, the fluxes from Fick´s law feel reasonable and match with the results from the sediment. Therefore has the choice been to believe more in the Fick´s law results than the core incubations in this case.

The core incubations with three and four cores from every station with same treatment, were supposed to receive an accurate flux. Unfortunately were the results scattered in every station which also can be understood by the large standard deviation. The replicates from every station had the same size but different between the stations. B1 had the smallest cores and the H2 the largest which were due to lack of smaller cores to subsample with. H2 had a water column height of 30 cm which is twice the length of the others which makes it difficult for the small sized magnet to stir the water. The result is inhomogeneity in the CH_4 concentration which affects the flux (too high concentration in the bottom waters change the gas partial pressure and if water gas concentration exceeds the one in the sediment CH_4 starts to diffuse down to the sediment). The size of the core is also an important factor due to the obvious reason; a larger core covers more sediment. A larger core should represent a more accurate flux due to a larger cover of the ocean floor but smaller cores give a more homogeny flux between the replicates which also seem to be the case in our investigation.

The thing that doesn't correlates is the fluxes and the bottom concentrations. As discussed before, the bottom concentration in February are similar between all stations with highest values in B1. This seems strange considering that the flux in B1 only reached 0,013 mmol $m^{-2}d^{-1}$, a 133 times lower flux than in H6. Looking at $\delta^{13}C$ maybe could help us to see how/if it differed between the sediment, lower and upper water column.

6.2.1 Water column nitrous oxide

In February, all stations shows supersaturation with the lowest nM in the bottom with a slight increase at the surface. B1 and H6 has a small decrease in the surface but the station

really pointing out is H4 with a saturation of 496,5% in the top. The second largest nM is 201,7% and is in the surface of H6. H6 and H4 has the largest concentrations and H2 the lowest and B1 only slightly higher. The oxygen has in many investigations proved to correlate with N_2O, that oxygen is essential to the production and that an increase of the N_2O concentration often results in a decrease of oxygen (*Andrew, P., (2011), Rönner, U., (1983), Bange, H.W*., (2006), *Dalsgaard, T., (2013)).* This correlation can´t be seen in February where the surface concentrations of oxygen in H4 doesn't decrease at all and looks unaffected through the water column except for a slow decrease towards the bottom. In H6 and H2 there´s a sharp decrease the last two meters but otherwise look unaffected whilst in B1 it increases at 15m, caused by the salinity- and temperature increase which causes the water to shift in density.

The results in April are now compared with the ones from February and all diagrams mentioned with ammonium and nitrite/nitrate concentrations can be seen in appendix 10.2.1;

In H6 the nM starts to decrease from the bottom but interrupts at 15m with increased nM until reaching 10m where there´s a decrease towards the surface. The difference from bottom to surface is a 14% decrease in surface waters. In February there was an increase of 17% but in total is the concentration higher in the water column in April. The ammonium concentration is under detector limit through the whole water column in 2013 and had peak values during the autumn 2012 (diagram 20). Simultaneously there was a decrease in the concentration of NO^-_3/NO^-_2 in the top 0-10 m, from the middle of February and reached the lowest values in. The concentration further down remained unchanged between 20-30m (diagram 21).

In H4, the lowest concentration is in the bottom (176%*)* with increasing values up to 10m where there´s a sharp decrease until 5m and the values starts to increase again towards the surface. The total increase from bottom to surface water in April was 70% whilst in February there was an increase of 232%. The bottom values were higher in April but altogether the concentration was higher in February due to the extreme increase in the upper half of the water column. In the 0-10 m surface waters, the ammonium had a peak in February and started to decrease again until undetectable concentration in March (diagram 22). The NO^-_3/NO^-_2 was at highest in February but decreased rapidly until April (diagram 23).

In H2 the concentration in April increased up to 15m and then started to decrease towards the surface. The surface waters a 3% higher concentration comparing to the surface whilst in February the increase was 15%. The concentration was higher in April though. In both February and April 2012, the Ammonium concentration was close to zero through the water column (diagram 24). In the same time had the concentration of NO^-_3/NO^-_2 a peak but decreased to zero during the first week in April (diagram 25).

In B1 the three depths show an increase from bottom to surface of 15% and in February the increase was 4%. The concentration was higher in April on this station as well. The ammonium concentration were low in the upper column the both samplings but in the lower

part there was a small peak in April (diagram 26). The NO^-_3/NO^-_2 starts to decrease in February/March and reached zero values in middle of April (diagram 27).

So in February in all station, except for H4, the bottom to surface concentrations had a small increase with a few percent. The trend is the highest values towards the surface which could be due to the effect of ice in February but doesn´t seem to have such a large affect as for the CH_4 which could have to do with the overall lower concentrations of N_2O. The decrease in B1 could be due to lack of ice which allows the gas to diffuse into the atmosphere.

Due to the presence of oxygen, dentrification isn´t the N_2O source in neither February nor April in the water column (*Andrew, P., (2011), Rönner, U., (1983), Bange, H.W*., (2006), *Dalsgaard, T., (2013)).* It would have been easy to say that nitrification alone is responsible but this is not supported by the unaffected oxygen in the water column. *Rönner, U., 1983* stated that N_2O generally increases whilst the oxygen decreases but in very low oxygen concentrations dentrification are the producers but a switch to anoxic environments a consumer. Both *Rönner, U., (1983)* and *Bange, H.W*., (*2006)* also stated that N_2O increases together with the NO^-_3/NO^-_2 but the results shows higher concentrations in April (except in H4) and a simultaneously decrease of the NO^-_3/NO^-_2.

