CO_2 dynamics along Danish lowland streams: water–air gradients, piston velocities and evasion rates

Kaj Sand-Jensen · Peter Anton Staehr

Abstract We measured CO_2 concentration and determined evasion rate and piston velocity across the water–air interface in flow-through chambers at eight stations along two 20 km long streams in agricultural landscapes in Zealand, Denmark. Both streams were 9–18-fold supersaturated in CO_2 with daily means of 240 and 340 μM in January–March and 130 and 180 μM in June–August. Annual CO_2 medians were 212 μM in six other streams and 460 μM in four groundwater wells, while seven lakes were weakly supersaturated (29 μM). Air concentrations immediately above stream surfaces were close to mean atmospheric conditions except during calm summer nights. Piston velocity from 0.4 to 21.6 cm h^{-1} was closely related to current velocity permitting calculation of evasion rates for entire streams. CO_2 evasion rates were highest in midstream reaches (170–1,200 mmol m^{-2} day^{-1}) where CO_2-rich soil water entered fast stream flow, while rates were tenfold lower (25–100 mmol m^{-2} day^{-1}) in slow-flowing lower reaches. CO_2 evasion mainly derived from the input of CO_2 in soil water. The variability of CO_2 evasion along the two lowland streams covered much of the range in sub-Arctic and temperate streams reported previously. In budgets for the two stream catchments, loss of carbon from soils via the hydrological cycle was substantial (3.2–5.7 mmol m^{-2} day^{-1}) and dominated by CO_2 consumed to form HCO_3^- by mineral dissolution (69–76%) and export of organic carbon (15–23%) relative to dissolved CO_2 export (7–9%).

Keywords Lowland streams · CO_2 concentrations · CO_2 release to atmosphere · Piston velocity

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Introduction

Streams are usually supersaturated with CO_2 due to inflow of CO_2-rich soil water and predominance of respiration relative to photosynthesis due to degradation of organic matter received from land (Kelly et al. 1983; Sand-Jensen et al. 1995; Battin et al. 2008). Extensive CO_2 supersaturation supports photosynthesis and growth of numerous amphibious plants which are unable to use HCO_3^- for photosynthesis (Sand-Jensen et al. 1992; Sand-Jensen and Frost-Christensen 1998). Extensive CO_2 supersaturation of turbulent stream water should also lead to substantial evasion to the atmosphere of CO_2 originally derived from the soil as CO_2 or degradable organic matter. This loss is

seldom included in budget calculations of soil CO_2 loss (Sand-Jensen et al. 2007). Moreover, in studies of local, regional and global carbon cycles, the rapid CO_2 exchange with the atmosphere in the turbulent stream flow has rarely been measured directly and included in a wider CO_2 flux perspective. Our overall objective was to evaluate the magnitude of CO_2 evasion from streams in a carbon flux perspective for the stream and the catchment.

Evasion of CO_2 to the atmosphere is highly variable temporally and spatially due to the complexity of hydrological, biological and physical processes determining the gradient and exchange coefficient (piston velocity) of CO_2 from water to air (Hope et al. 2001; Worall and Burt 2005). High evasion rates have been reported from turbulent upper reaches of streams draining temperate forests and peat land while evasion rates are 5–15 times lower in deeper downstream reaches of lower turbulence and CO_2 concentration (Hope et al. 2001; Silvennoinen et al. 2008). This difference shows the importance of CO_2 supply in soil water and contact time with the atmosphere for evasion rates along the streams. To confirm the magnitude of estimated evasion rates derived indirectly from general hydraulic formulae or use of trace gases, direct measurements are needed. Our second aim was to analyze daily and seasonal variations in CO_2 supersaturation along two lowland Danish streams in fertile agricultural landscapes and measure CO_2 evasion rates directly in flow-through flux chambers. This approach can constrain the true variability of evasion rates within and among streams and provide integrated values for entire streams that can be used in mass balances of the external terrestrial and internal stream sources of CO_2 to atmospheric release.

We calculated piston velocity directly from measurements of evasion rates and gradients of CO_2 across the air–water interface using flux chambers and tested the relationship of piston velocity to common hydraulic parameters (e.g. current velocity, water depth, and stream slope) known to influence surface turbulence (Thyssen and Erlandsen 1987; Sand-Jensen and Pedersen 1999). Near-surface turbulence drives the exchange of gases across the water–air interface (Jähne et al. 1987; Wanninkhof et al. 2009), but many individual processes can influence surface turbulence and gas transfer; for example, surface renewal (Komori et al. 1993), surface penetration (Atmane

et al. 2004), surface divergence (Turney et al. 2005) and thickness of the near-surface layer (Harriott 1962). Mechanistic approaches attempting to describe the turbulence have so far had limited applicability (Zappa et al. 2007; Vachon et al. 2010). A formula relating piston velocity to turbulent dissipation rate to the 1/4 power has some predictive power for rivers, estuaries and oceans combined (Zappa et al. 2007), but its application requires measurements with advanced Doppler velocimeters and improved prediction of piston velocity to ensure reliable calculations of evasion rates (Vachon et al. 2010). Estimates of piston velocity for CO_2 derived from measurements on trace gases still suffer from limited replication and uncertainties when converted to CO_2 (Genereux and Hemond 1992; Raymond and Cole 2001). This is an important problem because CO_2 reacts with water and water vapor (Ho et al. 1997) and reactions and transport depend on pH, temperature and organic surface films (Frew 1997) in ways that may differ from those of other trace gases. Moreover, correct determination of evasion rate requires knowledge of both piston velocity and the CO_2 gradient across the water–air interface and, thus, direct CO_2 measurements in water and air are needed anyway.

The CO_2 concentration above the water surface is usually assumed to be equal to the mean level in the atmosphere. This assumption has rarely been tested and it is violated if CO_2 accumulates in stagnant air receiving a high CO_2 flux from supersaturated waters below. This situation may arise in small, wind-protected streams receiving CO_2-rich soil water. Our final objective was to test whether CO_2 does accumulate in air above CO_2-rich small streams and how it influences the CO_2 gradient and the evasion rate.

