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Effects of the 2014 major Baltic inflow on methane and nitrous oxide dynamics in the water column of the central Baltic Sea

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This document contains the following supplementary materials:

Figure S1 – Establishment of the cut-off values below which data for CH_4 and N_2O are indistinguishable from blanks

Text S2 – Precision and accuracy of the reported data

Figure S2 – Diffusion experiment for gas loss from plastic syringes related to text S2.

Figure S3 – Figure exhibiting the changes in water column salinity at the Western Gotland Basin over a period of 16 years.

Table S4 – Table containing detailed information about the specific sampling sites, depths and coordinates.

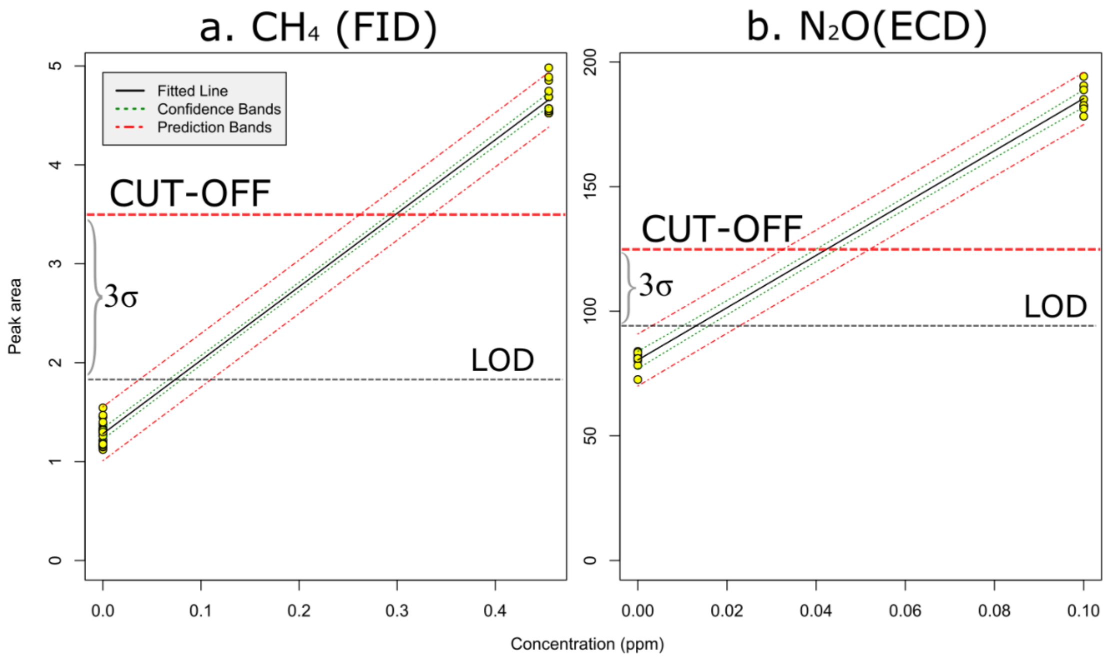

Figure S1. Establishment of cut-off concentrations of CH_4 (left) and N_2O (right), below which measured sample values are regarded as indistinguishable from those of blank pre-evacuated Exetainers. Note the different y-axis scales of the panels, which are due to the different detectors used for the GC measurement of each gas (FID vs. ECD). Yellow points represent measured peak areas of CH_4 and N_2O from blank pre-evacuated Exetainers (i.e. Exetainers from the supplier, subsequently filled with N_2, nominal CH_4 and N_2O concentrations = 0 ppm) and measured peak areas of the lowest standards for each gas, also stored in pre-evacuated Exetainers (CH_4 and N_2O concentrations 0.45 ppm and 0.1 ppm, respectively). A total of 22 replicate blanks and 14 replicate low standards were measured for CH_4 and 8 blanks and 8 low standards for N_2O. The linear fits (peak area vs. ppm) derived from the blanks and the low standards are shown for both gases, with the corresponding 95% confidence and prediction bands. Note that these fits are linear across the full range of standards (not shown). Limit of detection (LOD) was determined according to Armbruster and Pry (2008) ($\text{mean}_{\text{blank}} + 1.645 * \text{SD}_{\text{blank}}) + 1.645 * \text{SD}_{\text{low standard}}$. To determine the cut-off, a conservative additional margin was added to the LOD to account for the imprecision of real sample data (in contrast to standard measurements), in which multiple transfers of water and gas between Niskin bottles, syringes and pre-evacuated Exetainers introduce error between replicates. The mean standard deviation in peak area determined from all triplicate samples (n=N) was multiplied by 3 and added to LOD to estimate cut-offs of 3.49 and 125.82 peak area units for CH_4 and N_2O, respectively (3σ in the figure). Mean standard deviation of samples was calculated as the square root of mean variances of all sample triplicates: $\sqrt{\frac{\sum \sigma^2{}_{sample}}{n_{samples}}}$.