Rönner, U., (1983), also stated that oxidation of ammonium and nitrite are being inhibited by presence of light and that nitrification often are lacking in surface waters. The high increase in H4 could be explained by; the high oxygen content which are favorable conditions for nitrification, ice prevents the incoming light which is a limiting factor (the long and darker winter season also would favor nitrification in the upper water column), the high ammonium peak which all the other stations are lacking plus having one of the highest NO^-_3/NO^-_2 concentrations in the upper water column are all factor making it possible for enhanced N_2O concentrations in H4. However, taking the unaffected oxygen concentration in the upper water column, the simultaneously decrease of NO^-_3/NO^-_2 and increase of N_2O and the light inhibiting factor; points at another source than nitrification in the water column. In February the ice prevented the light which could allow nitrification in the top 10 m but as said before, this isn´t seen in either the oxygen or ammonium concentration. The steadily decrease of the NO^-_3/NO^-_2 and the zero concentrations of ammonium through the winter month takes away a river input explanation for H4; a river input would have been correlated with peaks of respective concentration or at least higher them. The main source could then be the sediment which on other hand is difficult to prove without sediment samples but the explanation is the same as for CH_4; when the water column is short this allows the sediment dynamics to have a bigger role in the release of N_2O. Another corresponding result pointing at sediment as a source is the oxygen uptake. In comparison is the oxygen uptake much larger in H6 than B1 and could mean a higher nitrification activity in the sediment and further a higher N_2O. This is supported by the highest saturation of N_2O in the bottom in H6 in February. If the sediment acts as a source the enhanced concentrations in April could be explained by a higher microbial activity in the sediment due to higher temperatures and a higher amount of gas released into the water.

Because of lacking oxygen-, sediment concentration- and isotope data, it´s impossible to do good statements about the N_2O in the water column. However, the really low concentrations of both ammonium and NO^-_3/NO^-_2 in all stations, the areas with increasing gas concentration have to be explained by something else than nitrification. According to *Dalsgaard et al* sulfide inhabits the reduction of N_2O to N_2 and would be interesting to investigate in the future. The mystery in H4 remains but *Rönner, U., (1983),* had the same phenomena in his investigation in the photic zone. He suggested in his report that some nitrate reducing bacteria (heterotrophic organism) are known to produce N_2O and that they maybe co-operates together some algae. Whatever this is valid for H4 considering the season is difficult to know but still could be worth to have in mind for future investigations.

6.2.2 Air-sea gas exchanges

The fluxes in April decreased with 47% in H4, increased with 26% in H2 and increased with 15% in B1. Because the same calculations were done for the N_2O as CH_4, the same factors are affecting the flux; the lower temperature increases the Schmidt number which decreases the piston velocity and therefore the flux. The higher temperatures in April decreased the Schmidt number which together with the higher nM in surface waters, causes the fluxes to increase in April. The wind speeds is lower in April which probably decreased the fluxes a bit. The only exception is H6 with a higher wind speed in April but with a lower surface concentration which counteracts the flux. H4 also has both lower wind speed and much lower concentration, which is the main reason for the lower flux in April. The others station has lower wind speeds but counteracts with higher temperatures and concentrations in the surface which gave higher fluxes in April.

7 Conclusions

The trend of CH_4 in the water column between February and April is increasing concentrations in the bottom which is counteracted with higher activities of AOM in the surface at H6 and H2. The conclusion has been that high gas concentration attracts higher numbers of AOM. B1 and H4 have both decreased concentrations in April and a less AOM activity which can´t be explained by salinity, temperature or oxygen changes. B1 had the largest change between the samplings and the high saturations on this station in February can`t be explained by a sediment flux and a river input isn´t a reasonable explanation due to the distance from the estuary.

According to the depth profiles the ice seems to trap the gas which has escaped the AOM. It seems like the stations with less CH_4 are more irregular but to know the sources with high certainty, more continuous data from winter are needed together with isotope measurements.

To get an accurate flux from the wind speed model, the choice to whether take an average wind speed over a longer time period or just take a single measurements is important and affects the flux very radically. The ice is probably the reason for the higher fluxes in February but wind speed is the main factor determining the flux together with surface concentrations,

at least in this method of calculations. The N_2O fluxes increased in April and is probably related with higher temperature and surface concentrations even though that the wind speeds were overall lower in April. Comparing wind speed and the chamber approach shows that the wind speed model seems to enhance the flux with roughly 50%. Of course this needs to be measured a lot more and continuous to be able to with high certainty determine this.

The Fick´s law calculations made in the sediment correlates with earlier results in Himmerfjärden with high CH_4 fluxes in H6 and the smallest in B1. The core incubation results are scattered even though it´s in situ measurements. However, the errors could be due to small stirrers (causing inhomogeneity) and disturbing of sediments during sampling which could affect the flux. The CH_4 increase in the water in April is probably due to warmer temperatures which enhances the degradation rate of organic and further the CH_4 production. Looking at the short water column, sediment probably matters more in the CH_4 production than the water column (*Abril and Iversen, 2002)*.

