Supplementary Material

Methane analysis

120 ml glass bottles were filled in duplicate with overflowing water, closed with butyl lined stoppers and stored at 4°C until analysis, generally within 4 weeks. CH4 concentrations were determined via head-space method by adding 20 ml of N2 as headspace. Headspace CH4 concentrations were analyzed in the home laboratory at the Alfred-Wegener-Institute in Helgoland with a gas chromatograph (GC 2014, Shimadzu) equipped with a flame ionization detector and a Shinycarbon column (Restek, USA). The temperatures of the oven, the injector, and detector were 100, 120, and 160°C, respectively. The carrier gas (N2) flow was 20 mL min-1, with 40 mL min-1 hydrogen and 400 mL min-1 synthetic air. Gas standards (Air Liquide) with CH4 concentrations of 5 ± 0.5 ppm and 10 ± 1 ppm were used for calibration. The calculation of the CH4 concentration was performed according to (Magen et al., 2014). The precision of the calibration line was r2 = 0.99 and the reproducibility of the samples was < 5%.

Calculation of the point of inflection

To calculate the point of inflection for a dilution plot (salinity versus methane concentration), the data were sorted for “salinity” and therewith the associated methane concentration, then the slope (x1-x2/y1-y2) was determined for each pair of values, then the median of subsequent values was calculated until it turned negative. The corresponding salinity values was defined as the inflection point.

Suppl. Table 1. Summary of linear regression statistics and associated LMP value in percent contribution to the overall R2 of the regression. Calculations were done by the R package “relaimpo” (Grömping 2006).

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| coefficients | Estimate | Std. Error | t value | Pr(>|t|) | LMP (%) |
| intercept | 113.00 | 5.21 | 21.69 | \*\*\* |  |
| Salinity | -2.24 | 0.07 | -31.40 | \*\*\* | 50.34 |
| temperature | 2.48 | 0.21 | 11.7 | \*\*\* | 28.84 |
| oxygen saturation | -0.76 | 0.05 | -14.12 | \*\*\* | 20.81 |

Suppl Table 2. Diffusive flux of methane from surface waters at different locations from June 20219 (this study) in comparison with data from June 20210 -2014.

|  |  |  |
| --- | --- | --- |
|  | mean diffusive flux ± std  (µmol /d/ m2) | |
|  | continuous measurements  (this study) | single stations in June 2012-2014 |
| marine  S > 30 | 40 ± 29 (n = 591)§ | 27 ± 5 (n = 4) |
| mixing area Elbe | 86 ± 34 (n = 118)§ | 50 ± 5 (n = 3) |
| Elbe river | 124 ± 42 (n = 297)\* | 87 ± 48 (n = 14) |
| mixing area Weser | 122 ± 40 (n = 53) |  |
| Weser river | 222 ± 49 (n = 25) |  |

§ no significant difference as tested with Wilcoxon Rank Sum Test

\* Significantly different as tested with Wilcoxon Rank Sum Test