



## **Seasonal and spatial variability of aquatic N<sub>2</sub>O, CH<sub>4</sub> and CO<sub>2</sub> concentrations and their contribution to the overall greenhouse gas budget of the river Tay catchment, NW Europe**

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River networks act as a link between components of the terrestrial landscape with the atmosphere and oceans, and are believed to contribute significantly to global budgets of carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O). However, knowledge of flux magnitudes and drivers of seasonal and spatial variability required to understand their contribution to the overall catchment greenhouse (GHG) flux is only available for relatively few river systems. For this reason we conducted a two year study of monthly GHG concentration measurements from the river Tay.

The river Tay is the largest river in Scotland, in terms of discharge and can be considered typical for many North European river systems. The Tay and its tributaries drain peat dominated uplands and agricultural lowlands before entering the North Sea via the large intertidal estuary. We collected water samples from 9 locations along the river monthly and analysed these samples for dissolved concentrations of N<sub>2</sub>O, CH<sub>4</sub> and CO<sub>2</sub>, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, O<sub>2</sub>, total organic carbon and nitrogen, pH and turbidity. Fluxes across the air water interface were calculated using published gas transfer equations.

All GHGs showed considerable spatial and seasonal variation. Nitrous oxide emissions ranged from 176 to 1850 μg N m<sup>-2</sup> d<sup>-1</sup> over the almost two year period February 2009 to December 2010. Emissions were highest in the lowland tributaries related to higher nutrient concentrations associated with more intensive agricultural activity. Methane emissions ranged from 1720 to 15500 μg C m<sup>-2</sup> d<sup>-1</sup>, and in general decreased from upland to lowland sites. Variation in sediment quality was the predominant driving factor. Carbon dioxide emissions ranged from 517 to 2550 mg C m<sup>-2</sup> d<sup>-1</sup> and generally increased from upland to lowland sites. Emissions were highest in late summer and autumn and lowest in winter at most sites, highlighting the role of seasonal environmental controls such as temperature, light, and substrate availability.

Terrestrial emissions for the Tay catchment were estimated from information on the landuse distribution (forest, moorland, grassland and arable land) and Tier 1 IPCC emission factors for the agricultural components and literature values for UK forests and moorlands. Aquatic N<sub>2</sub>O emissions accounted for 2.1 % of the total catchment emissions. The freshwater flux (both dissolved export and atmospheric emission of C) accounted for up to 38 % of the terrestrial carbon sink. Evasion of CO<sub>2</sub> dominated the freshwater flux (46 %) of carbon and accounted for 17.2 % of the terrestrial net C sink.