N_2O has been shown in earlier investigations to correlate with NO^-_3/NO^-_2 and oxygen but since oxygen data is lacking in April, it´s difficult so do a similar statement. The results showing an unchanged oxygen concentration, a simultaneously decrease of NO^-_3/NO^-_2 with an increased N_2O concentration and the light inhibiting factor points at another source than nitrification in the water column (*Rönner, U., (1983)*, *Bange, H.W.*, (*2006)*). The concentration in April has increased in the stations besides H4 and the explanation for the higher concentrations is the same as for CH_4; enhanced degradation rates of organic matter in the sediment. River input and prevented ice can´t explain the increase in H4 and without any visible correlation between oxygen, N_2O and NO^-_3/NO^-_2 nitrification doesn´t seem to be the source. It has been suggested that nitrate reducing bacteria could co-operates with algae to produce N_2O in the photic zone (*Rönner, U., 1983)*. This hypothesis needs to be tested and investigated a lot more, but could be good to have in mind in future investigations.

Considering the short water column, sediment seems to be the source of N_2O in the water but isotope data, sediment concentrations of N_2O, NO^-_3/NO^-_2, H_2S, N_2O fluxes from sediment and oxygen concentrations are needed to do an accurate conclusion of the sources of N_2O in the water column.

8 Acknowledgements

I'd like to thank all the stuff on Askö for the help during the sampling, you neither complained when the weather worked against us or when the sampling delayed due to the rough environment. Many thanks to Barbara Deutsch for the help during the sampling, you saved many hours with your competence. I´d also want to thank Heike Sigmund for the help in measuring the organic matter content and Carina Johansson for letting me use the freeze drier. I`d also want to thank Johan for the patience with my many English- and mathematical questions. Finally I want to thank my two supervisors; Volker Brüchert and Joanna Sawicka for all the coaching and patience during the whole time even though you both had a lot of

other things to do. Especially to you Joanna, for the incredible patience you have showed me even during my mistakes and many questions. Thank you so much for the many long and learning talks which has been very precious for me!

9 References

9.1 Electronic sources

The Syvab webpage, See Himmerfjärdsverket, 2011, Available:
http://www.syvab.se/himmerfjardsverket/anlaggningsdata (collected 2013-03-18)

The Syvabs webpage, see links on Himmerfjärden projects, Available:
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10 Appendix

10.1.1. Bunsen solubility from February

Through the paper written by Denis A. Wiesenburg and Norman L. Guinasso from 1979, the constants in the Bunsen solubility calculations of CH_4 were achieved. The constants for the N_2O calculations, taken from the paper of R.F Weiss and B.A Price, 1979 are together in table 18. The Bunsen calculations for CH_4 are seen in tables 20-23 (February) and 28-31 (April). N_2O calculations are seen between table 24-27 (February).

Constants CH_4		***Constants N_2O***	
A_1	-415,2807	**A_1**	-165,8806
A_2	-596,8104	**A_2**	222,8743
A_3	379,2599	**A_3**	92,0792
A_4	-62,0757	**A_4**	-1,48425
B_1	-0,059160	**B_1**	-0,056235
B_2	0,032174	**B_2**	0,031619
B_3	-0,0048198	**B_3**	-0,0048472

Table 18

Explanations	
Salinity	‰
ppm f_G	Dry mole fraction in air for Bunsen solubility calculations
X	Dry mole fraction in air for saturation calculations
x`	Measured ppm in headspace
Cw	β*x`
Ca	β*x
%	Cw/Ca*100

Table 19

Bunsen solubility calculations of CH_4 in H6									
Salinity	Kelvin	ppm f_G	Depth (m)	β	x	x`	Cw	Ca	Sat. %
4,61	273,3	1,88	0,03	15,34	1,88	5,04	145,39	54,23	259,0
5,85	274,53	1,88	5,07	15,30	1,88	3,23	92,89	54,07	162,2
5,99	274,63	1,88	10,08	15,29	1,88	2,33	66,99	54,05	114,4
6,03	274,53	1,88	15,03	15,30	1,88	2,13	61,25	54,06	104,3
6,05	274,59	1,88	20,05	15,29	1,88	2,58	74,18	54,05	127,7
6,06	274,62	1,88	25,01	15,29	1,88	3,12	89,70	54,05	156,4
6,07	274,64	1,88	30,08	15,29	1,88	3,28	94,30	54,05	165,4
6,08	274,6	1,88	32,56	15,29	1,88	3,55	102,07	54,05	179,3
5,42	274,77	1,88	34,11	15,29	1,88	8,00	230,00	54,05	416,0

Table 20

Bunsen solubility calculations of CH_4 in H4

Salinity	Kelvin	ppm f_G	Depth (m)	β	x	x`	Cw	Ca	Sat. %
5,70	273,66	1,88	0,00	15,08	1,88	4,14	62,43	28,35	210,6
5,97	274,06	1,88	4,94	15,05	1,88	2,82	42,45	28,30	141,0
6,13	274,21	1,88	10,05	15,04	1,88	3,29	49,47	28,27	165,4
6,19	274,47	1,88	15,03	15,03	1,88	2,70	40,57	28,25	134,0
6,21	274,66	1,88	20,01	15,02	1,88	2,77	41,60	28,24	137,8
6,27	275,27	1,88	25,01	15,00	1,88	2,50	37,49	28,19	123,4
6,28	275,52	1,88	27,54	14,99	1,88	5,65	84,69	28,18	291,0

