Impact of Land Cover Types on Riverine CO_2 Outgassing in the Yellow River Source Region

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Introduction

The supporting information provides additional information on the description of the correction of headspace equilibration method (Text S1).

Datasets S1 to S6: Sampling results for streams in April, June, August and October 2016.
Sampling results for streams in April, June, August, and October 2016 are tabulated in Datasets S1 to S6, respectively.
Column 'Sampling site': name of sampling site; Column 'Land cover type' : the land cover type around sampling sites; Column 'Coordinates': longitude (E) and latitude (N); Column 'Elevation': elevation above sea level (m); Column 'pH': pH (unitless); Column 'DIC': Dissolved inorganic carbon (mmol/L); Column 'DO': dissolved oxygen (mg/L); Column 'DOC': dissolved organic carbon (mg/L); Column 'pCO_2': partial pressure of CO_2 (μatm); Column 'FCO_2': CO_2 evasion across water-air interface (g C/m^2/yr).
Note: the symbol '-' denotes no data, and GL1, GL4, and GL5 in June were not sampled due to road condition, logistical problems, and instrument failures.

Text S1: Correction of headspace equilibration method

The cited method developed by Dickson et al. (2007) to corrected pCO_2.

The reactions that take place when carbon dioxide dissolves in water can be represented by the following equilibria:

$$CO_2(g) \rightleftarrows CO_2(aq) \tag{1}$$
$$CO_2(aq) + H_2O \rightleftarrows H_2CO_3(aq) \tag{2}$$
$$H_2CO_3(aq) \rightleftarrows H^+(aq) + HCO_3^-(aq) \tag{3}$$
$$HCO_3^-(aq) \rightleftarrows H^+(aq) + CO_3^{2-}(aq) \tag{4}$$

The notations (g), (l), and (aq) refer to the state of the species, *i.e.*, a gas, a liquid, and in aqueous solution, respectively. The sum of the CO_2 (aq) and H_2CO_3(aq) concentrations is expressed as CO_2^* (aq).

Redefining (1), (2), and (3) in terms of this species gives (5) and (6)

$$CO_2(g) \rightleftarrows CO_2^*(aq) \tag{5}$$
$$CO_2^*(aq) + H_2O(l) \rightleftarrows H^+(aq) + HCO_3^-(aq) \tag{6}$$

The equilibrium relationships between the concentrations of these various species can then be written as

$$K_0 = [CO_2^*]/pCO_2 \tag{7}$$
$$K_1 = [H^+][HCO_3^{2-}]/[CO_2^*] \tag{8}$$
$$K_2 = [H^+][CO_3^{2-}]/[HCO_3^-] \tag{9}$$

The calculation of $\ln(K_0/k^\circ)$ is given by the expression (10) below (Weiss,1974):

$$\ln(K_0/k^\circ) = 93.4517 \left(\frac{100}{\mathrm{K}}\right) - 60.2409 + 23.3585\ln\left(\frac{\mathrm{K}}{100}\right)$$

$$+S[0.023517 - 0.023656\left(\frac{\mathrm{K}}{100}\right) + 0.0047036\left(\frac{\mathrm{K}}{100}\right)^2] \quad (10)$$

The calculation of $\log_{10}(K_1/k^\circ)$ is given by the expression below (Lueker et al., 2000):

$$\log_{10}(K_1/k^\circ) = \frac{-3633.86}{\mathrm{K}} + 61.2172 - 9.67770\ln(\mathrm{K})$$

$$+0.011555\mathrm{S} - 0.0001152S^2 \quad (11)$$

The calculation of $\log_{10}(K_2/k^\circ)$ is given by the expression below (Lueker et al., 2000):

$$\log_{10}(K_2/k^\circ) = \frac{-471.78}{\mathrm{K}}) - 25.9290 + 3.16967\ln(\mathrm{K})$$

$$+0.01781\mathrm{S} - 0.0001122S^2 \quad (12)$$

Where, k° =1 mol kg-soln^{-1}, K is the kelvin of the water, S is the salinity.
The dissolved inorganic carbon content of water is defined as (13)

$$C_\mathrm{T} = [\mathrm{CO}_2^*] + [\mathrm{HCO}_3^-] + [\mathrm{CO}_3^{2-}] \quad (13)$$

Redefining (7), (8), and (9) in terms of this species gives (13)

$$= pCO_2^{headspace,f} \times K_0 \times [1 + \frac{K_1}{[H^+]} + \frac{K_1 \cdot K_2}{[H^+]^2}] \quad (14)$$

Where, the brackets represent total concentrations of these constituents in solution (in mol kg^{-1}) and [CO_2*] represents the total concentration of all unionized carbon dioxide, whether present as H_2CO_3 or as CO_2.

