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CO_2 evasion along streams driven by groundwater inputs and geomorphic controls

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Supplementary Information

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Empirical models

We used empirical models from Raymond *et al*. (2012) to estimate gas transfer velocities in the two studied streams. Four models were chosen based on their predictive performance (models 1, 2, 5 and 7; $0.55 < R^2 < 0.76$). We ran the models at each site and derived an uncertainty range for each of the modelled evasion flux estimates based on a Monte-Carlo approach (Fig.S1).

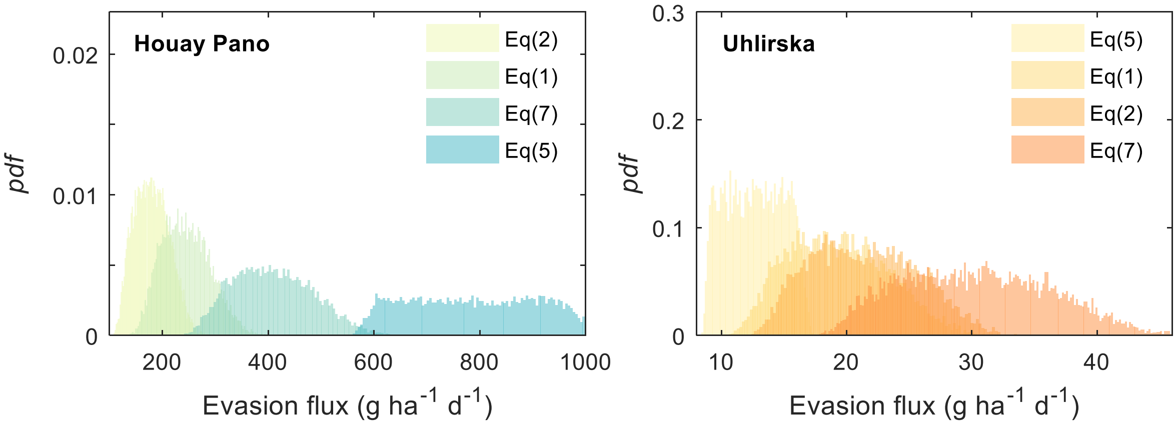

Figure S1. Evasion estimates according to four selected models. Probability density function (*pdf*) of each model output based on 10,000 Monte-Carlo simulations. Eq(1), Eq(2), Eq(5) and Eq(7) refer to models in Raymond *et al.* (2012).

Mass balance

Our mass balance relies on measurements of dissolved CO_2 at repeated intervals along the stream as well as in entering groundwater. We also measured discharge at each stream location so that groundwater inflow rates could be estimated through differential gauging (Fig.S2).

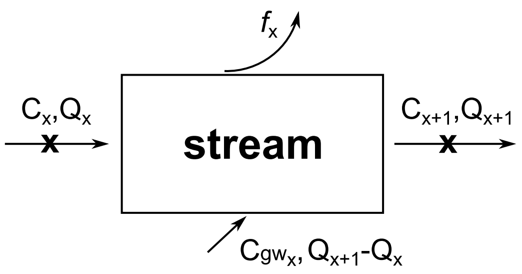

Figure S2. Illustration of the mass balance approach between two stream locations.

The uncertainties related to CO_2 and discharge measurements were quantified and propagated to our evasion flux estimates based on the mass balance framework. We then compared these evasion estimates to the estimates obtained via empirical equations (Fig.S3).

