

Figure S1. Establishment of cut-off concentrations of CH₄ (left) and N₂O (right), below which measured sample values are regarded as indistinguishable from those of blank pre-evacuated Exetainers. Yellow points represent measured peak areas of CH₄ and N₂O from blank pre-evacuated Exetainers (i.e. Exetainers from the supplier, subsequently filled with N₂, nominal CH₄ and N₂O concentrations = 0 ppm) and measured peak areas of the lowest standards for each gas, also stored in pre-evacuated Exetainers (CH₄ and N₂O concentrations 0.45 ppm and 0.1 ppm, respectively). A total of NN replicate blanks and NN replicate low standards were measured. 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 CH₄ and N₂O, respectively (3σ in the figure). Mean standard deviation of samples was calculated as the square

root of mean variances of all sample triplicates: $\sqrt{\frac{\sum \sigma^2_{\text{sample}}}{n_{\text{samples}}}}$.

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).

Reference:

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

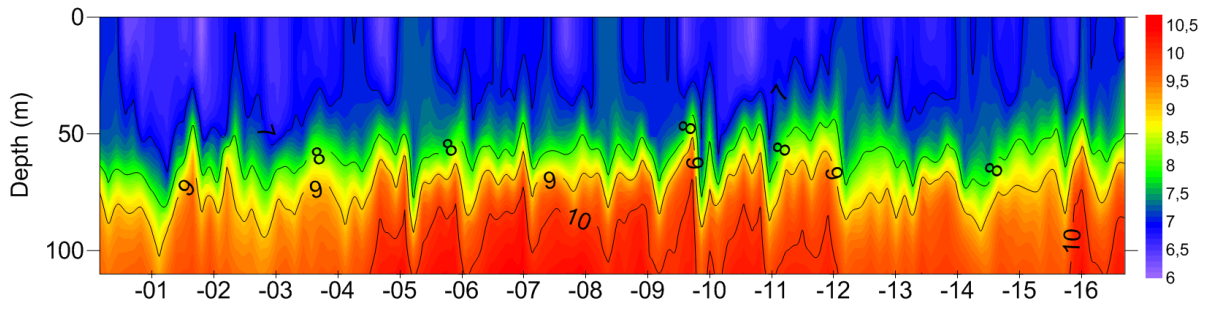


Figure S2. Water column salinity at western Gotland Basin station BY38 from 2000 to 2016, based on CTD salinity data retrieved from the SMHI Shark database (<http://www.smhi.se/klimatdata/oceanografi/havsmiljodata/marina-miljoovervakningsdata>). Note the annual to multi-annual oscillations in halocline depth.