The CO_2 in water that emits into the headspace during the shaking process can be express:

$$D_C = \frac{Vh}{Vw}(pCO_2^{headspace,f} - pCO_2^{headspace,i})/(RT) \quad (15)$$

Redefining (13), the original pCO₂ of water could be calculated by (16)

$$pCO_2 = \frac{C_T + D_C}{[1+\frac{K_1}{[H^+]}+\frac{K_1 \cdot K_2}{[H^+]^2}] \cdot K_0} \quad (16)$$

Finally, the pCO_2 was corrected by water vapor pressure

$$pCO_2^{Correct} = pCO_2^{Dry}\,(1 - pH_2O) \quad (17)$$

Where, pCO_2^{Dry} is the corrected pCO_2 value in dry air, pH_2O is the water vapor pressure over a water sample of given salinity at the temperature of equilibration, $pCO_2^{Correct}$ is the final corrected pCO_2.

Dataset S1. Land cover type, longitude, latitude and above sea level (ASL) of the 36 stream sites within the Yellow River source region, expressed in the order of April, June, August, and October in 2016.

Sampling sites	Land cover type	Coordinates		
		E	N	Elevation (m)
M1	grassland	99.75829	33.80749	3944
M2	permafrost	102.07888	33.95922	3413
M3	grassland	100.26164	35.68511	2608
GR1	grassland	101.30032	33.39361	3851
GR2	grassland	100.25924	34.37431	3847
GR3	grassland	102.35835	33.97419	3418
GR4	grassland	101.75893	34.11458	3494
GR5	grassland	100.89919	35.52327	3204
GR6	grassland	101.48157	35.01245	3631
GR7	grassland	101.53469	34.58753	3588
GR8	grassland	101.68369	33.76026	3506
GR9	grassland	101.62235	34.12661	3437
GR10	grassland	101.41593	34.18555	3506
GR11	grassland	101.28440	34.22831	3433
Pt1	peatland	102.7302	34.07592	3209
Pt2	peatland	102.23709	33.75737	3423
Pt3	peatland	102.62729	32.91428	3484
Pt4	peatland	102.95628	33.75627	3444
Pt5	peatland	103.18163	33.42880	3558
Pt6	peatland	103.35088	33.00639	3799
Pt7	peatland	103.17970	32.93623	3560
Pt8	peatland	102.90696	33.05994	3546
Pt9	peatland	102.80032	33.53649	3442
Pt10	peatland	102.48113	33.39488	3437
GL1	glacier	99.56724	34.84405	4036
GL2	glacier	99.61596	34.63389	4125
GL3	glacier	99.64521	34.6244	4022
GL4	glacier	99.64952	34.62556	4009
GL5	glacier	99.69093	34.77461	3704
GL6	glacier	99.68733	34.72751	3778
Pm1	permafrost	98.34296	34.82945	4226
Pm2	permafrost	97.91049	35.09445	4265
Pm3	permafrost	97.30228	35.01677	4309
Pm4	permafrost	99.46102	33.67272	4040
Pm5	permafrost	100.12988	34.11357	4126
Pm6	permafrost	100.07277	33.46087	4154

Table S2. pH, DIC, DOC, pCO_2, and FCO_2 of the main stream and grassland sites within the YRSR, expressed in the order of April, June, August, and October in 2016.