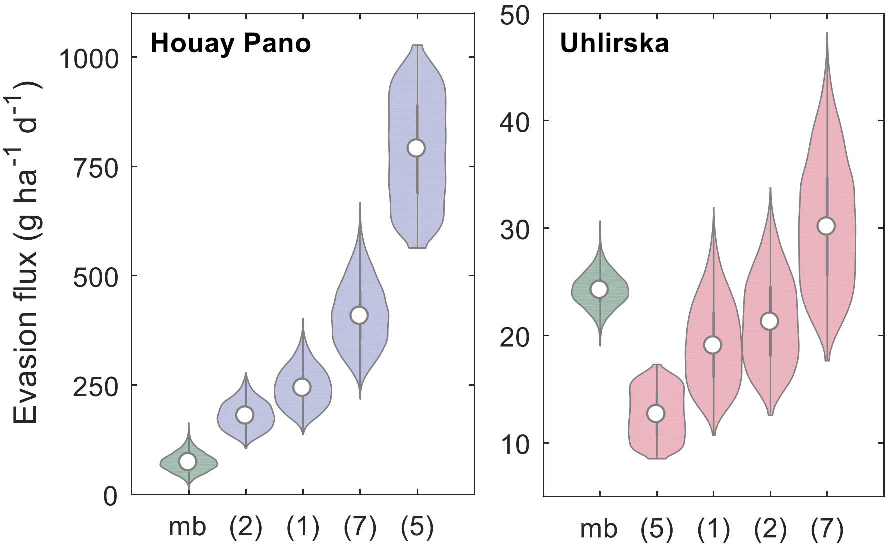

Figure S3. Evasion estimates and their uncertainty for the mass balance approach and comparison with empirical models. The violin plots outline the complete distribution of results based on 10,000 Monte-Carlo simulations. White circles represent the median while grey boxes represent the interquartile range. 'mb' refers to mass balance and (1), (2), (5) and (7) refer to models in Raymond *et al.* (2012).

All the empirical models performed poorly in Houay Pano relative to our mass balance results, with consistent overestimations that can be attributed to an average slope that is beyond the range of calibration of these models (0.14 m m^{-1}). The modelled evasion estimates for Uhlirska were closer to our mass balance results, despite large uncertainties within and between models.

Literature review

We gathered data from the literature to provide evidence that groundwater-derived CO_2 fluxes can be remarkably constrained spatially, making these contributions challenging to capture via discrete measurements. Table S1 summarises the references used in Figs 2a and 2b.

At Howard Spring, pCO_2 values were obtained using an eosGP infrared gas analyser (Eosense) connected to a CR3000 datalogger (Campbell Scientific). The sensor was calibrated before and after fieldwork using zero, 5,000 and 10,000 ppm Calgaz standards.

Table S1. Summary of studies used for Fig.2. Studies with both pCO_2 and flow rate measurements appear in both Figs 2a and 2b. Please refer to main text for reference numbers.

location	climate	$p\,CO_2$	flow	site refs (up; down)	relative σ	reference
Falling Spring Creek (USA)	temperate	+	+	D1 (springs S1, S2, S3); F4	±0.03 log CO2; ±15% Q	(68)
Falling Spring Run (USA)	temperate	+	+	S2; F1B	±0.03 log CO2; ±15% Q	(69)
Forma Sprofondata (Italy)	temperate	+	+	FS1; FS2	±0.03 log CO2; ±15% Q	(70)
Brocky Burn (Scotland)	temperate	+	+	upper; middle	±5% pCO2; ±15% Q	(71)
Juruena headwaters (Brazil)	tropical	+	+	mina2; bacia2	±5% pCO2; ±15% Q	(23); M.S. Johnson (pers. comm.)
Sleepers River (USA)	temperate	+	+	site 5 (at seepage); site 6	±8% pCO2; ±15% Q	(72); D.H. Doctor (pers. comm.)
Vastrabacken (Sweden)	boreal	+	+	soil; stream	±5% pCO2; ±15% Q	(24)
Vastrabacken (Sweden)	boreal	+	+	riparian; stream	±5% pCO2; ±15% Q	(14)
Leyre headwaters (France)	temperate	+	+	spring; 40m downstream	±5% pCO2; ±15% Q	(22)
Uhlirska (Czech Republic)	temperate	+	+	POR; UHL	±21% pCO2; ±15% Q	this study
Houay Pano (Laos)	tropical	+	+	station 58; station 56	±21% pCO2; ±15% Q	this study
Montseny (Spain)	temperate	+	-	SP; TM9	±20% pCO2	(73)
Stag Burn (Scotland)	temperate	+	-	site 1; site 8	±5% pCO2	(74)
Wiesent River (Germany)	temperate	+	-	Steinfeld; Wiesentfels	±21% pCO2	(75)
Howard Spring (Australia)	tropical	+	-	spring; 140m downstream	±5% pCO2	this study

Groundwater inflows linked to increases in stream CO_2

In Houay Pano, our very detailed stream survey allowed us to estimate groundwater-derived CO_2 input rates for each stream reach. Despite large scattering due to measurement uncertainties and the overlapping with other driving factors, there is a clear link between the rate of subsurface-derived CO_2 input for each stream reach (F_{gw}) and the corresponding spatial increase in the stream CO_2 flux (ΔF_{stream}) (Fig.S4).

