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Spatial and temporal variability of $p\mathrm{CO_2}$ and $\mathrm{CO_2}$ emissions from the Dong River in south China

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Introduction

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Text S1 Comparative analysis of the syringe and bottle headspace method

Both large volume bottle and small volume syringe were used in headspace equilibration method (Yoon et al., 2016). In this study, a 625 mL reagent bottle and a 100 ml syringe equilibrator were chosen for headspace extraction to investigate the impact of headspace volume and shaking time on the result of pCO_2 measurement. For the bottle equilibrator, 400 ml of sample water was collected with 225 ml ambient air, while 50 ml of sample water was collected with 50 ml of ambient air for the syringe equilibrator. According to Hope et al. (1995), equilibrium in the headspace could be achieved after 1 min of vigorous shaking when adapting the rapid headspace analysis technique developed by Kling et al. (1991). However, 5–10 min were also used for pCO_2 determination (Abril et al., 2015). Therefore, we measured the pCO_2 value in the headspace after shaking the equilibrator for 1–5 min at the one-minute interval. The average of triple replicates was then calculated for comparative analysis (Table S2). The experiment showed that syringe and bottle equilibrator gave very consistent results. Overall, the average pCO_2 value of syringe headspace was 1.2% larger than that of the bottle headspace, which was less than the 1.5% error of Li-850. However, it could take more time for a large volume equilibrator to achieve equilibrium. The pCO_2 results of the small volume syringe headspace are not significantly different after more than two minutes of shaking, while it took the large volume bottle equilibrator three minutes to achieve a similar pCO_2 value. Therefore, for rapid field measurement of surface water pCO_2, shaking for two minutes when using syringe headspace and three minutes when using the bottle headspace could yield reliable test results (Figure S3). In this study, we vigorously shake the bottle equilibrator for at least 1 minute (usually 1-3 minutes), which might cause a 1–5% underestimate of the pCO_2 result. Furthermore, Koschorreck et al. (2021) found that reducing the headspace ratio could significantly increase the accuracy of the headspace method. Therefore, a large volume equilibrator might be more suitable for the field measurement since a low headspace ratio could be easier to achieve.

Table S1 Seasonal variation in stream width for streams from first to seventh order.

Stream size	Stream order	Stream width (m)						
		January	April	July	August	October	Wet season	Dry season
small		13.5 ± 9.9	16.9 ± 10.1	17.1 ± 10.6	15.1 ± 9.7	14.5 ± 10.9	16.3 ± 10.0	14.0 ± 10.3
	1	2.9 ± 1.5	4.7 ± 2.7	6.0 ± 2.1	5.6 ± 2.7	4.7 ± 2.0	5.4 ± 2.4	3.8 ± 1.9
	2	8.3 ± 5.2	12.7 ± 7.8	12.5 ± 7.2	10.1 ± 2.8	8.4 ±3.2	11.8 ± 6.1	8.4 ± 4.1
	3	21.1 ± 7.4	24.7 ± 5.5	24.6 ± 8.5	22.1 ± 8.8	22.2 ± 10.3	23.8 ± 7.6	21.7 ± 8.8
large		173.9 ± 161.7	184.4 ± 164.0	187.2 ± 158.5	181.1 ± 162.4	175.1 ± 165.1	184.2 ± 159.1	174.5 ± 161.4
	4	67.6 ± 38.5	73.0 ±47.1	87.0 ±54.7	82.3 ±64.4	66.2 ± 54.3	80.7 ± 54.2	66.9 ± 45.8
	5	164.3 ± 46.4	187.7 ± 69.6	166.6 ±37.6	157.0 ±54.9	164.6 ± 45.4	170.4 ± 53.2	164.5 ± 43.3
	6	226.5 ± 23.3	235.5 ±37.5	241.3 ±45.7	231.5 ±44.5	243.9 ±38.4	236.1 ± 33.4	235.2 ± 27.6
	7	425.2 ± 207.3	433.4 ± 200.0	436.5 ±192.3	433.3 ±196.8	426.2 ±206.8	434.4 ± 177.6	425.7 ± 191.7

Table S2 Comparison of measured pCO_2 using two headspace extraction methods.

Equilibrator		Shaking time				
		1 min	2 min	3 min	4 min	5 min
Bottle	Test 1	637.9	642.3	669.1	664.6	673.1
	Test 2	645.3	651.7	658.2	666.5	680.0
	Test 3	634.4	645.8	665.2	662.1	664.6
	Average	639.2	646.6	664.2	664.4	672.6
Syringe	Test 1	640.6	662.7	664.9	681.5	681.5
	Test 2	639.5	670.4	670.4	674.8	680.3
	Test 3	648.4	660.5	664.9	669.3	666.0
	Average	642.8	664.5	666.7	675.2	675.9