Table 21

Bunsen solubility calculations of CH_4 in H2

Salinity	Kelvin	ppm f_G	Depth (m)	β	x	x`	Cw	Ca	Sat. %
6,16	273,30	1,88	0,06	15,33	1,88	1,94	29,75	28,83	103,2
6,16	273,41	1,88	5,02	15,33	1,88	1,83	28,05	28,82	97,3
6,19	273,32	1,88	10,06	15,33	1,88	1,30	19,93	28,82	69,1
6,23	273,70	1,88	15,07	15,32	1,88	1,68	25,74	28,80	89,4
6,33	275,47	1,88	19,98	15,26	1,88	5,55	84,72	28,70	295,2
6,43	275,49	1,88	25,02	15,26	1,88	5,75	87,76	28,70	305,9
6,62	275,77	1,88	30,02	15,25	1,88	7,19	109,67	28,68	382,4

Table 22

Bunsen solubility calculations of CH_4 in B1

Salinity	Kelvin	ppm f_G	Depth (m)	β	x	x`	Cw	Ca	Sat. %
6,23	273,42	1,88	0,10	15,33	1,88	2,97	45,53	28,82	158,0
6,25	273,47	1,88	5,01	15,33	1,88	3,09	47,36	28,81	164,4
6,26	273,51	1,88	10,10	15,33	1,88	4,09	62,68	28,81	217,6
6,49	274,12	1,88	15,14	15,30	1,88	4,97	76,06	28,77	264,4
6,7	276,07	1,88	20,02	15,24	1,88	6,07	92,53	28,66	322,9
6,82	276,39	1,88	25,11	15,23	1,88	6,07	92,47	28,64	322,9
6,92	276,59	1,88	30,08	15,23	1,88	6,34	96,54	28,63	337,2
6,97	276,69	1,88	31,63	15,22	1,88	7,88	119,96	28,62	419,1
7,02	276,83	1,88	35,04	15,22	1,88	8,90	135,45	28,61	473,4

Table 23

Bunsen solubility calculations of N_2O in H6

Salinity	Kelvin	ppm f_G	Depth (m)	F	β	x	x`	Cw	Ca	Sat. %
4,61	273,30	325	0,03	-2,87	-932,40	325	655,47	-611163,12	-303030,43	201,7
5,85	274,53	325	5,07	-2,93	-951,58	325	670,22	-637765,87	-309263,95	206,2
5,99	274,63	325	10,08	-2,93	-953,20	325	639,86	-609917,56	-309790,22	196,9
6,03	274,53	325	15,03	-2,93	-951,93	325	592,58	-564096,22	-309377,32	182,3
6,05	274,59	325	20,05	-2,93	-952,78	325	585,44	-557796,29	-309652,84	180,1
6,06	274,62	325	25,01	-2,93	-953,20	325	581,52	-554304,24	-309790,50	178,9
6,07	274,64	325	30,08	-2,93	-953,49	325	560,16	-534104,41	-309884,33	172,4
6,07	274,60	325	32,63	-2,93	-952,95	325	560,03	-533682,01	-309709,22	172,3
5,42	274,77	325	34,11	-2,94	-953,98	325	557,69	-532028,86	-310044,14	171,6

Table 24

Bunsen solubility calculations of N_2O in H4										
Salinity	Kelvin	ppm f_G	Depth (m)	F	β	x	x`	Cw	Ca	Sat. %
5,7	273,66	325	0,00	-2,89	-939,47	325	1613,72	-1516045,14	-305328,49	496,5
5,97	274,07	325	5,00	-2,91	-945,59	325	927,37	-876912,04	-307315,67	285,3
6,13	274,21	325	10,05	-2,92	-947,80	325	734,14	-695817,58	-308034,18	225,9
6,19	274,47	325	15,03	-2,93	-951,43	325	570,63	-542914,69	-309214,99	175,6
6,21	274,66	325	20,01	-2,94	-954,03	325	496,80	-473964,58	-310059,93	152,9
6,27	275,27	325	25,01	-2,96	-962,32	325	495,75	-477067,33	-312753,62	152,5
6,29	275,65	325	28,03	-2,98	-967,41	325	482,92	-467181,47	-314408,29	148,6

Table 25

Bunsen solubility calculations of N_2O in H2										
Salinity	Kelvin	ppm f_G	Depth (m)	F	β	x	x`	Cw	Ca	Sat. %
6,16	273,30	325	0,06	-2,66	-863,22	325	461,25	-398157,86	-280546,22	141,9
6,16	273,41	325	5,02	-2,66	-864,67	325	439,50	-380020,01	-281018,17	135,2
6,19	273,32	325	10,06	-2,66	-863,19	325	431,46	-372431,70	-280536,86	132,8
6,23	273,70	325	15,07	-2,67	-867,80	325	581,32	-504473,57	-282035,32	178,9
6,33	275,43	325	20,06	-2,74	-889,19	325	428,80	-381284,90	-288987,21	131,9
6,43	275,49	325	25,02	-2,74	-888,96	325	418,36	-371905,93	-288911,12	128,7
6,5	275,79	325	27,63	-2,74	-892,07	325	415,18	-370364,74	-289921,51	127,7
6,62	275,77	325	30,02	-2,74	-890,61	325	400,51	-356697,36	-289448,45	123,2

*Table 26. The first replicate is not included due to unavailable N_2O calibration gas during measurements. In the second replicate samples in 5 and 15m is lacking

