Longitudinal discontinuities in riverine greenhouse gas dynamics generated by dams and urban wastewater

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Table S1. Water quality data measured along the Han River by monthly monitoring from July 2014 to July 2015 (n = 11) and in an outlet of the urban tributary Joongnang (HR 12) from May 2015 to December 2017 (n = 13).

Site	pH	DO (mg L^{-1})	EC (μS cm^{-1})	DOC (mg L^{-1})	HIX	FI	$SUVA_{254}$ (L mg-C^{-1} m^{-1})	C1/ DOC	C2/ DOC	C3/ DOC	NO_3-N (mg L^{-1})	NH_4-N (mg L^{-1})	PO_4^{3-} (mg L^{-1})	Chl *a* (μg L^{-1})
HR1	6.85	9.10	40	1.18	7.67	1.26	3.72	0.86	0.98	0.50	1.48	0.01	BDL	0.85
	(0.16)	(1.49)	(5)	(0.68)	(3.13)	(0.04)	(2.11)	(0.18)	(0.17)	(0.08)	(0.60)	(0.02)		(0.39)
HR2	7.33	9.59	148	1.33	4.32	1.40	2.58	0.93	1.29	1.09	4.02	0.04	0.03	3.63
	(0.34)	(1.74)	(41)	(0.37)	(2.08)	(0.06)	(0.72)	(0.19)	(0.24)	(0.36)	(1.19)	(0.04)	(0.06)	(4.14)
HR4	7.31	8.86	98	1.36	4.43	1.29	3.03	0.73	0.96	0.71	1.92	0.01	BDL	6.75
	(0.21)	(1.64)	(20)	(0.40)	(1.78)	(0.03)	(1.83)	(0.20)	(0.23)	(0.12)	(0.42)	(0.02)		(6.02)
HR8	7.43	9.93	122	1.61	2.70	1.35	1.89	0.54	0.83	0.84	1.54	0.03	BDL	6.26
	(0.58)	(1.78)	(19)	(0.20)	(0.73)	(0.02)	(0.50)	(0.15)	(0.20)	(0.11)	(0.41)	(0.05)		(7.59)
HR11	7.77	9.78	197	1.83	2.24	1.40	2.18	0.67	1.05	1.24	2.15	0.04	BDL	9.81
	(0.78)	(1.47)	(41)	(0.22)	(1.04)	(0.04)	(0.33)	(0.18)	(0.22)	(0.25)	(1.39)	(0.04)		(8.23)
HR12	6.71	5.97	538	4.40	2.05	1.70	2.13	1.32	2.31	3.51	6.82	3.99	1.14	5.78
	(0.33)	(1.38)	(95)	(0.70)	(0.88)	(0.08)	(0.33)	(0.17)	(0.38)	(0.74)	(1.45)	(2.13)	(1.35)	(2.70)
HR14	7.42	8.52	263	2.35	2.06	1.53	2.19	0.86	1.41	1.80	2.47	0.54	0.38	27.32
	(0.35)	(1.93)	(69)	(0.28)	(0.70)	(0.06)	(0.30)	(0.13)	(0.17)	(0.29)	(0.75)	(0.25)	(0.19)	(28.29)

Values below detection limits are indicated by BDL. The numbers in parentheses indicate one standard deviation.

Table S2. Summary of water quality data measured during the wet-season survey along the Han River in July 2014.

