GHG collection and measurement

Surface water samples were collected with 120 mL glass serum bottles at wrist depth for the determination of CH4 concentrations; samples were collected in triplicate at each site. After poisoning with a saturated solution of NaCl for CH4, the serum bottle was sealed with butyl stoppers below the water surface, crimped with aluminum caps, and stored at ambient temperature in the dark. CH4 concentrations were measured using the headspace equilibration method44 on a gas chromatography equipped with a flame ionization detector for CH4 (Agilent 7890B GC-FID). The partial pressure of CO2 (pCO2) in surface water was measured in-situ using a Qubit Dissolved CO2 System equipped with an internal pump and a pCO2 probe (S157-P, Qubit Biology Inc., Canada). The pCO2 probe is coated with a polytetrafluoroethylene membrane sleeve that is permeable to CO2 gases but not to water. The system was calibrated with standard CO2 gases ranging from 0 to to 10,000 μatm. Recalibration of the system was done before each round of fieldwork.

Fluxes of CO2 and CH4 were measured simultaneously with surface water sample collection. Local ambient air samples were also collected at the same time. At each site, four floating chambers were deployed from the shallow water near the river bank to the deep water in the mid-channel to measure carbon gas fluxes. These chambers were of the same size and shape and streamlined with a flexible plastic foil collar to minimize the effects of chamber-induced turbulence when measuring fluxes. Also, each chamber was covered with aluminum foil to reflect sunlight and minimize internal heating. Chambers were allowed to drift and each chamber measurement lasted for 60 to 80 min. After mixing the chamber content 3 times, 50 mL of gas were extracted from inside the chambers to air-tight gas sampling bags at the 0, 5, 10, 20, 40, 60, 80 min time intervals. This multi-chamber method and prolonged deployment not only increased the probability of capturing ebullition but also incorporated spatiotemporal variability in both diffusion and ebullition within and among streams and rivers. CO2 and CH4 concentrations of gas samples were determined as described above.

In addition to gas sampling, surface water samples were collected for physicochemical analyses at each sampling sites. Sediment samples were collected simultaneously alongside every gas and surface water sampling for physicochemical and microbial analyses unless there were only gravels/cobbles in the riverbed, and a total of 80 sediment samples were obtained. Air temperature, atmospheric pressure, and wind speed were measured in situ with a portable anemometer (Testo 480, Germany). Water temperature, pH, DO, ORP, and conductivity were measured in situ with portable field probes (Hach HQ40d). Precipitation and solar radiation were obtained from National Meteorological Information Center (http://data.cma.cn/). Flow velocity, discharge, width, and mean depth of streams and rivers were provided by hydrological stations at each sampling site.

Flux calculation

Total gas fluxes were calculated according to the following equation:

Ft = (nt – n0)/(A x t)

where, nt and no are the number of moles of carbon gases in the chamber at time t and time zero (mol), respectively; A is the surface area of water covered by the chamber (m2); and t is the measurement duration time of drifting (min). Diffusive and ebullitive fluxes for CH4 were separated using the Campeau et al. approach. Briefly, the Ft for CO2 is assumed to be exclusively diffusive (that is, the CO2 ebullition is negligible). Only the linear section of the pCO2 increase curve during the first 10 min of chamber deployment was used for FCO2 calculation to eliminate possible biases due to gas accumulation in the chambers which will affect the flux rates. The theoretical diffusive k for CH4 was calculated based upon kCO2 as follows:

kCH4/kCO2 = (ScCH4/ScCO2)^-n

where, kCH4 and kCO2 are the gas transfer velocity of CH4 and CO2; Sc is the Schmidt number and n is assigned a value of 1/2 for wind speed > 3.6 m s^-1 or 2/3 for wind speed < 3.6 m s^-1. We then calculated the theoretical diffusive flux for CH4 according to:

Fd = k (Cwater – Ceq)

where k is the gas transfer velocity (m·d^-1), Cwater is the water gas concentration (mol·m^-3), and Ceq is the gas concentration in water in equilibrium with the local atmosphere corrected for temperature induced changes in solubility according to the Henry’s law (mol m^-3). Thus, the difference between the total and diffusive fluxes is attributed to ebullition.