Bunsen solubility calculations of N_2O in B1										
Salinity	Kelvin	ppm f_G	Depth (m)	F	β	x	x`	Cw	Ca	Sat. %
6,23	273,42	325	0,10	-2,88	-937,22	325	429,16	-402214,40	-304596,87	132,0
6,25	273,47	325	5,01	-2,89	-937,95	325	447,96	-420158,43	-304832,39	137,8
6,26	273,51	325	10,10	-2,89	-938,51	325	459,52	-431262,80	-305016,86	141,4
6,39	273,97	325	15,00	-2,91	-945,04	325	452,93	-428043,59	-307139,61	139,4
6,7	276,07	325	20,02	-3,00	-973,75	325	424,06	-412929,24	-316467,38	130,5
6,82	276,39	325	25,11	-3,01	-978,18	325	426,95	-417634,82	-317908,11	131,4
6,92	276,59	325	30,08	-3,02	-980,99	325	435,33	-427050,80	-318820,53	133,9
7,02	276,82	325	34,87	-3,03	-984,18	325	409,55	-403069,84	-319857,17	126,0
7,05	276,89	325	37,05	-3,03	-985,14	325	415,34	-409167,84	-320171,69	127,8

Table 27

10.1.2 Bunsen solubility from April

Bunsen solubility calculations of CH_4 in H6									
Salinity	Kelvin	ppm f_G	Depth(m)	β	x	x`	Cw	Ca	Sat. %
4,8	275,85	1,88	0	15,07	1,88	4,70	70,81	28,39	249,4
4,8	275,75	1,88	5	15,07	1,88	4,09	61,60	28,39	216,9
5,6	275,05	1,88	10	15,05	1,88	3,06	46,11	28,35	162,7
5,7	275,15	1,88	15	15,04	1,88	3,02	45,43	28,33	160,4
5,8	274,75	1,88	20	15,04	1,88	2,66	39,94	28,34	140,9
5,8	274,85	1,88	25	15,04	1,88	2,37	35,57	28,33	125,5
5,8	274,95	1,88	30	15,04	1,88	2,08	31,35	28,33	110,6
5,9	274,85	1,88	32	15,03	1,88	3,28	49,26	28,32	173,9
5,9	274,95	1,88	35	15,03	1,88	30,01	451,02	28,32	1592,7

Table 28

Bunsen solubility calculations of CH_4 from H4									
Salinity	Kelvin	ppm f_G	Depth(m)	β	x	x`	Cw	Ca	Sat.%
5,5	275,35	1,88	0	15,04	1,88	3,77	56,73	28,24	200,87
5,6	274,95	1,88	5	15,05	1,88	3,32	50,00	28,25	176,97
5,6	274,95	1,88	10	15,05	1,88	3,61	54,33	28,25	192,28
5,8	274,45	1,88	15	15,05	1,88	3,69	55,51	28,26	196,43
5,9	274,15	1,88	20	15,05	1,88	3,37	50,78	28,27	179,65
5,9	274,15	1,88	23	15,05	1,88	3,39	51,00	28,27	180,41

Table 29

Bunsen solubility calculations of CH_4 from H2									
Salinity	Kelvin	ppm f_G	Depth(m)	β	x	x`	Cw	Ca	Sat. %
5,8	275,05	1,87	0	15,03	1,87	3,30	49,55	28,12	176,21
5,8	275,05	1,87	5	15,03	1,87	3,21	48,25	28,12	171,59
5,8	274,45	1,87	10	15,05	1,87	3,10	46,65	28,16	165,68
5,8	274,35	1,87	15	15,05	1,87	3,18	47,89	28,16	170,04
5	274,35	1,87	20	15,10	1,87	3,60	54,42	28,25	192,62
6	274,35	1,87	25	15,04	1,87	5,49	82,58	28,14	293,45
6,1	274,55	1,87	30	15,02	1,87	10,57	158,84	28,12	564,93
6,1	274,65	1,87	32	15,02	1,87	12,40	186,23	28,11	662,47

Table 30

Bunsen solubility calculations of CH_4 from B1									
Salinity	Kelvin	ppm f_G	Depth(m)	β	x	x`	Cw	Ca	Sat. %
5,9	274,65	1,90	0	15,05	1,90	2,30	34,59	28,59	120,97
5,9	274,45	1,90	5	15,05	1,90	2,41	36,31	28,61	126,92
6,5	275,55	1,90	38	14,99	1,90	2,30	34,54	28,47	121,30

Table 31

10.2.1 Ammonium and nitrate/nitrite from H6

The values are all taken from the webpage *www2.ecology.su.se* which can be found on a link in Syvabs webpage. The concentration can be seen in appendix and are an average between 0-10m and 20-30 m and expressed in mg m^{-3}.