Site	pH	DO (mg L^{-1})	EC (μS cm^{-1})	DOC (mg L^{-1})	HIX	FI	$SUVA_{254}$ (L mg-C^{-1} m^{-1})	C1/ DOC	C2/ DOC	C3 /DOC	NO_3-N (mg L^{-1})	NH_4-N (mg L^{-1})	PO_4^{3-} (mg L^{-1})	Chl *a* (μg L^{-1})
HR1	6.80	8.85	40	2.49	10.44	1.32	9.85	1.13	1.27	0.56	1.98	BDL	BDL	ND
HR2	7.44	8.22	100	1.73	6.18	1.34	3.55	1.10	1.39	0.83	3.07	0.06	0.14	ND
HR3	7.57	7.1	75	2.08	5.83	1.27	4.01	1.02	1.26	0.80	1.20	0.07	BDL	20.40
HR4	7.22	7.55	91	1.83	5.77	1.28	8.40	1.17	1.49	0.96	1.80	0.06	BDL	16.60
HR5	8.44	8.33	74	1.24	1.59	1.29	1.37	0.20	0.33	0.54	1.31	BDL	BDL	1.60
HR6	8.01	8.7	19	1.60	2.00	1.42	2.10	0.62	1.11	1.75	1.50	0.07	BDL	3.90
HR7	7.6	10.31	105	1.46	1.65	1.36	2.18	0.61	1.15	2.03	1.22	BDL	BDL	13.50
HR8	8.83	11.27	106	1.73	2.74	1.34	1.87	0.49	0.73	0.83	1.30	BDL	BDL	6.80
HR9	9.07	10.5	217	2.02	1.91	1.37	2.51	0.78	1.40	2.48	1.14	BDL	BDL	34.40
HR10	9.27	13.03	223	1,97	2.80	1.37	2.19	0.68	1.12	1.41	0.93	BDL	BDL	7.70
HR11	7.78	9.68	179	1.81	2.43	1.39	1.96	0.64	1.02	1.15	1.20	BDL	BDL	32.00
HR12	6.89	2.2	505	4.39	1.50	1.81	1.99	1.37	2.27	3.55	4.42	4.06	1.31	17.80
HR13	7.06	7.6	236	1.98	2.10	1.53	2.08	0.89	1.53	1.89	1.69	0.25	0.26	10.10
HR14	6.95	7	221	2.15	2.33	1.51	2.11	0.92	1.49	1.73	1.61	0.46	0.61	26.00
HR15	7.06	6.3	558	2.32	0.76	1.49	2.25	1.11	1.88	4.72	0.25	276.08	BDL	42.20

Values below detection limits are indicated by BDL, while ND refers to values not determined.

Table S3. Summary of water quality data measured during dry-season survey along the Han River in May 2015.

Site	pH	DO (mg L^{-1})	EC (μS cm^{-1})	DOC (mg L^{-1})	HIX	FI	$SUVA_{254}$ (L mg-C^{-1} m^{-1})	C1/ DOC	C2/ DOC	C3/ DOC	NO_3-N (mg L^{-1})	NH_4-N (mg L^{-1})	PO_4^{3-} (mg L^{-1})	Chl *a* (μg L^{-1})
HR1	6.98	9.94	39	0.95	8.19	1.22	3.32	0.97	1.06	0.49	1.60	BDL	BDL	BDL
HR2	8.00	10.57	159	1.22	4.32	1.37	2.56	0.93	1.30	1.02	4.06	BDL	BDL	9.13
HR3	7.90	9.02	85	1.23	3.29	1.32	2.55	0.68	0.91	0.94	1.23	0.03	BDL	2.03
HR4	7.42	8.06	99	1.04	3.81	1.28	2.44	0.68	0.94	0.77	1.89	BDL	BDL	0.75
HR5	7.60	10.00	85	1.20	3.17	1.34	1.86	0.44	0.68	0.60	1.52	BDL	BDL	0.66
HR6	8.61	9.90	121	1.67	2.06	1.43	1.73	0.47	0.75	1.10	1.64	BDL	BDL	10.34
HR7	6.76	9.60	122	1.37	2.89	1.40	1.94	0.54	0.82	0.86	1.84	0.05	BDL	1.65
HR8	7.24	7.37	124	1.35	2.38	1.33	1.93	0.49	0.76	0.85	1.94	BDL	BDL	3.62
HR9	8.30	11.42	247	1.69	2.82	1.44	2.02	0.61	0.96	1.00	1.96	BDL	BDL	10.43
HR10	9.00	11.60	198	1.73	2.57	1.39	2.03	0.53	0.84	0.96	1.88	BDL	BDL	5.83
HR11	7.50	7.88	184	1.62	2.32	1.39	2.00	0.58	0.93	1.07	1.96	0.04	BDL	5.96
HR12	6.97	3.47	578	5.14	1.37	1.77	1.99	1.23	2.14	3.49	5.80	6.49	1.88	7.42
HR13	7.52	7.64	272	2.27	1.70	1.55	2.07	0.79	1.32	1.84	2.34	0.80	0.13	11.08
HR14	7.50	8.70	281	2.32	1.55	1.57	1.97	0.76	1.26	1.88	2.12	0.81	0.27	85.10
HR15	7.34	6.24	170	2.41	0.81	1.50	1.80	0.75	1.32	2.62	1.91	111.83	0.09	3.43

Values below detection limits are indicated by BDL, while ND refers to values not determined.