Methods

Study sites

Pøle and Havelse are two small lowland streams located in an open calcareous moraine landscape in North Zealand, Denmark (Fig. 1; Sand-Jensen et al. 2007). The Pøle stream is 21 km long and drains 92 km^2 of mixed agricultural (57%), urban (30%) and forested (13%) area. Pøle stream receives purified treated sewage (mechanically, biologically, and chemically) from the large town of Hillerød (35,000
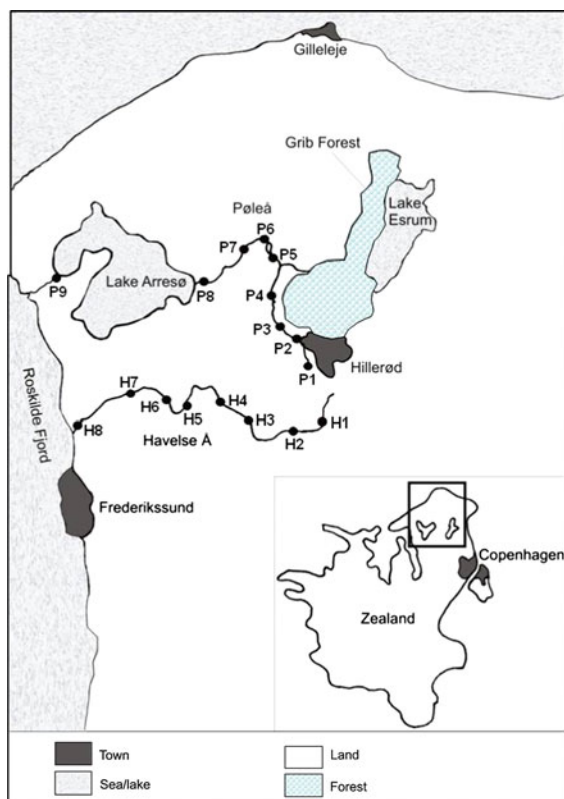
Fig. 1 Map over North Zealand, Denmark showing the location of the two streams, Pøle and Havelse with sampling sites and the largest cities and beech forest in the otherwise agricultural landscape

inhabitants). The percentage of lakes is about 1% of the Pøle catchment. Including the large Lake Arresø (38 km^2) located downstream of Pøle stream raises the percentage to 22. The Havelse stream is 22.6 km long and drains 130 km^2 of mixed agricultural (85%), urban (10%) and forested (5%) area and receives chemically and biologically purified sewage from small villages (about 5,000 inhabitants). The Havelse catchment is devoid of lakes.

Eight stations were located equidistantly along the length of the Pøle and the Havelse streams. The uppermost stations in the Pøle stream (P1 and P2) and the Havelse stream (H1 to H3) were very shallow (mean depth <0.2 m) and narrow (mean width <1.5 m). The lowermost station in the Pøle stream (P8) was 9.7 m wide and 0.9 m deep, while the lowermost station in the Havelse stream (H8) was 6.6 m wide and 0.5 m deep. Both streams are channelized, have relatively uniform depths and the banks

are without trees but support tall emergent herbs during summer offering shading and wind protection.

The annual average discharge for the last 30 years is similar for both streams; 26.5 for Pøle and 24.7 10^6 m^3 for Havelse (Frederiksborg 1996). High discharge and low surface irradiance during winter reduce aquatic plant growth while substantial growth of benthic microalgae and submerged macrophytes takes place in May–August (Sand-Jensen et al. 1988; Sand-Jensen and Frost-Christensen 1998). Daily mean discharge and water depth and transversal depth profiles across the stream were available for six hydrometric stations in the Pøle stream (P3–P8) and three stations in the Havelse stream (H3, H5 and H7) continuously operated by the county for more than 30 years (unpublished reports from Frederiksborg Amt). This information permitted calculation of daily mean current velocity (U, m s^{-1}) throughout the year as daily mean discharge (Q, m^3 s^{-1}) divided by daily mean transversal area (A, m^2), i.e. $U = Q A^{-1}$. Discharge, water depth and current velocity at the remaining stations were estimated by measuring the hydraulic parameters twice a month, establishing close relationships to hydrometric stations nearby and estimating the daily hydraulic parameters from these relationships. Oxygen consumption of the input of easily degradable organic matter (BOD) over 24 h is expected to take place within the streams and these rates were measured at the same eight stations along both streams at monthly intervals and converted to CO_2 release using a molar quotient of CO_2 to O_2 of 1.0 (Pedersen 2004).

To obtain an overall picture of the regional freshwater CO_2 concentration we performed year-round measurements during 1999 at several stations arranged equidistantly along six other streams, in the outlet from seven large eutrophic lakes, in four groundwater wells and in soil water leaving the drain pipes (Sand-Jensen et al. 1995). All localities were within 30 km from the town of Hillerød. The median CO_2 concentration in groundwater was 460 μM (88% of 133 measurements were between 320 and 640 μM, see later) and concentrations in drain water were at the same level for the same average bicarbonate alkalinity as in the streams (4,500–5,500 μeq l^{-1}, Sand-Jensen et al. 2007). This agreement was anticipated due to the equilibrium of calcite dissolution by CO_2 in carbonate-rich soils (Dreybrodt 1988). Silicate weathering only contributes ∼10% to HCO_3^- formation in the

soils, while 90% derive from dissolution of carbonates (unpublished data). In the dissolution of silicate in the soil one CO_2 molecule is produced for every HCO_3^- molecule formed and in the dissolution of carbonates one CO_2 molecule is consumed for every two HCO_3^- molecule formed permitting determination of total CO_2 loss from the soils to the streams in dissolved CO_2 and HCO_3^- (Sand-Jensen and Staehr 2007). Including loss of terrestrial organic carbon to the streams (Pedersen 2004) permits construction of carbon budgets on a catchment scale.

CO$_2$ concentration, evasion rate and piston velocity

The CO_2 concentration was determined about monthly at all 16 stations over 1 year by measuring pH, alkalinity, temperature and conductivity in water samples collected just before noon (10.00–12.00) following standard methods (Mackereth et al. 1978; Sand-Jensen and Frost-Christensen 1998).

Air concentrations of CO_2 at 2 m above the stream surface were measured with a portable infrared gas analyzer (IRGA; LCA-3, Analytical Development Company, England) during daytime measurements of CO_2 evasion with a flow-through chamber (see below). Air CO_2 concentration was measured with greater spatial and temporal resolution during a calm summer night and day in a 4 m wide mid-stream station (P4) in the Pøle stream. Air samples were collected using PVC pipes (3 m long, 0.5 cm in diameter, and perforated with small holes) mounted horizontally 1, 2 and 4 cm above the stream. Air was sucked at a rate of 140 ml min^{-1} through air-tight tubing by a pump in the IRGA. Wind velocity was measured 2 m above the water surface using a Hobo anemometer.

CO_2 evasion from supersaturated stream waters was determined in repeated measurements from sunrise to the afternoon between June and November at 9 mid-stream and downstream stations in the Pøle (P4–P8) and the Havelse stream (H3–H8) representing the largest surface areas and emission rates from the streams. A full daily measurement program was performed at every station on three occasions in June–July, August–September and October–November. To save time, measurements were not performed at the most upstream stations because flow conditions here resemble those at mid-stream stations and piston velocity and CO_2

evasion rate can be calculated from measured current velocity and CO_2 concentration. Also, upstream stations are narrow and contribute less to the integrated stream evasion of CO_2 than wider stations further downstream. Measurements of evasion rates in the streams covered most of the range in water depths (0.09–0.90 m) and current velocity (0.01–0.82 m s^{-1}) that is observed at the stream reaches over the year.