Name	Land cover types	Apr						Jun						Aug						Oct					
		pH	DIC	DO	DOC	pCO_2	FCO_2	pH	DIC	DO	DOC	pCO_2	FCO_2	pH	DIC	DO	DOC	pCO_2	FCO_2	pH	DIC	DO	DOC	pCO_2	FCO_2
			mmol L^{-}	mg L^{-}	mg L^{-}	μatm	mmol m^{-2} d^{-}		mmol L^{-}	mg L^{-}	mg L^{-}	μatm	mmol m^{-2} d^{-}		mmol L^{-}	mg L^{-}	mg L^{-}	μatm	mmol m^{-2} d^{-}		mmol L^{-}	mg L^{-}	mg L^{-}	μatm	mmol m^{-2} d^{-}
M1	grasslan	8.	4.4	7.4	4.6	662	99	8.	2.5	6.4	2.5	513	51	7.	-	6.6	4.7	758	181	8.	2.9	8.1	-	643	72
M2	glacier	8.	3.5	8.6	5.4	550	42	8.	1.9	7.2	3.6	483	185	7.	-	6.6	3.5	514	48	7.	2.3	8.2	5.4	678	45
M3	grasslan	8.	4	7.5	3.9	525	103	8.	3.1	6.8	9.5	572	6	7	-	6.4	3.8	715	113	7.	3.1	-	1.3	535	85
GR1	grasslan	7.	1.7	8.6	3.7	886	70	8.	2.1	6.6	1.2	538	42	7.	2.4	7.1	3.6	105	366	7.	1.8	7.4	1.4	830	134
GR2	grasslan	8.	4.8	6.8	5.9	571	133	8.	-	7.3	5.3	488	11	7.	-	6.5	-	109	367	7.	3.7	7.6	3.1	822	165
GR3	grasslan	8.	2.8	7.1	10	686	68	8.	2.1	8.6	5.1	149	22	7.	2.8	5.9	8.2	611	27	8	1.6	5.9	4.7	719	46
GR4	grasslan	8.	4.2	6.7	3.6	614	40	8.	3	6.7	5.4	479	16	7	2.7	6	6.9	552	120	7.	3.9	8	6.6	510	311
GR5	grasslan	8.	4.4	7.5	-	969	326	8.	2.9	6.8	3.8	545	64	7.	2.9	5.8	2.7	119	447	7.	3.9	8.1	1.7	-	-
GR6	grasslan	8.	5.6	8.4	4.7	762	114	8.	3.7	7.6	9.6	628	166	7.	3.9	6.3	8.4	186	370	7.	5.1	8.4	4.2	108	496
GR7	grasslan	8.	6.3	7	2.5	139	203	8.	3.2	6.5	3	608	100	7	3.5	6.9	2.8	219	337	7.	5.5	8.2	1.7	121	530
GR8	grasslan	8.	2.6	8.3	7.4	720	45	8.	1.9	9	7.8	478	76	7.	2.8	7.3	2.6	141	211	7.	2.8	7.4	5.3	593	104
GR9	grasslan	8.	2.3	8.7	4.8	921	32	8.	1.6	7	6.8	493	146	7.	1.7	6.4	2	585	120	7.	1.9	7.6	6.7	515	122
GR1	grasslan	8	3.4	8	3.5	112	237	8.	2.2	6.7	2.3	469	104	7.	1.9	6.2	2.7	676	40	7.	2.4	7.9	2.4	496	54
GR1	grasslan	8.	4.6	7.9	4.9	547	53	8.	3	6.9	-	482	41	7.	-	6.2	6.6	700	92	7.	4.1	7.7	-	557	101

Table S3. pH, DIC, DOC, pCO_2, and FCO_2 of the peatland sites within the YRSR, expressed in the order of April, June, August, and October in 2016.