Text S2. Precision and accuracy of the reported data

Here we estimate the precision and accuracy of the reported data (above the cutoff value), caused by the residual air in the Exetainers, the potential effect of diffusive gas exchange in the plastic syringes and other sources of error, including transfer of samples between syringes.

Precision was estimated from triplicate analysis of all samples and was consistently <5% RSD (see main text). This implies that error introduced by syringe transfers and other sampling artefacts was acceptable for this study where concentrations of CH_4 and N_2O varied over several orders of magnitude.

The average volume of the residual air in the Exetainers was experimentally determined to be 0.7±0.1 mL (n = 20, different batches). The manufacturer (LabCo UK) confirmed that the Exetainers are not flushed with any inert gas prior to evacuation, implying that the residual air has atmospheric concentrations of CH_4 and N_2O (mean concentrations 1.834 ppm, 0.328 ppm, respectively (Blasing, 2016)). This introduces a potential source of inaccuracy in the sample data.

When mixing two varying concentrations of a given gaseous substance at constant temperature, the concentration of the resulting mixture can be calculated by mass balance:

$$C_3 = \frac{(C_1V_1)+(C_2V_2)}{V_1+V_2} \qquad (1)$$

The contaminating effect of residual air is expected to be greatest at low sample concentrations, such as those just above the cutoff value (Fig. S1). To estimate the error in accuracy of these samples, let C_1 be the mean atmospheric CH_4 concentration (1.834 ppm), V_1 be the mean volume of residual air in the Exetainers (0.7 mL), V_2 the mean volume of the samples (25 mL) and C_3 the measured mean concentration of CH_4 in the lowest reported samples (approximately 0.4 ppm). By solving eq. 1 for C_2, which is the true CH_4 concentration in these samples:

$$C_2 = \frac{C_3(V_1+V_2)-C_1V_1}{V_2} \qquad (2)$$

it can be calculated that without the contamination, the true mean concentration for a sample measured to contain 0.4 ppm CH_4 was in fact 0.35 ppm. These calculations suggest that the residual air in the Exetainers causes up to an 11.4% overestimation for CH_4 at the low end of our reported range. For N_2O, the overestimation is 10.1% for these samples.

When the sample concentration exceed atmospheric concentration, the effect of the residual air switches from enriching to diluting the true concentrations. Using eq 2. for the highest measured samples in this study (30.1 and 13.2 ppm for CH_4 and N_2O, respectively) there is a 2.6% underestimation in CH_4 and 2.7% for N_2O due to dilution caused by the residual air. The mean concentration in all samples was 2.67±4.11 ppm for CH_4 and 0.24±0.79 ppm for N_2O, meaning that on average, there is a 0.9% underestimation in the CH_4 samples and a 1.1% overestimation in the N_2O samples. We regard these values as acceptable for this study where concentrations of CH_4 and N_2O varied over several orders of magnitude.

The plastic syringes used in sampling (BD Plastipak, 60 mL Luer-Lok) are made of non-gas tight polypropylene, meaning that diffusive exchange with outside air is a potential further source of inaccuracy in the data. To test this, we conducted an experiment in which 15 syringes were filled simultaneously with the same standard gas mixture (5 ppm CH_4, 1.1 ppm N_2O) and subsequently measured after transfer to Exetainers in triplicate, at 30 minute intervals for 150 minutes (Fig. S2). Based on this experiment, we can conclude that the gas loss per hour is < 0.5% for CH_4 and approximately 1.6% for N_2O.