Measurements were made with a flux chamber which sealed off 19.1 dm^3 (V_{ch}) of atmospheric air above 11.68 dm^2 (A_{ch}) of stream surface area (Fig. 2). The accumulation of CO_2 in the enclosed air volume was measured with the IRGA while maintaining unaltered stream flow and turbulence. The rationale for construction and use of the chamber is that gas piston velocity (K_L) in these shallow and narrow streams is regulated by surface turbulence (Zappa et al. 2007) which, in turn, is determined by turbulence in the streaming water generated by current velocity and roughness elements at the bottom and along the banks. Wind exposure is small and its influence on surface turbulence and piston velocity is insignificant (Moog and Jirta 1999; Raymond and Cole 2001). Likewise, piston velocity of oxygen in small streams was predicted previously from hydrological parameters (e.g., current velocity, water depth and energy gradient; Thyssen and Erlandsen 1987; Thyssen et al. 1987).

The flux chamber was a half-cylinder 94 cm long and 18 cm in internal diameter made of gas-impermeable PVC painted white to prevent heating (Fig. 2). The chamber has end-walls that are 2 cm shorter than the chamber walls and are supplied with 4 cm long skirts of thin flexible plastic that rest on the water
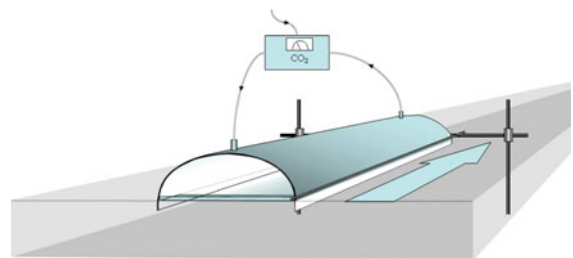
Fig. 2 Sketch of flux chamber made of a half-cylinder of gas-tight Perspex which is aligned with the flow, placed with the side walls 1 cm below the water surface and sealed by plastic flaps from the end walls floating on the water surface. Air within the chamber is circulated via a continuously measuring CO_2 analyzer

surface in the direction of flow and form a gas tight seal (Christensen 2000). The chamber was placed with the main axis oriented in the flow direction and the lower 1 cm under water. Thus, the maximum height of enclosed air was 8 cm. The chamber had two 120 cm long iron pegs glued to the outer wall and rested on iron pegs placed transversally across the stream. The transversal pegs were connected to vertical pegs bored into the sediment well away from the chamber to avoid interference with the flow. The height of the transversal pegs was adjusted such that the chamber side walls extended exactly 1 cm below the water and the plastic skirts of the end walls rested on the water surface.

The inlet and outlet of the IRGA was connected to the air volume in the chamber via air-tight tubing. Gas was circulated at a rate of 600 cm^3 min^{-1} and gas movements were sufficient to keep the chamber air mixed and ensure a linear rise in CO_2 concentration over time. The CO_2 concentration was analyzed every 10 s over 150 s and the linear rise based on 16 data points (α, µl CO_2 l^{-1} atmospheric air s^{-1}) was used to determine the CO_2 flux (F_A, mol CO_2 m^{-2} h^{-1}) according to

$$F_A = \alpha\, V_{ch}\, f\, V_{CO_2}\, (temp)^{-1}\, A_{ch}^{-1} \tag{1}$$

where f converts flux rates from seconds to hours and from dm^2 to m^2 and V_{CO2} (temp) is the volume of 1 mol of CO_2 at the actual temperature and one atmosphere. Pressure changes are small and can safely be neglected. V_{CO2} (temp) was corrected according to

$$V_{CO_2}\, (temp) = V_{STP}\, (Temp + 273.15)\, (273.15)^{-1} \tag{2}$$

where V_{STP} is 22.258 l CO_2 mol^{-1} at 0°C and one atmosphere and Temp is the actual temperature in °C (Waser et al. 1982).

Piston velocity (K_L, m h^{-1} = 100 cm h^{-1}) was calculated from flux measurements (F_A, mol m^{-2} h^{-1}) and the concentration difference of CO_2 between water and air (Thyssen et al. 1987)

$$K_L = F\, (CO_2^{mea} - CO_2^{equ})^{-1} \tag{3}$$

where CO_2^{mea} is the actual CO_2 concentration dissolved in the water calculated from continuous measurements of pH, conductivity and temperature (YSI-multisonde, 600 XL-100-0) and acidimetric Gran titration of total dissolved inorganic carbon (DIC) in water samples retrieved every 30 min and

analyzed following Mackereth et al. (1978). CO_2^{equ} is the concentration of CO_2 in water in equilibrium with the measured CO_2 concentration in the air 2 m above the stream surface. The air concentration was measured approximately every 20 min. CO_2^{equ} is calculated from the measured air concentration and Henry's constant corrected for the influence of temperature (Maberly 1996).

Measuring range of the IRGA was 0–1,600 µl CO_2 l^{-1} and measuring accuracy was ±0.5 µl CO_2 l^{-1}. Calibration was made by manufactured gases of known concentration. A total of 200 triplicate flux measurements (i.e. 600 single flux measurements) were made. Coefficients of determination (r^2) based on linear regression of CO_2 concentration versus time in the flux experiments averaged 0.99. Triplicate determinations of piston velocity were highly reproducible with an average CV (SD/mean) of only 5.3% in 200 series.

Measurements at each reach were performed from before sunrise to the afternoon at one to four positions of the flux chamber depending on physical heterogeneity across the stream. In wide, heterogeneous streams, the surface was divided into a near-bank section and a mid-stream section of equal sizes and two positions were selected in the middle of the two. Metal frames to support the flux chamber were set up at all positions and the chamber was moved between these positions such that 3–8 triplicate measurements were made at each position over the day. Current velocity was measured in replicate over 1 min at a position 0.5 m upstream of the flux chamber during each measurement series. Water depth was the mean of measurements at positions along the sides, upstream and downstream of the chamber. Piston velocity for an entire reach was calculated as the mean value of all piston velocities determined at different local sites and periods for an entire day. The mean slope of the water surface along the reach (m km^{-1}) was measured by filling a 12 m long flexible, transparent plastic tube with water and measuring the difference in hydraulic head between the downstream open end of the tube relative to the water surface with an accuracy of 1 mm. Mean current velocity over a 50 m reach was measured as the passage time of 50% of an added quantum of NaCl dissolved in 20 l of water. Salt passage was followed by continuously logging conductivity downstream of the reach. Mean depth was calculated from measurements at 25 cm intervals across 11 transversal sections placed 5 m between each other along the reach.