Name	Land cover types	Apr						Jun						Aug						Oct					
		pH	DIC	DO	DOC	pCO_2	FCO_2	pH	DIC	DO	DOC	pCO_2	FCO_2	pH	DIC	DO	DOC	pCO_2	FCO_2	pH	DIC	DO	DOC	pCO_2	FCO_2
			mmol L^{-}	mg L^{-}	mg L^{-}	μatm	mmol m^{-2} d^{-}		mmol L^{-}	mg L^{-}	mg L^{-}	μatm	mmol m^{-2} d^{-}		mmol L^{-}	mg L^{-}	mg L^{-}	μatm	mmol m^{-2} d^{-}		mmol L^{-}	mg L^{-}	mg L^{-}	μatm	mmol m^{-2} d^{-}
Pt1	peatlan	8.6	4.8	7.3	6.3	562	102	8.6	3.4	6	4.5	522	24	7	3.6	6.5	2.5	1970	310	-	3.5	7.1	5	876	272
Pt2	peatlan	8.2	5	8.5	6.3	1362	258	8.2	3.3	8.3	3	598	14	7.1	1.8	6.5	6.1	1461	75	7.3	2.6	7.6	3.8	862	286
Pt3	peatlan	7.4	1	7.6	-	1809	190	7.9	-	6.6	1.4	1139	120	7.4	1.1	6.4	2.4	862	1574	8	1.2	7.4	6.8	1370	415
Pt4	peatlan	8.4	5.9	8.4	5.3	511	87	8.6	3.5	8.2	2.6	509	57	7.3	3.5	7.5	3.8	882	29	7.3	4.2	8.8	0.2	517	40
Pt5	peatlan	7.7	1	7	5.1	576	64	8.6	1.5	7.1	7.6	660	62	7.1	1.8	6.3	4.2	523	21	7.2	1.7	7.8	4.4	856	148
Pt6	peatlan	7.5	0.6	8	4.3	1177	232	7.9	1.2	6.3	9.4	652	50	7.1	0.8	5.9	3.1	632	125	7.6	0.9	7	4.6	1206	346
Pt7	peatlan	7.6	0.7	8.2	-	612	335	8.2	1.5	7	-	490	61	7.2	1.3	5.5	3.5	755	406	7.5	1	8	3.2	685	28
Pt8	peatlan	7.6	1.1	7.8	6.3	712	104	8.2	1.3	6.4	-	567	39	7.2	1.2	6.2	2.1	2441	280	7.9	1.2	7.6	3.9	732	463
Pt9	peatlan	8.6	4.8	8.1	6.6	562	8	8.1	-	-	12.2	891	70	7.1	2.1	7.5	21.7	1268	14	7.3	-	7.1	5.1	1338	79

Pt10	peatlan	7.8	1	7.1	5.1	865	29	8.5	1.6	-	3	1891	20	7.1	-	7.5	3.4	761	53	-	1.1	7.2	-	815	109

Table S4. pH, DIC, DOC, pCO_2, and FCO_2 of the glacier sites within the YRSR, expressed in the order of April, June, August, and October in 2016.

Name	Land cover types	Apr						Jun						Aug						Oct					
		pH	DIC	DO	DOC	pCO_2	FCO_2	pH	DIC	DO	DOC	pCO_2	FCO_2	pH	DIC	DO	DOC	pCO_2	FCO_2	pH	DIC	DO	DOC	pCO_2	FCO_2
			mmol L^{-1}	mg L^{-1}	mg L^{-1}	μatm	mmol m^{-2} d^{-1}		mmol L^{-1}	mg L^{-1}	mg L^{-1}	μatm	mmol m^{-2} d^{-1}		mmol L^{-1}	mg L^{-1}	mg L^{-1}	μatm	mmol m^{-2} d^{-1}		mmol L^{-1}	mg L^{-1}	mg L^{-1}	μatm	mmol m^{-2} d^{-1}
GL1	glacier	8.4	3.9	7.2	4.4	656	272	-	-	-	-		-	7.6	1.2	8.3	2.1	273	–33	7.2	2.9	9.8	4.8	806	104
GL2	glacier	8.2	1.8	8.7	4.7	859	301	8.6	-	7.5	2	484	19	7.5	-	6.6	-	628	89	7.5	-	7.7	-	711	91
GL3	glacier	8.5	3.1	8.2	4.7	606	36	8.7	2.3	6.8	2.8	492	12	7.3	1.9	6.4	4.5	692	133	7.8	2.5	8	3.9	523	53
GL4	glacier	8.4	3.1	8.1	2.7	514	47	-	-	-	-	-	-	7.5	2.1	6.6	4.5	716	75	7.8	3.1	8.4	4.6	672	75
GL5	glacier	8.5	3.1	7.5	4.1	630	11	-	-	-	-	-	-	7.3	2.2	6.9	2.9	525	255	7.3	-	7.8		441	40
GL6	glacier	8.5	4	7.2	3.9	542	92	8.6	-	6.9	1.2	542	60	7.3	2.8	-	2.2	1592	561	-	2.3	7.9	4	640	144

Table S5. pH, DIC, DOC, pCO_2, and FCO_2 of the permafrost sites within the YRSR, expressed in the order of April, June, August, and October in 2016.