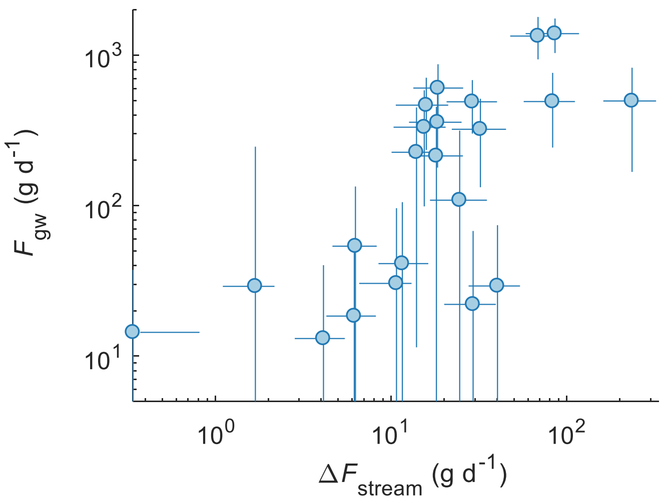

Figure S4. Relationship between groundwater CO_2 inputs and spatial increases in stream CO_2. Values correspond to subsurface-derived CO_2 input fluxes (F_{gw}) for each stream section along Houay Pano and their associated increases in stream CO_2 flux (ΔF_{stream}). Error bars correspond to the 10th–90th percentile range based on 10,000 simulations. Only stream reaches with positive ΔF_{stream} are shown.

Uncertainties associated with indirect measurement of pCO_2

Deriving pCO_2 from measurements of pH, temperature and alkalinity can yield highly biased results, particularly in acidic waters (Abril *et al.*, 2015). In our case, streamwater in Houay Pano was in the 6.9–8.1 pH range, and so less sensitive to potential overestimations. According to Abril *et al.* (2015) discrepancies between calculated and measured pCO_2 are relatively low for waters with pH > 7. At Uhlirska, streamwater was much more acidic (range 3.9–6.7), and so we chose to calculate pCO_2 from pH and DIC rather than alkalinity (Marx *et al.*, 2018). Despite the potential for systematic errors, deriving pCO_2 data from pH and DIC in acidic lake waters was shown to yield low random errors (Golub *et al.*, 2017). Overall, we applied a relative standard deviation of ±21% for all our pCO_2 indirect observations, based on a pH uncertainty of ±0.1 pH units. At both sites pH was carefully calibrated before and after fieldwork, and we think that a ±0.1 error on pH readings is a relatively conservative estimate.

Observatories

The Houay Pano catchment is part of M-TROPICS, a network of long-term critical zone observatories (CZO) located in the tropics (https://mtropics.obs-mip.fr) and funded by the French government. It also belongs to the wider French CZO program OZCAR (http://www.ozcar-ri.org).
The Uhlirska catchment observatory has been operating since 1982 and is now a leading Czech CZO for hydrological studies. It is monitored as part of joint initiative from the Czech Geological Survey and the Czech Hydrometeorological Institute, and also belongs to the European Representative Basins (ERB).

References

Abril G, *et al.* (2015) Technical Note: Large overestimation of pCO2 calculated from pH and alkalinity in acidic, organic-rich freshwaters. *Biogeosciences* 12:67-78.

Golub M, Desai AR, McKinley GA, Remucal CK, & Stanley EH (2017) Large uncertainty in estimating pCO2 from carbonate equilibria in lakes. *Journal of Geophysical Research: Biogeosciences* 122:2909-2924.

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Raymond PA, *et al.* (2012) Scaling the gas transfer velocity and hydraulic geometry in streams and small rivers. *Limnology and Oceanography: Fluids and Environments* 2:41-53.