The predictive relationships between piston velocity and hydraulic parameters were established for piston velocities at 20°C (K_L^{20}). Temperature correction from ambient temperature (K_L^{amb}) to 20°C was performed according to Thyssen and Erlandsen (1987)

$$K_L^{amb} = K_L^{20} \left(1.024^{(amb - 20)}\right) \qquad (4)$$

The annual integrated evasion rates for entire streams were estimated from measured mean monthly CO_2 concentrations and water temperatures at eight stations along the streams and mean piston velocity estimated from mean monthly current velocity and temperature at the same stations. The established empirical relationship between piston velocity and current velocity (see later in Table 2, line 1) and the temperature correction in Eq. 4 were used to calculate piston velocity. Stream surface areas between stations were calculated from measured stream width and distance between stations.

Net photosynthesis was measured between 9.00 and 13.00 during flux measurements according to Odum's single station method (Odum 1956). Dissolved oxygen in the water was recorded continuously (YSI, 600XL-100-0) and atmospheric exchange was calculated using Eq. 3 by substituting oxygen for CO_2 and converting measured piston velocity for CO_2 to oxygen following Thyssen and Kelly (1985).

Results

CO_2 concentration in air

During measurements with the flux chamber, the mean CO_2 concentration in the air at 2 m was 352 µl l^{-1} corresponding to equilibrium concentrations in Pøle stream of 16.2 ± 2.7 µM (SD, $n = 495$), while air and equilibrium concentrations were slightly higher in Havelse stream (17.0 ± 1.8 µM, $n = 305$). At wind-protected reaches with tall herbs on the banks, the air concentration had risen in the night and early morning on five of 24 occasions to 1.3–2.0 times above the typical atmospheric level (i.e. 20.0–31.9 µM in water at air equilibrium). These locally elevated air concentrations declined within 1–2 h when solar heating induced a weak wind (Fig. 3).

CO_2 at four vertical levels in the air during a very calm summer night rose to 580 µl l^{-1} at 1, 2 and 4 cm
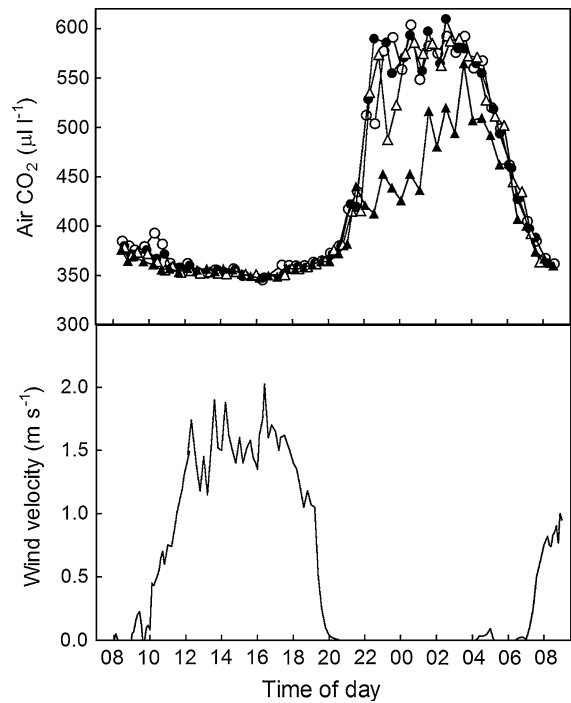
Fig. 3 Diurnal changes in CO_2 concentration measured in the air 1 cm (*open circle*), 2 cm (*filled circle*), 4 cm (*open triangle*) and 2 m (*filled triangle*) above the water surface (*upper*) and wind speed measured at 2 m (*lower*)

above the water surface, while CO_2 rose to 500 µl l^{-1} at 2 m (Fig. 3). Elevated CO_2 disappeared at low wind speeds in the morning (<0.2 m s^{-1}) and had a limited impact on CO_2 fluxes because they coincided with peak CO_2 concentration in the water (145–590 µM). The water–air CO_2 gradient was at most reduced by 11% due to CO_2 accumulation in still air and delayed CO_2 evasion for only 1–2 h.

CO_2 concentration in water

CO_2 was greatly supersaturated at all eight stations in both streams throughout the year (Fig. 4). The uppermost station in Pøle stream (P1) received soil water from fields and a refuse dump and had particularly high HCO_3^- and CO_2 concentrations (annual median 1490 µM CO_2). CO_2 concentration became significantly lower (annual median 115 µM at P6 and P7) at the relatively wide and shallow midstream reaches conducive to CO_2 evasion and photosynthesis. CO_2 concentration increased (median 170 µM) and became less variable towards the mouth of Pøle stream (P8),
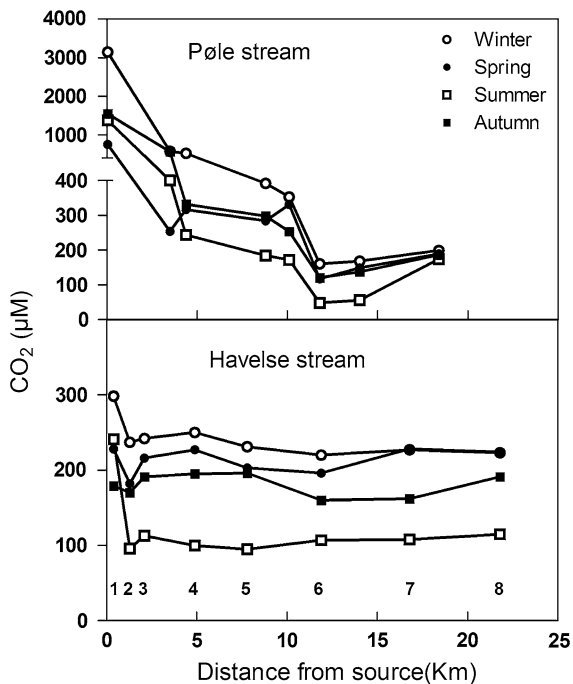
Fig. 4 CO_2 concentration at eight stations in the Pøle (*upper panel*) and Havelse streams (*lower panel*) in winter (January–March), spring (April–May), summer (June–September) and autumn (October–December). Data are means of 2 or 3 monthly measurements

which has deeper slow-flowing water that restricts CO_2 evasion. CO_2 concentration changed less along the Havelse stream, but as in Pøle stream, it was slightly higher at upper and lower reaches than at mid-stream reaches (Fig. 4). Over the year, median CO_2 concentration was highest in winter (Havelse = 210 μM; Pøle = 430 μM; Fig. 4) and lowest in mid-summer (Havelse = 116 μM; Pøle = 171 μM) because input of CO_2-rich soil water was higher and photosynthetic CO_2 consumption lower in winter than in summer.