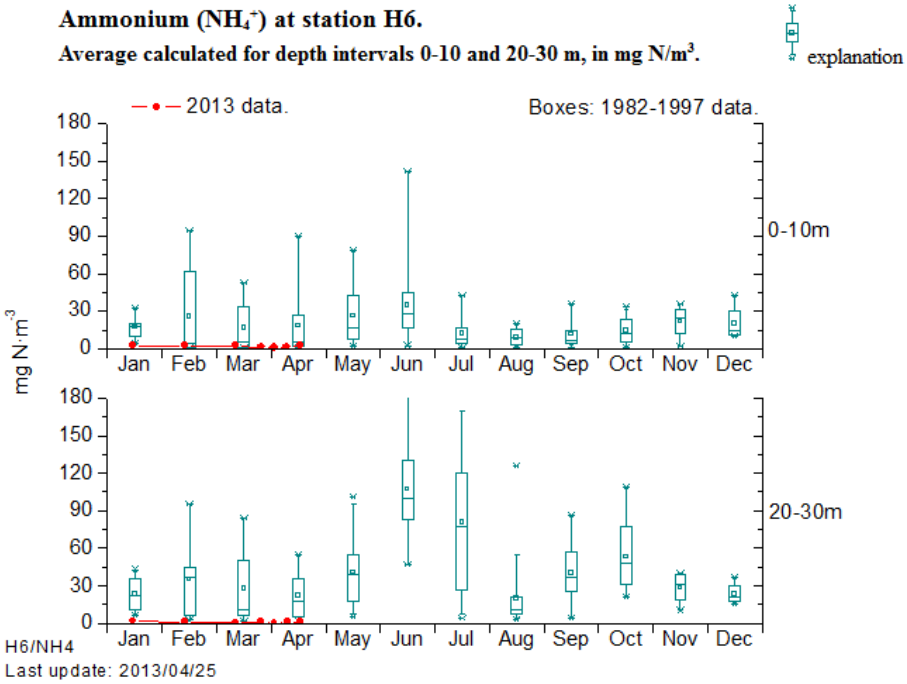

Diagram 20

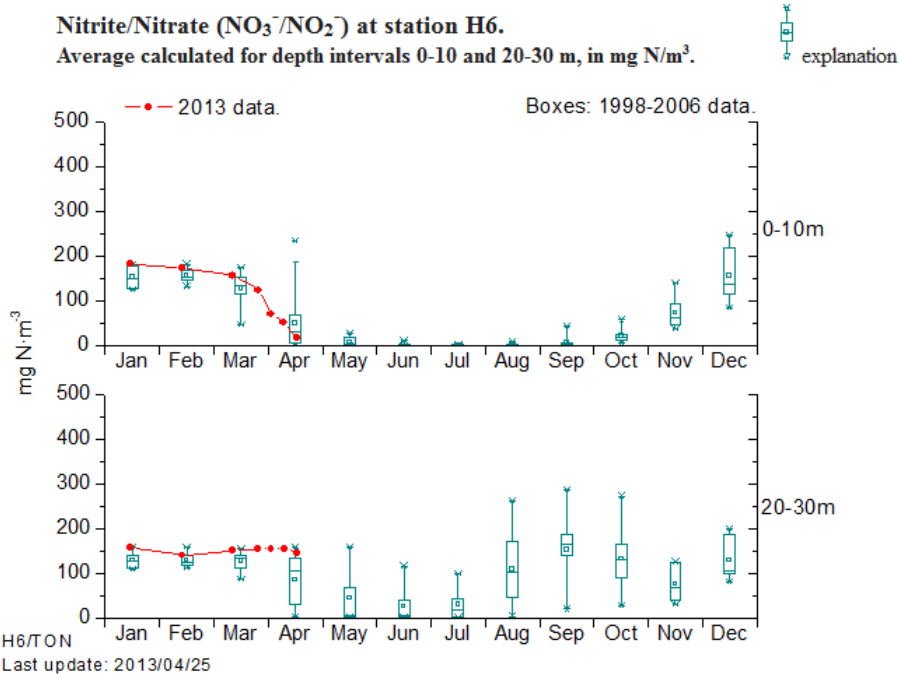

Diagram 21

10.2.2 Ammonium and nitrite/nitrate in H4

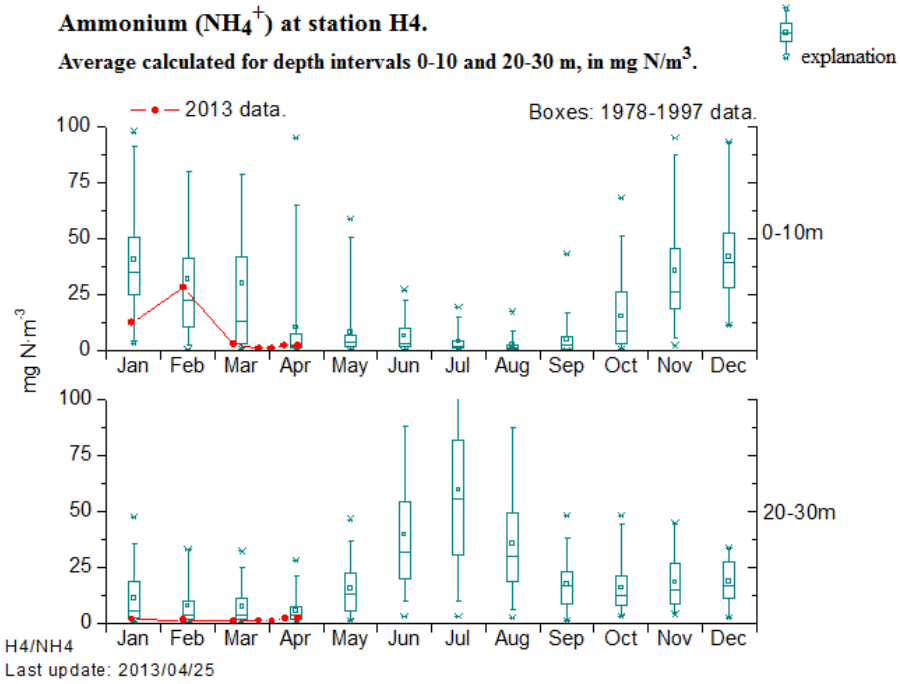