Nam e	Land cover types	Apr						Jun						Aug						Oct					
		pH	DIC	DO	DOC	pCO_2	FCO_2	pH	DIC	DO	DOC	pCO_2	FCO_2	pH	DIC	DO	DOC	pCO_2	FCO_2	pH	DIC	DO	DOC	pCO_2	FCO_2
			mmol L^{-}	mg L^{-}	mg L^{-}	μat	mmol m^{-2} d^{-}		mmol L^{-}	mg L^{-}	mg L^{-}	μat	mmol m^{-2} d^{-}		mmol L^{-}	mg L^{-}	mg L^{-}	μat	mmol m^{-2} d^{-}		mmol L^{-}	mg L^{-}	mg L^{-}	μat	mmol m^{-2} d^{-}
Pm1	permafros	8.	3.2	-	3.4	236	–32	10.	7.4	12.1	-	-	-	7.	2.9	6.7	6.5	560	4	7.	-	8.5	-	936	23
Pm2	permafros	8.	4.1	-	5.5	511	97	8.7	-	6.2	5.1	483	32	7.	3	5.7	8.2	538	62	8.	7.6	6.4	-	927	213
Pm3	permafros	8.	5.2	-	6.3	681	61	9	-	7.2	5	447	10	7.	-	6.9	7.1	554	34	-	4.1	7.2	3.8	365	–8
Pm4	permafros	8.	3.2	8	2.8	495	58	8.5	-	6.7	1.5	508	29	7.	-	6.4	2.5	628	72	-	2.2	8.4	1.1	583	52
Pm5	permafros	8.	4.3	7.7	4.6	688	74	8.7	3.4	6.9	4.8	502	85	7.	3.1	7.4	7.1	726	173	7.	4.4	8	10.6	859	184
Pm6	permafros	8.	2.1	7.3	7.4	181	-50	8.5	2.5	6.2	4.6	989	109	7.	1.8	9.2	6.5	540	22	-	2.6	7	1.4	866	282

Table S6. Mean pH, DO, DOC, pCO_2, and FCO_2 of 4 land cover types.

Land cover type	Time	pH	DIC mmol L^{-1}	DO mg L^{-1}	DOC mg L^{-1}	pCO_2 μatm	FCO_2 mmol m^{-2} d^{-1}
Grassland	April	8.3±0.2	3.9±1.4	7.7±0.7	5.1±2.2	836±258	120±96
	June	8.5±0.2	2.6±0.7	7.2±0.8	5±2.6	609±297	72±52
	August	7.2±0.3	2.7±0.7	6.4±0.5	4.7±2.6	1086±551	227±154
	October	7.4±0.3	3.3±1.3	7.7±0.7	3.8±2	734±253	206±178
Peatland	April	7.9±0.5	2.6±2.2	7.8±0.5	5.7±0.8	875±437	141±108
	June	8.3±0.3	2.2±1	7±0.9	5.5±3.8	792±436	52±31
	August	7.2±0.1	1.9±1	6.6±0.7	5.3±5.9	1156±630	289±472
	October	7.5±0.3	1.9±1.2	7.6±0.5	4.1±1.8	926±285	219±159
glacier	April	8.4±0.1	3.2±0.8	7.8±0.6	4.1±0.7	635±122	127±127
	June	8.6±0.1	2.3±2.3	7.1±0.4	2±0.8	506±31	30±26
	August	7.4±0.1	2±0.6	7±0.8	3.2±1.2	738±449	180±209
	October	7.5±0.3	2.7±0.4	8.3±0.8	4.3±0.4	632±132	85±38
Permafrost	April	8.5±0.2	3.7±1.1	7.7±0.4	5±1.7	465±216	35±61
	June	9±0.8	4.4±2.6	7.6±2.3	4.2±1.5	586±227	53±42
	August	7.2±0.1	2.7±0.6	7.1±1.2	6.3±2	591±74	61±60
	October	7.5±0.5	4.2±2.1	7.6±0.8	4.2±4.4	756±231	124±118

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