Downstream decline of CO_2 concentration can be explained by the increased retention time of supersaturated water in the stream which facilitates release to the atmosphere, while net photosynthesis did not change significantly along Pøle stream ($r = -0.46$, $P = 0.44$) and Havelse stream ($r = 0.75$, $P = 0.25$). CO_2 loss to the atmosphere from a given stream water volume and unit time is given by the concentration difference multiplied by the time-specific piston velocity ($K_2 = K_L H^{-1}$, where H is mean water depth). K_2 declined during summer to almost zero in the deeper, lowermost reaches (P8 and H8: $0.02 \, h^{-1}$)

compared to higher values at shallower midstream reaches in Pøle ($0.23-0.39 \, h^{-1}$) and Havelse streams ($0.38-0.98 \, h^{-1}$). This pattern permitted input of CO_2 from soil water to exceed atmospheric loss in the deep, lowermost reaches and, thereby, stream CO_2 concentration to increase (Fig. 4).

A compilation of 539 measurements of CO_2 from six other streams in North Zealand corresponded to those from the Pøle and Havelse streams (median 212 μM, Fig. 5). Groundwater was markedly supersaturated and more than 80% of 133 measurements had CO_2 concentration between 320 and 640 μM (median 460 μM). CO_2 measurements in the outlets from seven eutrophic lakes ($n = 1755$) ranged from below air saturation during summer to above air saturation in winter and the annual median (29 μM) exceeded air saturation.

CO_2 evasion rate and sources

During summer, CO_2 supersaturation declined tenfold from sunrise to the afternoon at stream stations with intense photosynthesis and CO_2 evasion declined similarly (data not shown). At other stations with reduced photosynthesis, CO_2 concentration and evasion varied much less over the day (i.e. threefold, see Fig. 6). Piston velocity varied much less diurnally than CO_2. Evasion of CO_2 was much larger at high current velocity in the middle of the stream profile than in slower flowing water with low piston velocity close to the banks (Fig. 6).
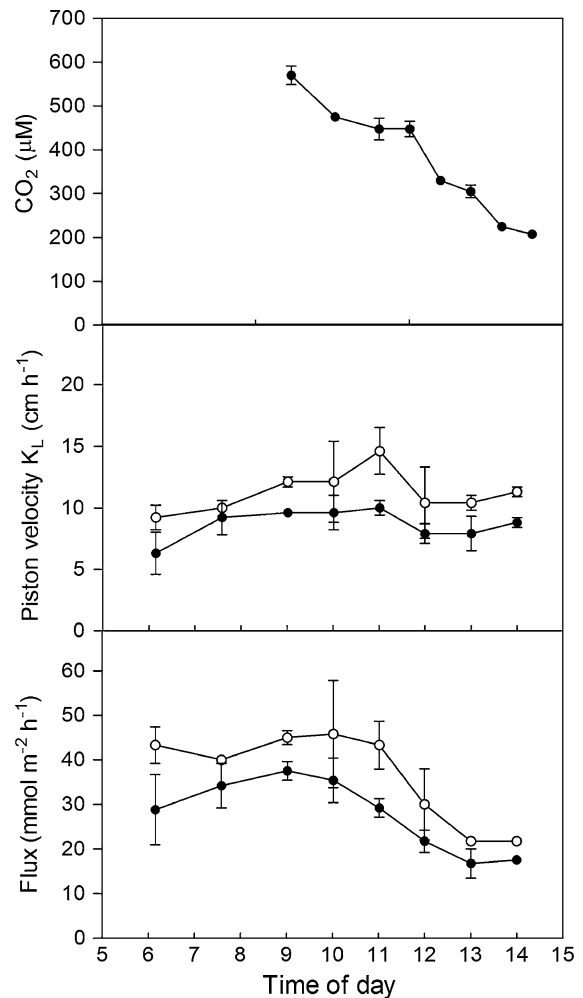
Mean daily concentration, evasion and piston velocity of CO_2 changed downstream during June–August (Fig. 7). In the Pøle stream, concentration and evasion of CO_2 ($500-1,200 \, \text{mmol m}^{-2} \, \text{day}^{-1}$) were highest at the two first mid-stream stations (P4 and P5). As a consequence of these high losses, CO_2 depletion and lower evasion rates occurred downstream at the two following stations (P6 and P7). At the stream mouth (P8), CO_2 evasion remained low ($100 \, \text{mmol m}^{-2} \, \text{day}^{-1}$) because of low piston velocity in the deeper, slow-flowing water. In the Havelse stream, CO_2 evasion stayed relatively constant (i.e. $210-265 \, \text{mmol m}^{-2} \, \text{day}^{-1}$) at mid-stream stations (H5 and H7) located 8 and 17 km from the source, but as in the Pøle stream, evasion tended to be higher upstream ($235-470 \, \text{mmol m}^{-2} \, \text{day}^{-1}$ at H3) and markedly lower ($25 \, \text{mmol m}^{-2} \, \text{day}^{-1}$) in slow-flowing water at the outlet (H8, Fig. 7).
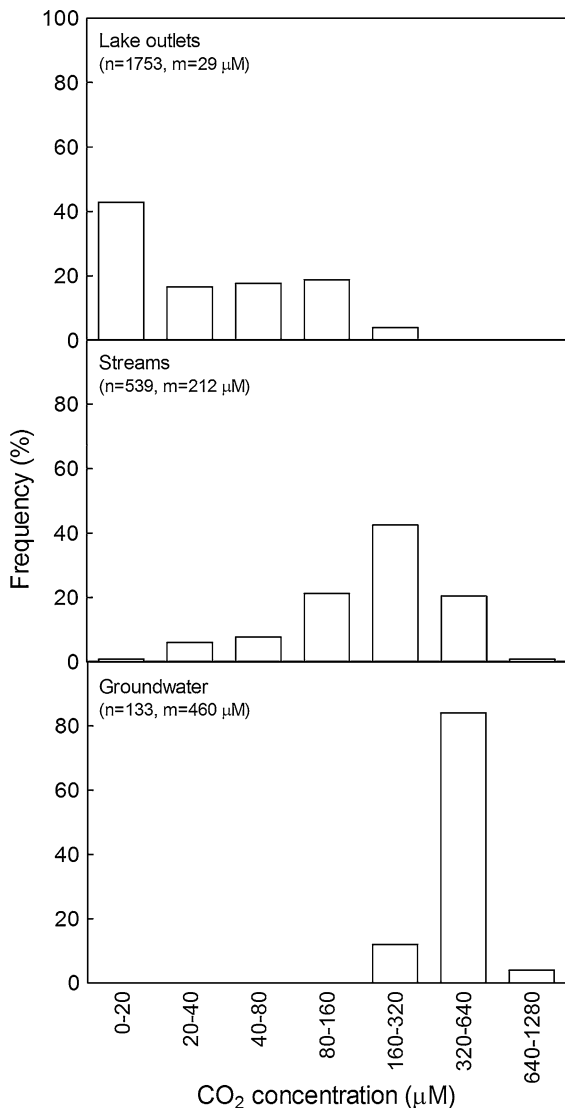
Fig. 5 Frequency distribution of daily mean CO_2 concentration (μM) in seven large eutrophic lakes, six streams and four groundwater wells studied throughout the year in North Zealand, Denmark. Medians (*m*) and number of measurements (*n*) are shown