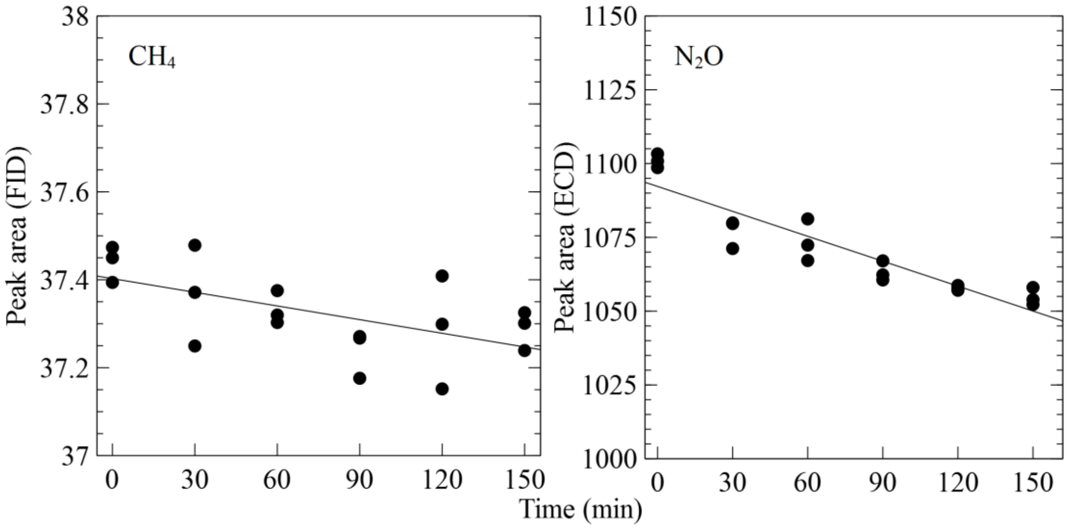

Figure S2. The loss of CH_4 and N_2O from a plastic syringe over 150 minutes in a standard gas mixture containing 5 ppm CH_4 and 1 ppm N_2O. Note the different y-axes.

Thus, given that sample gas remained in the syringes for a maximum of 40 minutes, it can be concluded that diffusive exchange was a relatively small factor in the overall inaccuracy (<1%).

References:

Armbruster, D. A. and Pry, T.: Limit of blank, limit of detection and limit of quantitation., Clin. Biochem. Rev., 29 Suppl 1(August), S49-52 [online] Available from: http://www.pubmedcentral.nih.gov/articlerender.fcgi?artid=2556583&tool=pmcentrez&rendertype=abstract, 2008.

Blasing, T. J.: Recent Greenhouse Gas Concentrations (Updated April 2016), Carbon Dioxide Inf. Anal. Cent., doi:10.3334/CDIAC/atg.032, 2016.

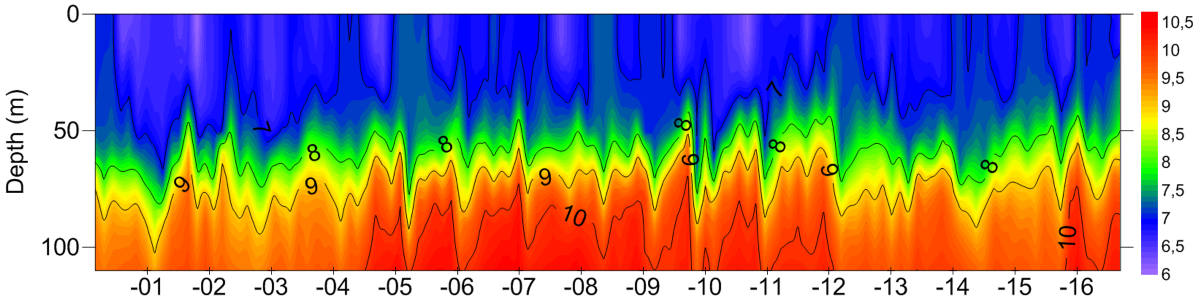

Figure S3. Water column salinity at Western Gotland Basin station BY38 from 2000 to 2016, based on CTD salinity data retrieved from the SMHI Shark database (http://www.smhi.se/klimatdata/oceanografi/havsmiljodata/marina-miljoovervakningsdata), exhibiting the typical annual to multi-annual oscillations in halocline depth in this area. These oscillations were likely contributing to the changes in the halocline depth observed during 2015 in the Western Gotland Basin.

Table S4. Sampling dates and depths of gas samples, along with exact sampling station coordinates in decimal minutes (WGS 84).