Table S4. Summary of Kendall rank correlation (τ) between all the measurements of GHGs and water quality parameters in the upper, middle, and lower reaches of the Han River.

	pCO_2			CH_4			N_2O		
	Upper	Middle	Lower	Upper	Middle	Lower	Upper	Middle	Lower
pH	-0.19	**-0.64**	**-0.42**	**0.47**	0.24	-0.21	-0.02	-0.13	0.20
DO	-0.20	-0.20	**-0.64**	0.05	-0.04	**-0.27**	0.25	-0.04	0.11
Water Temp.	0.10	**-0.24**	**0.40**	0.28	**0.34**	**0.30**	-0.14	-0.13	**-0.28**
EC	0.20	-0.21	-0.03	**0.42**	0.12	0.03	**0.36**	-0.08	**0.56**
DOC	-0.05	-0.13	0.10	0.15	**0.31**	0.17	0.05	0.00	**0.56**
TSS	0.16	-0.13	**0.24**	**0.52**	0.15	0.08	0.24	0.11	0.12
TA	**0.33**	**-0.24**	-0.08	**0.51**	0.29	0.00	**0.40**	-0.01	**0.66**
Na^+	0.23	**-0.41**	-0.06	**0.52**	**0.33**	0.10	0.22	-0.07	**0.61**
NH_4-N	0.16	0.25	0.13	0.27	0.16	0.21	0.32	0.14	**0.73**
K^+	0.14	**-0.28**	0.06	**0.51**	**0.35**	0.06	0.11	-0.04	**0.67**
Ca^{2+}	0.21	-0.23	0.01	**0.53**	**0.36**	0.04	0.27	-0.09	**0.48**
Mg^{2+}	0.17	**-0.28**	-0.07	**0.53**	**0.33**	-0.01	0.22	-0.14	**0.61**
F^-	0.06	0.00	**0.26**	-0.30	**0.34**	0.20	-0.06	0.13	**-0.23**
Cl^-	0.12	**-0.33**	-0.01	**0.54**	**0.44**	0.09	0.26	-0.04	**0.58**
Br^-	**0.27**	-0.16	**0.28**	0.20	0.19	-0.05	0.21	-0.10	-0.15
NO_3-N	0.18	0.08	**-0.23**	0.28	0.15	0.01	**0.42**	0.14	**0.49**
PO_4^{3-}	0.16	1.00	**0.47**	1.00	1.00	**0.36**	1.00	1.00	0.13
SO_4^{2-}	0.03	**-0.24**	0.07	**0.45**	0.26	-0.05	0.05	-0.10	**0.51**
FI	**0.26**	-0.13	-0.07	**0.53**	0.25	0.11	**0.41**	**0.34**	**0.67**
HIX	-0.07	**0.31**	**0.23**	-0.29	-0.10	0.04	-0.10	0.05	**-0.49**
$SUVA_{254}$	-0.08	0.23	**0.28**	-0.25	0.00	0.19	-0.21	0.13	**-0.40**
C1/DOC	0.11	**0.27**	**0.62**	-0.01	-0.05	**0.38**	0.11	0.17	-0.11
C2/DOC	0.21	**0.26**	**0.61**	0.19	-0.07	**0.36**	0.15	0.16	0.08
C3/DOC	0.19	-0.14	0.00	**0.47**	0.16	0.09	**0.33**	0.19	**0.66**
Chl *a*	-0.16	-0.11	**-0.27**	0.19	0.25	0.05	-0.05	-0.03	0.21

All data collected in two basin-wide surveys, monthly samplings, a cruise, and tributary samplings were analyzed separately for each of three reaches. Significant correlations at $P < 0.05$ are indicated by bold numbers.

Table S5. Summary of three GHGs and water quality data measured along the tributary Joongnang (JN; HR12) during two synoptic samplings.