Fig. 6 Concentration (μM, *upper panel*), evasion rate (mmol m^{-2} h^{-1}, *middle panel*) and piston velocity for CO_2 (cm h^{-1}, *lower panel*) during the day at positions close to the shore (*filled circles*) and at faster flow in the middle of the stream (*open circles*) at P4 in Pøleå on a day of sustained CO_2 supersaturation. Mean values and SD

The main annual input of CO_2 to the streams (79–94%) was as dissolved free CO_2 in soil water, while CO_2 release from degradation of easily degradable organic matter in the water (BOD) was a minor source (Table 1). Output of CO_2 through evasion to the atmosphere (70–74%) and export via the outlet (26–30%) approximately matched the input.

Total annual carbon loss from terrestrial soils to Pøle and Havelse streams was dominated by CO_2 consumed in dissolution of minerals to form HCO_3^- (1,596 and 1,395 tons C, respectively) and organic carbon export (539 and 281 tons C) compared to export of dissolved CO_2 (172 and 160 tons, Table 1). These annual export rates are substantial when scaled to catchment area of Pøle (25.1 g C m^{-2}) and Havelse streams (14.1 g C m^{-2}).

Piston velocity and empirical models

Repeated measurements during the day for every location of the flux chamber yielded 55 mean daily

Fig. 7 Mean daily concentration (μM, *first panel*), piston velocity (cm h^{-1}, *second panel*) and evasion rate for CO_2 (mmol m^{-2} day^{-1}, *third panel*) at different distances downstream in the Pøle and Havelse streams in June–July (*closed circles*) and August (*open circles*). Mean values and SD
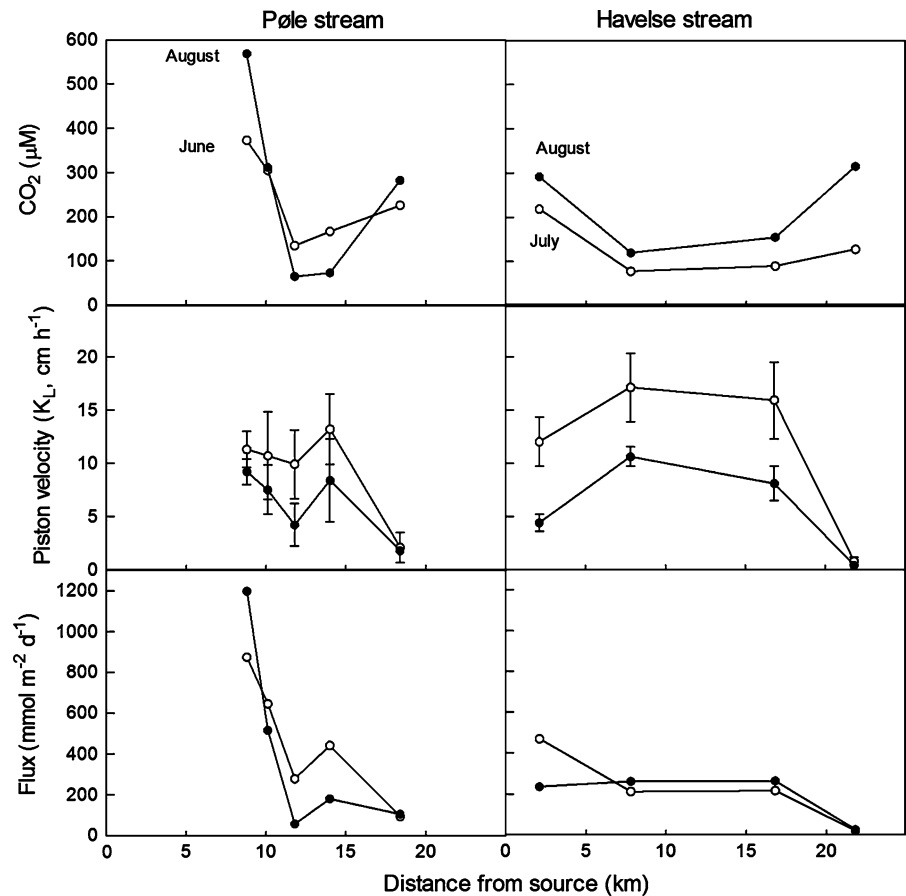
Table 1 Sources and rates of annual CO_2 import and export for Pøle and Havelse streams

	Havelse stream	Pøle stream
Soil water input	160	172
Input by in-stream BOD	11	45
Total input	171	217
Efflux to air	119	188
Downstream export	50	67
Total output	169	255

All values in 10^3 kg C stream^{-1} year^{-1}

Table 2 Significant relationships ($P < 0.0001$) of piston velocity (K_L at 20°C, cm h^{-1}) as a function of current velocity (U, m s^{-1}) and water depth (H, m)

I. Means of all daytime measurements at local sites (n = 55)

Log K_L = 1.257(0.041) + 0.742(0.055) log U (r^2 = 0.77)

II. Means of every triplicate experiment at local sites (n = 200)

Log K_L = 1.286(0.029) + 0.776(0.035) log U (r^2 = 0.71)

Log K_L = 0.282(0.077) − 0.812(0.122) log H (r^2 = 0.18)

Log K_L = 1.170(0.064) + 0.743(0.038) log U − 0.159(0.079) log H (r^2 = 0.72)

Relationships to the energy gradient (S, m km^{-1}) were not significant, I. Relationships between means of all measurements at a given position of the flux chamber during the day, II. Relationships between means of triplicate measurements at different times during the day

SE standard error (in parenthesis), r^2 coefficient of determination, *n* number of measurements

values of evasion rate and piston velocity. Piston velocity (K_L^{20}) ranged from 0.4 to 21.6 cm h^{-1} and had an approximately normal distribution with most values (63%) between 4 and 12 cm h^{-1}. Piston velocity increased significantly with current velocity according to a log–log linear least square regression ($P < 0.0001$, slope 0.742; Table 2). The negative influence of increasing water depth on piston velocity was not significant ($P = 0.11$).

Almost the same relationship of piston velocity to current velocity was found for 200 triplicate measurements (slope 0.776), but the negative relationship to water depth was significant as "*n*" was greater,

although it accounted for only 18% of the variability (Table 2). In multiple regression models, current velocity contributed most and water depth less to the prediction of piston velocity, but the total variability accounted for was almost the same (72%) as that attained by current velocity alone.

