



Seasonal, inter-annual and decadal changes of carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) in the Scheldt estuary (Belgium, The Netherlands)

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We carried out monthly cruises to study the seasonal and spatial variations of the partial pressure of carbon dioxide CO₂ (pCO₂), methane (CH₄) and nitrous oxide (N₂O) concentrations in the Scheldt estuary, a strongly human impacted system located in Belgium and the Netherlands. This survey was initiated in 2008 for pCO₂, and from 2009 onwards for methane (CH₄) and nitrous oxide (N₂O). In the lower estuary, pCO₂ strongly decreased and oxygen saturation level (%O₂) strongly increased during the spring phytoplankton bloom. In the upper estuary, two yearly maxima of pCO₂ coinciding with minima of %O₂ occurred in spring and fall due to enhanced nitrification and/or net heterotrophy. In the upper estuary, pCO₂ decreased in winter due to lower temperature (affecting solubility and inhibiting biological activity). pCO₂ also decreased in summer due to increase in primary production and decrease of net heterotrophy. In the upper estuary, maxima of CH₄ were observed in winter due to enhanced river inputs (high discharge) while in the lower estuary higher CH₄ was observed in summer. This was probably due to inputs of CH₄ from inter-tidal areas at the mouth of estuary that increased in summer due to higher temperatures and higher organic matter availability. N₂O also showed higher values during winter in the upper estuary, but in summer N₂O was low in the lower estuary due to decreased solubility due to higher temperature. During winter 2009, extremely high N₂O values were observed in the upper estuary, up to 3257 nM (23738% saturation). This was related to the problems encountered by the Brussels North waste water treatment plant (WWTP) in late 2009. One of the collectors of the station was shut down in 25 November 2009, and by 8 December 2009, the whole WWTP was shut down and the waste-water was delivered directly to the Rupel. Extremely high N₂O values were observed in the upper estuary on 7 December 2009, and abnormally high N₂O values (compared to other years) persisted until April 6 2010. The comparison of present day N₂O values with historical data obtained in 1993-1997 and 1978 shows a spectacular decrease of N₂O levels from maximal values of about 350 nmol L⁻¹ in the 1990's to 50 nmol L⁻¹ in 2009-2012. This decrease reflects the collapse of NH₄⁺ concentrations in the estuary due to the overall improvement of water quality in relation to the implementation of WWTPs, leading to a decrease of nitrification rates. The maximum of N₂O concentration in 1978 was located between salinities 10-15, in the 1990's it was located between salinities 2 and 5, and nowadays it is located at salinities < 2.5. This suggests that the maximum of nitrification has migrated upstream in the estuary.