Site	Coordinates	Distance from the confluence (km)	pCO_2 (µatm)	CH_4 (nmol L^{-1})	N_2O (nmol L^{-1})	pH	DO (mg L^{-1})	EC (µS cm^{-1})	DOC (mg L^{-1})	HIX	FI	$SUVA_{254}$ (L mg-C^{-1} m^{-1})	C1/ DOC	C2/ DOC	C3/ DOC	NO_3-N (mg L^{-1})	NH_4-N (mg L^{-1})	PO_4^{3-} (mg L^{-1})
November 2015																		
Forested headwater stream	37°48', 127°1'	36	2759	4.7	25.8	6.53	8.88	71	0.97	3.41	1.33	2.30	0.68	0.79	0.50	3.19	BDL	BDL
Peri-urban	37°48', 127°2'	34	2151	713.7	44.1	6.63	8.51	276	2.12	4.73	1.37	2.61	0.96	1.22	1.21	2.64	0.26	0.24
Peri-urban	37°46', 127°2'	31	4160	65.8	75.8	4.20	8.03	355	2.07	3.99	1.48	2.26	1.11	1.69	1.30	2.80	0.12	0.21
Urban	37°44', 127°3'	26	3785	5436.8	88.4	7.20	7.03	440	3.82	2.02	1.55	1.99	1.21	1.87	2.69	3.56	1.66	0.50
Urban	37°41', 127°3'	20	3400	279.2	56.6	6.13	8.40	517	3.15	2.43	1.67	2.10	1.36	2.46	2.95	5.63	0.30	BDL
Urban	37°38', 127°3'	14	3610	5837.7	65.3	6.44	5.40	592	3.67	1.82	1.63	2.14	1.17	1.90	2.79	3.89	1.91	0.32
Urban	37°34', 127°4'	7	1952	1827.8	32.0	7.04	7.00	515	2.47	2.30	1.65	2.10	1.08	1.95	2.19	5.10	0.13	BDL
WWTP	37°33', 127°3'	4	11758	424.9	487.0	6.72	6.88	663	5.03	1.42	1.77	2.07	1.44	2.59	3.72	7.31	6.41	4.38
Urban	37°33', 127°2'	2	8219	1170.9	400.1	6.70	5.81	607	4.21	1.46	1.74	2.02	1.31	2.38	3.46	7.00	3.67	3.48
May 2016																		
Forested headwater stream	37°48', 127°1'	36	1239	10.0	15.7	6.07	10.15	58	0.56	5.88	1.36	2.17	0.67	0.91	0.50	2.69	0.03	BDL
Peri-urban	37°48', 127°2'	34	1142	101.9	19.8	6.56	9.07	151	1.14	4.71	1.31	2.70	0.98	1.24	0.95	2.57	0.06	BDL
Peri-urban	37°46', 127°2'	31	2987	80.2	46.2	7.02	7.30	273	1.66	3.52	1.49	2.39	1.11	1.63	1.36	2.44	0.14	BDL
Urban	37°44', 127°3'	26	1712	495.9	26.4	7.39	8.80	349	2.08	2.57	1.53	2.26	1.02	1.62	1.84	3.28	0.19	BDL
Urban	37°41', 127°3'	20	6192	353.2	98.1	6.63	7.65	431	2.69	1.82	1.63	2.29	1.08	1.96	2.77	5.22	0.48	0.22
Urban	37°38', 127°3'	14	1489	2746.2	39.2	7.37	7.50	421	2.50	1.97	1.56	2.53	0.98	1.70	2.27	4.89	0.37	0.18
Urban	37°34', 127°4'	7	2667	5198.2	23.0	7.07	7.70	405	2.42	2.02	1.60	2.42	1.03	1.80	2.30	4.68	0.46	BDL
WWTP	37°33', 127°3'	4	11827	1908.0	285.7	6.00	6.61	631	4.64	1.21	1.71	2.16	1.44	2.67	4.44	7.20	9.57	0.32
Urban	37°33', 127°2'	2	8598	2488.9	218.5	6.70	6.49	536	3.90	1.16	1.72	2.17	1.16	2.16	3.81	6.50	5.10	0.26

Values below detection limits are indicated by BDL.

Table S6. $\delta^{13}C$ and $\Delta^{14}C$ measured in the dissolved organic matter collected along the Han River (HR1, HR4, HR8, HR11, HR14), the urban tributary Joongnang (JN), and wastewater treatment plant (WWTP) effluents.

Site	Age (years B.P.)	$\Delta^{14}C_{DOC}$ (‰)	$\delta^{13}C_{DOC}$ (‰)
July 2014			
HR1	Modern	58.91	-28.16
HR4	115	-22.08	-26.09
HR8	300	-43.92	-21.51
HR11	Modern	66.84	-26.41
HR12 (JN)	1050	-129.07	-24.98
HR14	590	-78.21	-20.58
WWTP effluent	765	-97.87	-25.75
May 2015			
HR1	180	-29.56	-28.16
HR4	635	-83.24	-20.34
HR8	350	-49.91	-26.91
HR11	540	-72.30	-26.79
HR12 (JN)	850	-107.61	-23.61
HR14	675	-87.87	-23.18
WWTP effluent	905	-113.48	-25.79

Table S7. Summary of three GHGs and water quality data measured along the lower Han River during a boat cruise in June 2016.

