



## **Riverine GHG emissions: one year of CO<sub>2</sub>, <sup>13</sup>CO<sub>2</sub> and CH<sub>4</sub> flux measurements on Vistula river in Krakow, southern Poland**

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Terrestrial surface waters are generally considered to be sources of carbon dioxide and methane, because respiration of organic matter via aerobic and anaerobic pathways causes supersaturation of surface waters with respect to CO<sub>2</sub> and CH<sub>4</sub>, respectively. In rivers, these processes are influenced by such anthropogenic factors as changes of land-use, wastewater and alteration of river channels.

The research object is Vistula, the largest Polish river. It has the length of 1047 km and annual runoff of  $6.2 \times 10^{10} \text{ m}^3$ . The urban section of Vistula in Krakow receives large amounts of organic matter from highly urbanized catchment and point discharges of urban waste waters within the city limits. The river was sampled regularly at three points: the entrance to the city, the center and the point where Vistula leaves the agglomeration. A floating chamber coupled with Picarro G2101-*i* analyzer was applied to quantify CO<sub>2</sub>, <sup>13</sup>CO<sub>2</sub> and CH<sub>4</sub> fluxes leaving the surface of the river. A floating chamber was equipped with sensors to measure air pressure, temperature and humidity inside the chamber and the temperature of water. The chamber was equipped with a set of floats and an anchor. The measurements started in October 2011, and were repeated with approximately monthly frequency. Physicochemical properties of water (temperature, conductivity, pH, CO<sub>2</sub> partial pressure over the water surface and alkalinity) were also measured during each measurement campaign. In addition, at each site short-term variability of the measured fluxes was also investigated. Additionally, short-term variability of the measured fluxes of CO<sub>2</sub>, <sup>13</sup>CO<sub>2</sub> and CH<sub>4</sub> were performed in all three sites.

The results indicate that fluxes of CO<sub>2</sub> released from the river are comparable with the soil emissions of this gas measured in Krakow area. The  $\delta^{13}\text{C}$  signature of riverine CO<sub>2</sub> flux allowed to identify decomposition of C3 organic matter as the major source of this gas. No distinct seasonal variability of the CO<sub>2</sub> emission and its stable isotope composition was observed, suggesting that main factors controlling emission of CO<sub>2</sub> from the river are not related to meteorological conditions as well as to physicochemical water parameters.

It turned out that ebullition of methane from the river bed contributes significantly to the overall flux of CH<sub>4</sub>. The waterborne flux of CH<sub>4</sub>, after correcting for ebullition remained positive (in the order of  $3\text{--}20 \text{ mmol m}^{-2}\text{h}^{-1}$ , depending on the site), which shows that urban river is an important emitter of this gas.

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