Discussion

CO_2 supersaturation in streams

Havelse, Pøle and other streams in North Zealand were greatly supersaturated with CO_2 due to the year-round inflow of CO_2-rich soil water, the short retention time (<24 h) and the surplus of respiration to photosynthesis (Simonsen 1974; Sand-Jensen 1997). Increasing contact time with the atmosphere can account for the decline of CO_2 from upstream to midstream reaches of the Havelse and Pøle streams, while declining evasion rates can account for the increased CO_2 concentration in the slow-flowing lowermost reaches.

The widespread CO_2 supersaturation in lowland streams is a prerequisite for the existence of a diverse community of amphibious plants (Riis et al. 2001) which are unable to use HCO_3^- and, therefore, require high CO_2 concentration to attain sufficient photosynthesis (Sand-Jensen and Frost-Christensen 1998). The amphibious species are unable to grow in lake outlets because long water retention time and phytoplankton photosynthesis in the lakes often reduce CO_2 to below air saturation during summer resulting in negative net photosynthesis by the amphibious species (Sand-Jensen and Frost-Christensen 1998).

Photosynthesis of aquatic species in the two study streams contributed to the lower CO_2 concentration during summer than winter (Fig. 4) and caused a mean 2.7-fold reduction of CO_2 from sunrise (105–749 µM) to late afternoon (25–479 µM) during 24 diurnal summer measurements. In no instance did the CO_2 concentration fall below air saturation. Thus, CO_2 exchange was consistently directed from the stream waters to the atmosphere in accordance with previous studies in temperate lowland (Rebsdorf et al. 1991; Neal et al. 1998) and upland streams (Hope et al. 2001) and in boreal streams (Sobek et al. 2003).

The contrast between annual median CO_2 concentration in groundwater (460 µM), streams (212 µM) and lake outlets (29 µM) in North Zealand has several important implications. Soil water is the main contribution to the systematic CO_2 supersaturation in the streams and to the substantial CO_2 evasion as confirmed by mass balances (Table 1). CO_2 concentration in the lakes are only slightly above air saturation suggesting that the annual CO_2 flux is usually directed from the lake water to the atmosphere, though at much lower rates than from the streams, due to the 10–20 times lower water–air CO_2 gradient and the lower piston velocity compared to streams. For the largest and most wind-exposed of the seven lakes in North Zealand (Lake Arresø, area = 38 km^2), the annual mean piston velocities (K_L) were estimated to 6.9 cm h^{-1} for 2 years using the model by Jonsson et al. (2008) and continuous wind measurements. For the two streams the mean piston velocity of 8.4 cm h^{-1} was 1.2 times higher. The larger air–water gradient and piston velocity in the streams imply that the mean CO_2 evasion rates per m^2 are at least 15-fold higher from streams than large lakes.

Piston velocity

There are several advantages of directly measuring CO_2 evasion rates and concentration differences between water and air and calculating piston velocity from the two parameters instead of relying on indirect methods. First, direct measurements were highly accurate and reproducible. Second, establishment of close relationships between piston velocity and current velocity permitted up-scaling of evasion rates to entire streams and annual rates. Third, several uncertainties associated with indirect methods and conversion from measurements of trace gases to CO_2 were avoided.

Direct measurements of CO_2 evasion rate and CO_2 concentration in air and water were fast, sensitive and highly reproducible. CO_2 concentrations were here derived from determination of alkalinity, pH and temperature in discrete water samples, but continuously operating and reliable pH and temperature sensors are available (e.g. Maberly 1996) and alkalinity can be derived from continuously operating conductivity probes (Sand-Jensen and Frost-Christensen 1998). New techniques are also available to directly measure dissolved CO_2 in freshwaters (Johnson et al. 2010).

There are also potential drawbacks in the use of CO_2 flux chambers, however. First, there are potential

errors by the use of flux chambers because water and air turbulence, air temperature and pressure can be influenced by the presence of the chamber (Bilett and Moore 2008). With the chamber construction used here, we could perform the measurement over very short time intervals and avoid changes in air temperature and pressure but we have no measurements of water turbulence to document that it was entirely unaffected by the presence of the chamber, although it was constructed with that purpose. Secondly, it may be difficult to apply flux chambers over very rough water surfaces in stream riffles which may be hot spots for CO_2 evasion. Such stream sections were not present in the channelized North Zealand streams studied here. Third, upscaling of variable evasion rates from the site specific location of flux chambers to entire stream reaches is time-consuming and may introduce error which is difficult to evaluate. Upscaling is avoided by the use of inert trace gases over long reaches.

Piston velocity increased in close correlation with current velocity across the wide range of velocities (0.01–0.82 m s^{-1}) and water depths (0.09–0.90 m) covered by this study. The relationship between piston velocity and current velocity can be used in most local physical settings in lowland streams over the year to predict piston velocity from current velocity and other hydrological features. Once piston velocity is known, evasion rates can be calculated from temperature and CO_2 concentration in air and water. Air measurement of CO_2 concentrations can apparently be left out in most cases because they are either very close to mean atmospheric levels or elevated concentration just above the stream surfaces only occur briefly during very calm nights and mornings when CO_2 concentration in the water is often so high that the outward CO_2 gradient is barely reduced. Water current velocity for prediction of piston velocity is either available from periodic measurements or it can be derived from measurements in a routine hydraulic program. As a result, it becomes realistic to determine annual CO_2 evasion rate for all streams within a catchment.

The relationship of piston velocity to current velocity in the stream may reflect a more direct coupling to surface turbulence (Moog and Jirta 1999) as previously documented for lowland streams (Sand-Jensen and Pedersen 1999). Thus, we cannot dismiss the possibility that a strong empirical relationship between piston velocity and current velocity, as established here for channelized streams, varies

appreciably between stream types depending on channel morphology, depth patterns and bed roughness influencing the turbulence regime. If so, more general predictors of piston velocity should be sought and near-surface turbulence appears to be a promising parameter (Zappa et al. 2007) although relationships of piston velocity to turbulent dissipation rate so far have not attained the same predictive power as that of piston velocity to current velocity presented here.

Measurements of evasion rate and piston velocity along reaches have the advantage of covering the relevant scale for budget calculation, but those available have the disadvantage of limited replication and use of gases (e.g., oxygen, propane, ethane, SF$_6$) which requires conversion to CO_2 (Cole and Caraco 1998). This conversion may induce error when the studied gases behave differently or unexpectedly to that of CO_2 in water, in air and over the interface separating them (Simonsen 1974; Thyssen and Kelly 1985). For example, CO_2 takes part in complex pH-dependent conversions in the stream water, in rainwater and in the dew that forms above streams during nights and early mornings (Ho et al. 1997). The resistance to passage of different gases through organic layers on stream surfaces (Frew 1997) is not predictable from molecular weight if differences in solubility between test gases and CO_2 influence passage across the interface. Consequently, there is room for subjectivity and analytical variability in the use of equations converting the piston velocity of, for example, propane to CO_2 (Genereux and Hemond 1992; Hope et al. 2001). One solution to these shortcomings and an independent check of the data could be to take advantage of the direct approach used here and combine it with full-scale measurements by covering entire reaches with transparent gas-tight material that encloses a large air volume for measurement of CO_2 accumulation rates over time.