Sampling		Coordinates (D M.m)			Max depth	Sampling depths (m)																																					
Date	Site	Long.	Lat.	Ship / org.	(m)	20	40	50	60	70	80	90	100	105	109	110	115	120	125	130	135	140	142	143	144	145	150	155	160	165	167	170	175	185	190	192	195	196	200	225	236	237	238
17.3.2015	BY20	57 59.89 N	019 52.73 E	Aranda / SMHI	195	x	x		x	x	x	x	x						x								x						x		x								
17.3.2015	BY15	57 18.73 N	020 04.57 E	Aranda / SMHI	239	x			x	x	x	x	x						x								x						x	x	x		x		x	x		x	
17.3.2015	BY10	56 38.02 N	019 35.09 E	Aranda / SMHI	145	x	x		x	x	x	x	x						x																								
22.3.2015	BY32	58 01.01 N	017 59.07 E	Aranda / SMHI	202	x	x	x	x	x	x	x	x						x								x						x										
22.3.2015	BY38	57 07.03 N	017 40.12 E	Aranda / SMHI	110	x	x	x	x	x	x	x	x		x																												
21.4.2015	BY20	57 59.89 N	019 52.74 E	Aranda / SMHI	195	x	x		x	x	x	x	x						x								x						x		x								
21.4.2015	BY15	57 18.89 N	019 56.03 E	Aranda / SMHI	225	x			x	x	x	x	x						x	x	x	x				x	x						x						x	x			
21.4.2015	BY10	56 38.02 N	019 35.09 E	Aranda / SMHI	144	x	x		x	x	x	x	x						x					x																			
26.4.2015	BY32	58 01.01 N	017 59.07 E	Aranda / SMHI	201	x	x	x	x	x	x	x	x						x								x						x					x					
26.4.2015	BY38	57 07.03 N	017 40.12 E	Aranda / SMHI	110	x	x	x	x	x	x	x	x		x																												
4.6.2015	BY32	57 59.99 N	017 59.81 E	Aranda / SYKE	171	x	x	x	x	x	x	x	x						x								x					x											
5.6.2015	BY20	58 00.00 N	019 53.81 E	Aranda / SYKE	193	x	x		x	x	x	x	x						x								x						x					x					
5.6.2015	BY15	57 19.20 N	020 03.00 E	Aranda / SYKE	239	x			x	x	x	x	x	x		x	x	x	x	x	x	x					x						x						x	x		x †	
6.6.2015	BY10	56 38.00 N	019 35.00 E	Aranda / SYKE	143	x	x		x	x	x	x	x						x				x																				
5.8.2015	BY20	58 00.00 N	019 53.81 E	Aranda / SYKE	195	x	x		x	x	x	x	x						x								x						x				x						
5.8.2015	BY15	57 19.20 N	020 03.00 E	Aranda / SYKE	238	x			x	x	x	x	x	x		x	x	x	x	x	x						x						x						x	x			x
6.8.2015	BY10	56 38.00 N	019 35.00 E	Aranda / SYKE	142	x	x		x	x	x	x	x						x				x																				
6.8.2015	BY38	57 07.00 N	017 40.00 E	Aranda / SYKE	109	x	x	x	x	x	x	x	x		x																												
7.8.2015	BY32	57 59.99 N	017 59.81 E	Aranda / SYKE	170	x	x	x	x	x	x	x	x						x								x					x											
24.10.2015	BY15	57 19.22 N	020 03.12 E	Salme / TTU	231	x			x	x	x	x	x			x		x	x	x	x						x						x						x	x			
25.10.2015	BY20	57 59.99 N	019 57.12 E	Salme / TTU	169				x	x	x	x	x						x								x				x												
8.12.2015	BY20	57 59.89 N	019 52.73 E	Aranda / SMHI	196	x	x		x	x	x	x	x						x								x						x			x							
8.12.2015	BY15	57 18.73 N	020 04.57 E	Aranda / SMHI	239	x	x	x	x	x	x	x	x						x								x	x	x	x		x	x						x	x	x		
9.12.2015	BY10	56 38.02 N	019 35.09 E	Aranda / SMHI	145	x	x		x	x	x	x	x						x						x																		
13.12.2015	BY38	57 07.03 N	017 40.12 E	Aranda / SMHI	111	x	x	x	x	x	x	x	x			x																											
13.12.2015	BY32	58 01.01 N	017 59.07 E	Aranda / SMHI	202	x	x	x	x	x	x	x	x						x								x						x						x				

† gas samples lost