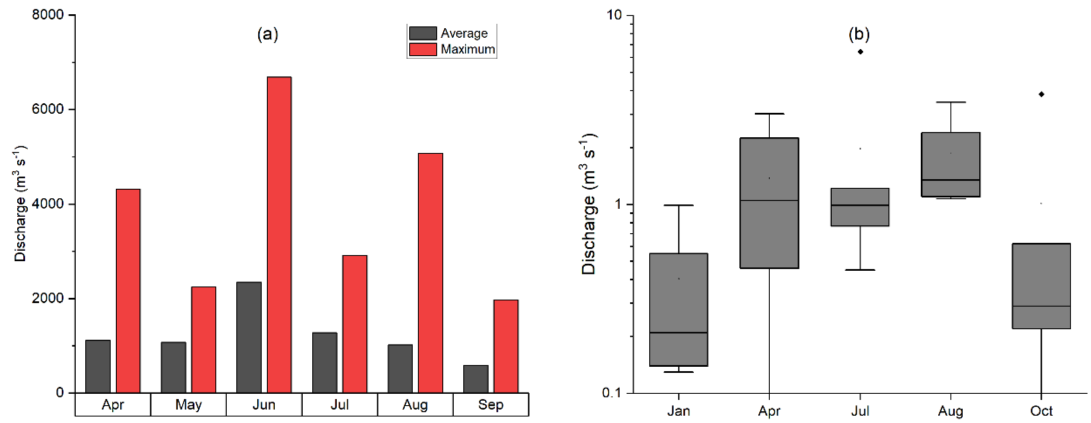

Figure S1 (a) Wet season discharge in Boluo station, based on data provided by the Hydrological Bureau of Guangdong Province. (b) discharge in first order streams.

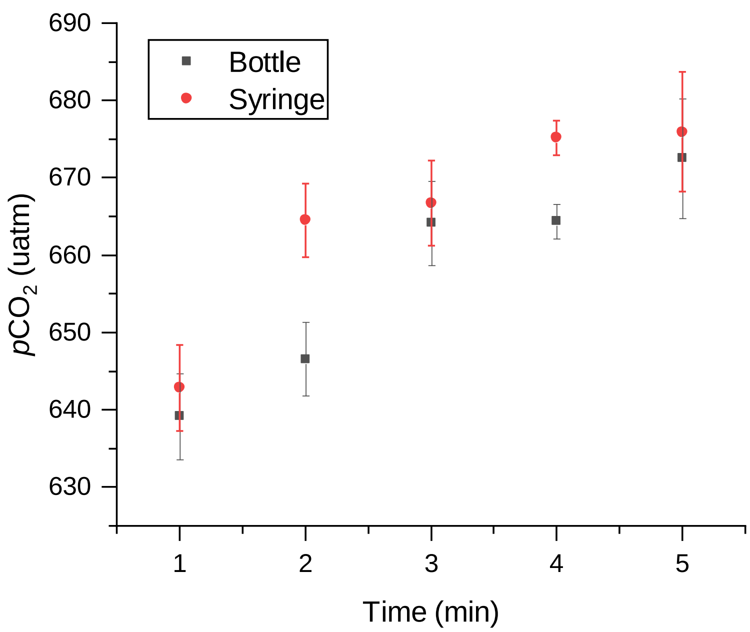

Figure S2 Measured $p\mathrm{CO_2}$ in headspace after shaking for 1-5 min.

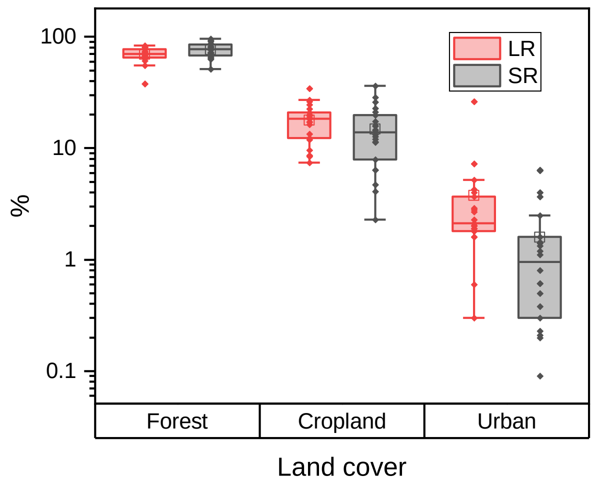

Figure S3 Forest, cropland, and urban cover respectively as a percentage of the catchment area. The box mid-lines represent medians; the interquartile range (IQR) is represented by top and bottom of the box, respectively; whiskers indicate the range of 1.5 IQR; the white square symbols represent means, and the other symbols represent Forest, cropland, and urban cover respectively as a percentage of catchment area.

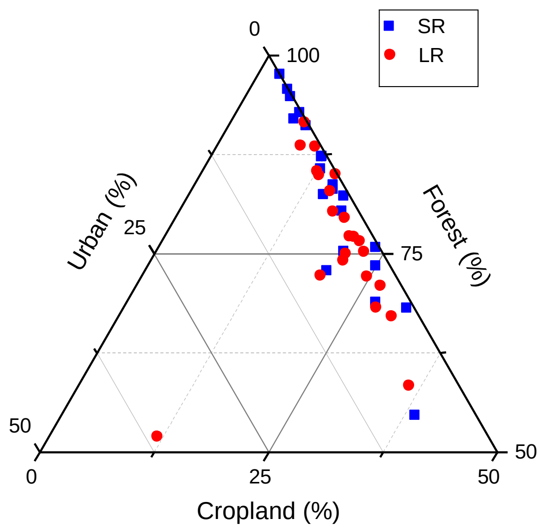

Figure S4 Forest, cropland, and urban cover respectively as a percentage of the total area of forest, cropland, and urban.

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