Diagram 22

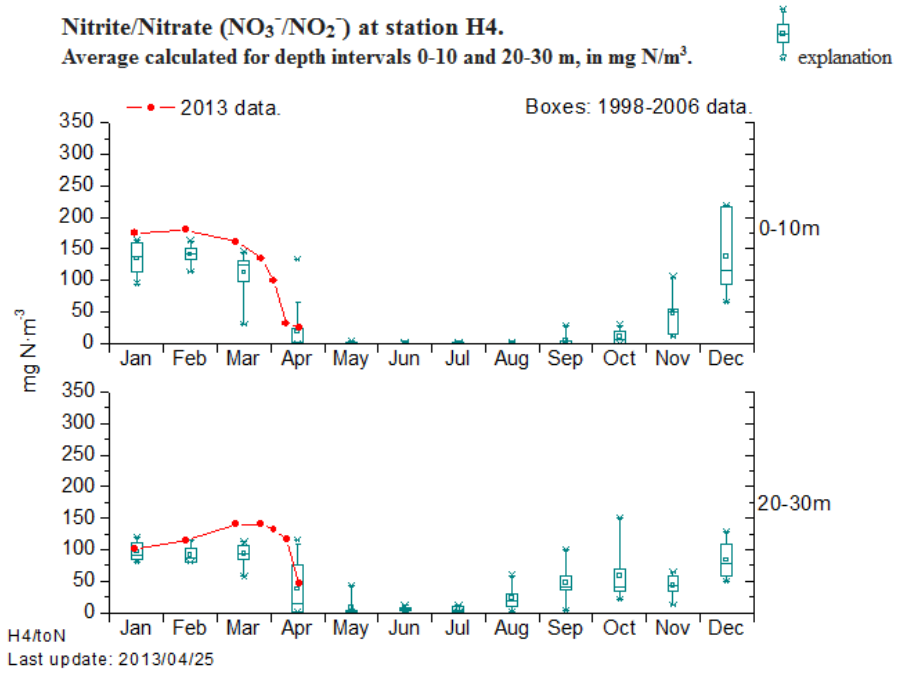

Diagram 23

10.2.3 Ammonium and nitrite/nitrate in H2

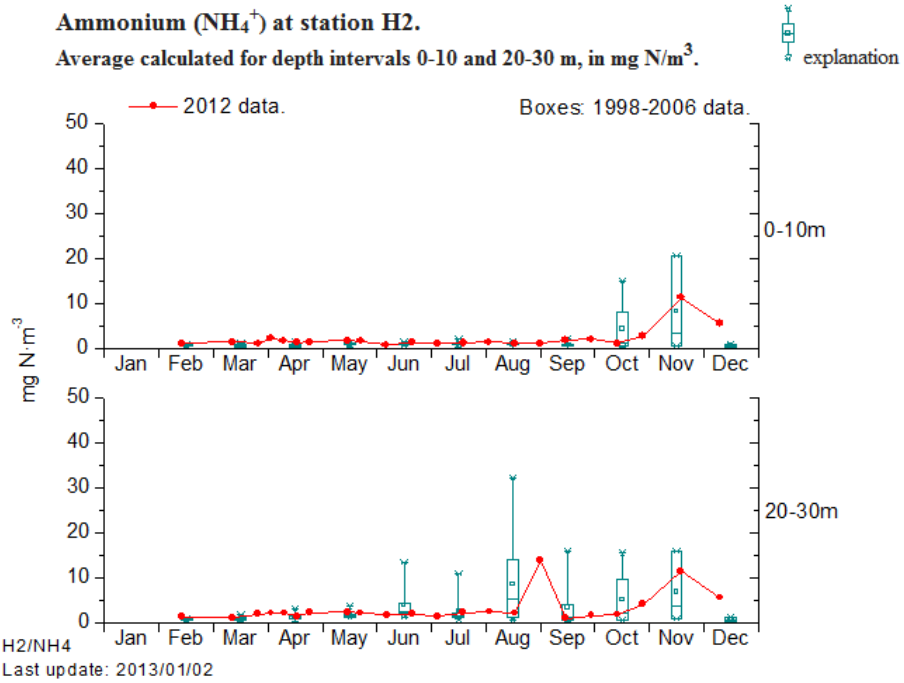

Diagram 24