CO$_2$ evasion from streams: a wider perspective

Daily evasion rates during summer were highest (170–1,200 mmol m^{-2}) in the middle parts of the Pøle and Havelse streams where CO_2-rich soil water entered shallow reaches with relatively fast flow. Rates were markedly lower (25–100 mmol m^{-2} day^{-1}) further downstream in the deeper, slow-flowing reaches because of the lower piston velocity (Table 3). The annual mean CO_2 evasion rate was 395 in the Havelse

Table 3 Daily mean CO_2 evasion to the atmosphere from selected sub-Arctic and temperate streams and rivers in different settings

Locations	CO_2 evasion (mmol C m^{-2} day^{-1})
Sub-Arctic streams	
Alaska[c]	10–115
Temperate lower stream reaches	
Hudson River, New York[d]	16–37[m]
Havelse stream (H8), Denmark[a]	25[l]
Pøle stream (P8), Denmark[a]	100[l]
Temmesjoki River, South Finland[e]	100–150
Brocky Burn, Scotland[g]	20–280[m]
Temperate mid and upper streams	
Midstream Havelse stream (H3–H7), Denmark[a]	235–355[l]
Upper Temmesjoki River, South Finland[e]	450
Midstream Pøle stream (P4-P7), Denmark[a]	170–1,200[l]
Midstream Brocky Burn, Scotland[g]	340–1720[m]
Upper Brocky Burn, Scotland[g]	545–3820[m]
Entire temperate streams	
River Tees, UK[f]	0–165
River Coquet, UK[f]	0–340
Öreälven, Sweden[h]	345
Xijiang River; China[i]	0–165
Walker Branch, Tennessee[j]	157–373
Entire Havelse stream, Denmark[b]	395
Entire Pøle stream, Denmark[b]	495
River Swale, UK[k]	100–1,000

[a] Direct measurements from June to November, this study

[b] Annual mean values

[c] Kling et al. (1991)

[d] Raymond et al. (1997)

[e] Silvennoinen et al. (2008)

[f] Worall and Burt (2005)

[g] Hope et al. (2001)

[h] Jonsson et al. (2007), 200 days with open stream flow

[i] Yao et al. (2007)

[j] Jones and Mulholland (1998)

[k] Neal et al. (1998)

[l] Direct measurements of evasion rate (this study)

[m] Estimates using direct measurements of piston velocity

stream and 495 mmol m^{-2} day^{-1} in the Pøle stream (Table 3). These values are about 5–10 times higher than the average formation of excess CO_2 within

systems as a result of greater ecosystem respiration than gross production in the compilation of data from 62 streams (100 mmol m^{-2} day^{-1}) and 37 rivers (55 mmol m^{-2} day^{-1}; Battin et al. 2008). This comparison supports our conclusion that the main CO_2 source to the evasion from the two lowland streams (79–94%) was dissolved free CO_2 in soil water, while CO_2 release from degradation of imported easily degradable organic matter (BOD) represented a minor source (Table 1). Input of degradable organic matter would make a greater contribution if the streams had been longer and more time had been available for degradation of imported organic material and if untreated sewage and not tertiary treated sewage had been received.

The 50-fold range of daily evasion rates at different reaches in the Pøle and Havelse streams (25–1,200 mmol m^{-2} day^{-1}) covers most of the global range of mean CO_2 evasion rates for different subarctic streams (10–115 mmol m^{-2} day^{-1}, Kling et al. 1991) and temperate streams in either open lowlands (20–3,820 mmol m^{-2} day^{-1}, Raymond et al. 1997; Worall and Burt 2005), forest-covered lowlands (Silvennoinen et al. 2008), and in upland peat lands (Hope et al. 2001; Table 3). CO_2 evasion rates are also highly variable from lake surfaces (e.g. 0.1–25 mmol m^{-2} day^{-1}, Sand-Jensen and Staehr 2009), but the levels are two orders of magnitude lower per surface area in lakes than streams because of lower concentrations of CO_2 in the surface waters. This contrast between streams and lakes also exists in the catchment areas of the Pøle stream. Thus, the mean evasion rate was 3 mmol m^{-2} day^{-1} from the large Lake Arresø located downstream (Fig. 1) and 14 mmol m^{-2} day^{-1} for 19 small lakes located within the catchment (Sand-Jensen and Staehr 2009). The 19 small lakes had an annual CO_2 evasion of 5×10^6 mol compared with 16×10^6 from the stream. The annual CO_2 evasion was larger from downstream Lake Arresø (42×10^6 mol) in the particular years. In the Havelse catchment lakes were absent and all aquatic CO_2 evasion was from the stream surfaces.

Scaled to surface area of the catchments, daily mean CO_2 evasion rates from freshwaters were 1.9 mmol m^{-2} day^{-1} for the Pøle catchment (including downstream Lake Arresø) and 0.21 mmol m^{-2} day^{-1} for the Havelse catchment. Similar CO_2 evasion rates from surface waters scaled to catchment area were estimated in a Canadian peatland (Bilett and

Moore [2008]). Total carbon loss from terrestrial soils via the hydraulic cycle in North Zealand are more substantial, however, because, in addition to dissolved CO_2, organic carbon is also exported and CO_2 is consumed in dissolution of minerals to form high HCO_3^- concentrations in the effluent water. Total carbon losses from terrestrial soils with the water flow amounted to daily means of 5.7 and 3.2 mmol m^{-2} day^{-1} for Pøle and Havelse catchments which are substantial rates in the carbon flux budget of terrestrial habitats amounting to 3–50% of the net production rates of beech forests (typically 11–125 mmol m^{-2} day^{-1}, Granier et al. [2000]).

In conclusion, our results document the considerable variability of CO_2 evasion rate from upstream to downstream reaches within streams, between different streams and among streams and lakes from the same region. To integrate evasion rates into overall budgets for all water bodies within catchments requires programs for measuring or predicting CO_2 concentration and piston velocity with a high spatial and temporal resolution that has now become practically possible thanks to continuously operating sensors and formulation of general empirical predictions of piston velocity. From the catchment fluxes presented here it is evident that considerable amounts of carbon are lost from terrestrial soils as CO_2, HCO_3^- and organic carbon via the hydrological cycle and must be included in the carbon budgets of streams, lakes as well as terrestrial ecosystems to attain reliable results.

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