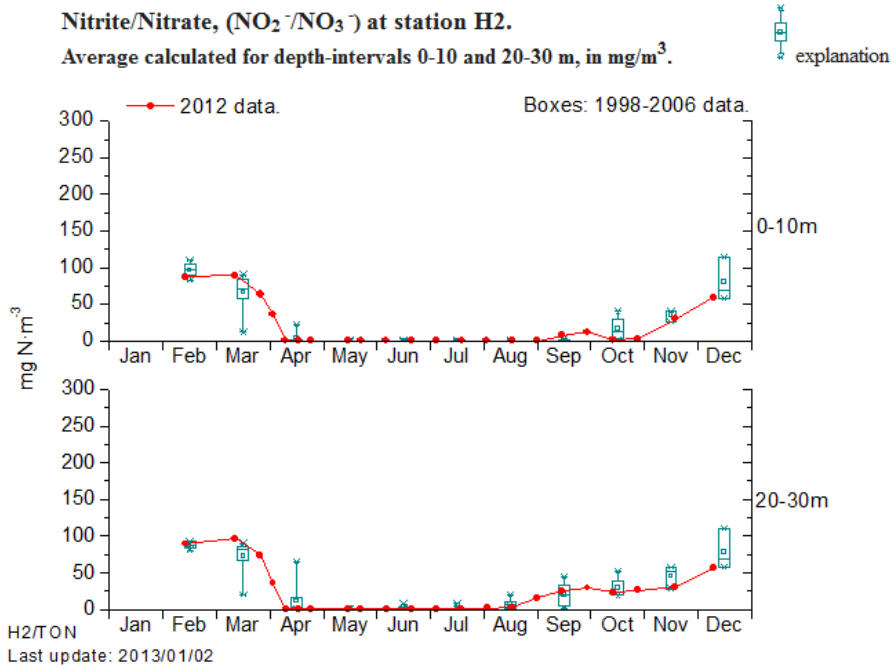

Diagram 25

10.2.4 Ammonium and nitrate/nitrite in B1

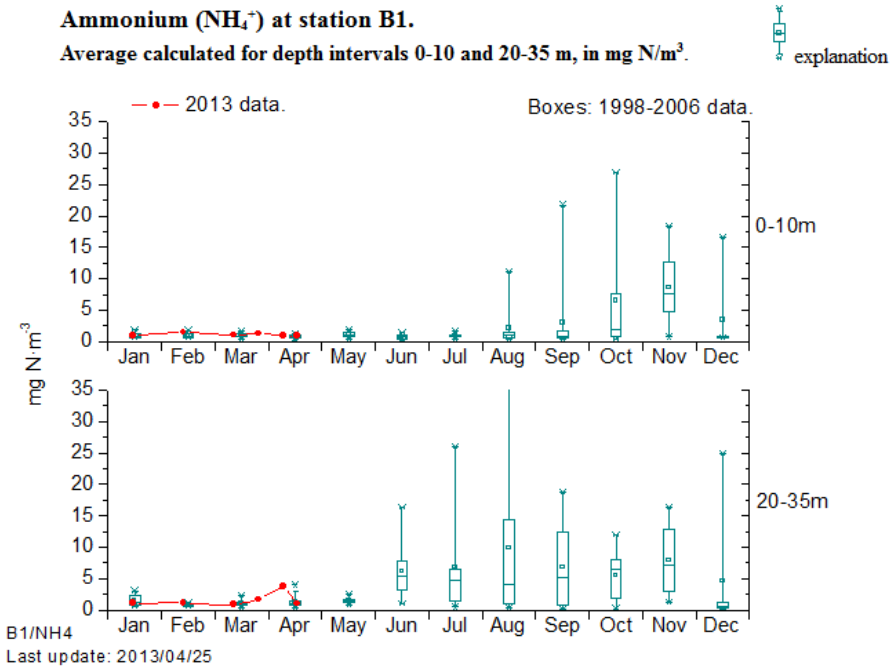

Diagram 26

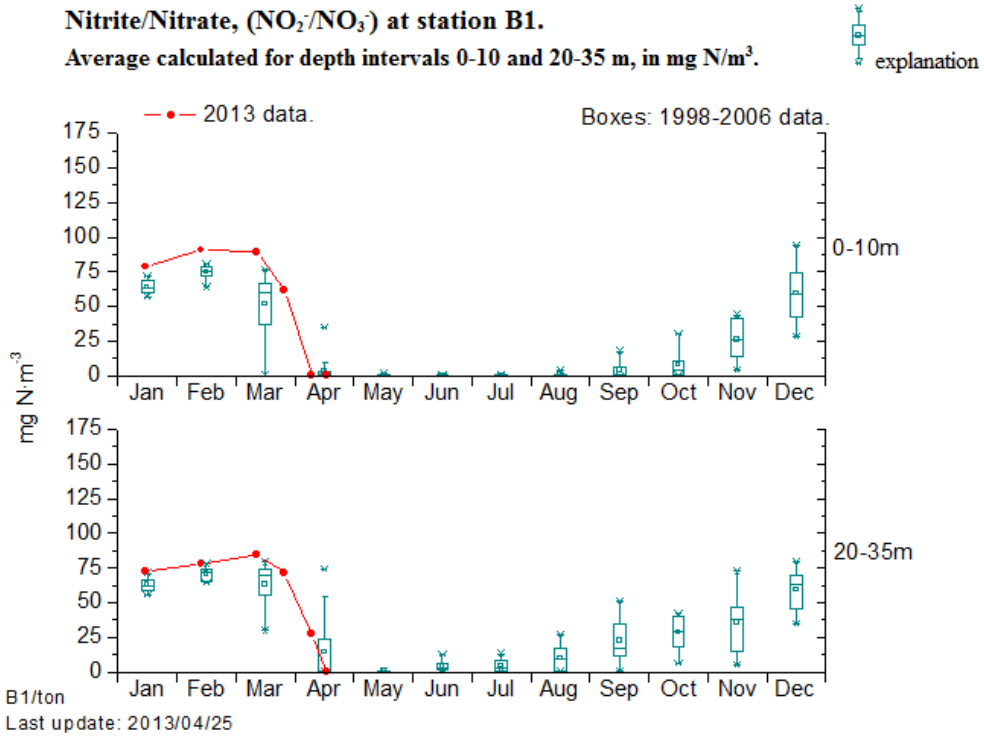

Diagram 27