Coordinates	Distance to mouth (km)	pCO_2 (μatm)	CH_4 (nmol L^{-1})	N_2O (nmol L^{-1})	pH	DO (mg L^{-1})	EC (μS cm^{-1})	DOC (mg L^{-1})	HIX	FI	$SUVA_{254}$ (L mg-C^{-1} m^{-1})	C1/ DOC	C2/ DOC	C3/ DOC	NO_3-N (mg L^{-1})	NH_4-N (mg L^{-1})	PO_4^{3-} (mg L^{-1})	Chl *a* (μg L^{-1})
Mainstem																		
37°33'N, 127°7'E	76	289	870.2	16.6	7.80	ND	149	1.88	2.43	1.39	1.90	0.47	0.73	0.86	1.33	0.13	BDL	13.92
37°31'N, 127°5'E	69	89	135.7	11.4	7.45	10.67	164	1.92	2.09	1.44	1.81	0.48	0.79	0.92	1.40	0.07	BDL	7.29
37°32'N, 127°2'E	67	774	695.9	47.1	7.36	9.95	210	1.99	1.97	1.53	1.89	0.69	1.20	1.40	1.84	0.26	BDL	8.48
37°32'N, 127°1'E	64	7979	3088.2	199.4	ND	5.87	556	4.16	1.23	1.75	2.11	1.16	2.20	3.70	5.43	7.30	0.31	ND
37°31'N, 127°0'E	63	1661	ND	ND	ND	8.59	224	2.07	1.65	1.58	2.00	0.72	1.26	1.64	1.99	0.73	BDL	11.54
37°31'N, 126°57'E	57	2713	1758.5	69.7	ND	7.67	243	2.03	1.63	1.56	0.39	0.81	1.44	1.83	2.47	0.58	0.18	5.99
37°32'N, 126°55'E	53	2741	1257.3	88.5	ND	7.15	253	2.11	1.81	1.56	2.07	0.86	1.53	1.84	2.32	0.62	0.21	18.89
37°33'N, 126°53'E	50	2150	776.2	78.7	7.40	7.21	262	2.08	1.88	1.57	2.08	0.87	1.53	1.82	2.28	0.53	0.21	23.37
Tributary																		
37°30'N, 127°5'E	68	4828	368.9	181.3	5.87	ND	520	3.79	1.68	1.67	2.19	1.13	2.15	3.03	4.49	0.60	0.18	6.43
37°33'N, 127°2'E	66	8206	1320.5	165.7	5.78	ND	524	3.86	1.24	1.79	2.11	1.26	2.42	4.01	6.19	6.42	0.23	5.83
37°32'N, 126°52'E	48	2120	4344.9	389.9	7.36	ND	656	4.74	0.94	1.72	2.16	1.01	1.96	3.48	5.95	0.93	BDL	60.04

Values below detection limits are indicated by BDL, while ND refers to values not determined.

Table S8. $\delta^{13}C$ in dissolved CO_2 and CH_4 collected during a boat cruise conducted along the lower Han River in June 2016.

Coordinates	Distance to mouth (km)	$\delta^{13}C_{CO2}$ (‰)	$\delta^{13}C_{CH4}$ (‰)
Mainstem			
37°33'N, 127°7'E	76	-20.87	-43.78
37°31'N, 127°5'E	69	ND	-36.59
37°32'N, 127°2'E	67	- 19.15	ND
37°32'N, 127°1'E	64	-18.04	-48.62
37°31'N, 127°0'E	63	-17.73	ND
37°31'N, 126°57'E	57	-17.39	-36.38
37°32'N, 126°55'E	53	-16.68	-35.60
37°33'N, 126°53'E	50	-16.73	-32.59
Tributary			
37°30'N, 127°5'E	68	-18.33	-52.14
37°33'N, 127°2'E	66	-18.20	-45.89
37°32'N, 126°52'E	48	-14.69	-45.86

ND indicates values not determined.

S2: Supplementary figure

Fig. S1. Seasonal mean concentrations of 3 GHGs measured at 6 sites across the Han River basin. Error bars indicate one standard deviation. Monitored seasons include: summer (July 2014 and June and July 2015 for CO_2; and June and July 2015 for CH_4 and N_2O), fall (September–November 2014), winter (December 2014), and spring (March–May 2015 for CO_2; March 2015 for CH_4 and N_2O). Note that CH_4 concentrations at HR1 were lower than 10 nmol L^{-1}.

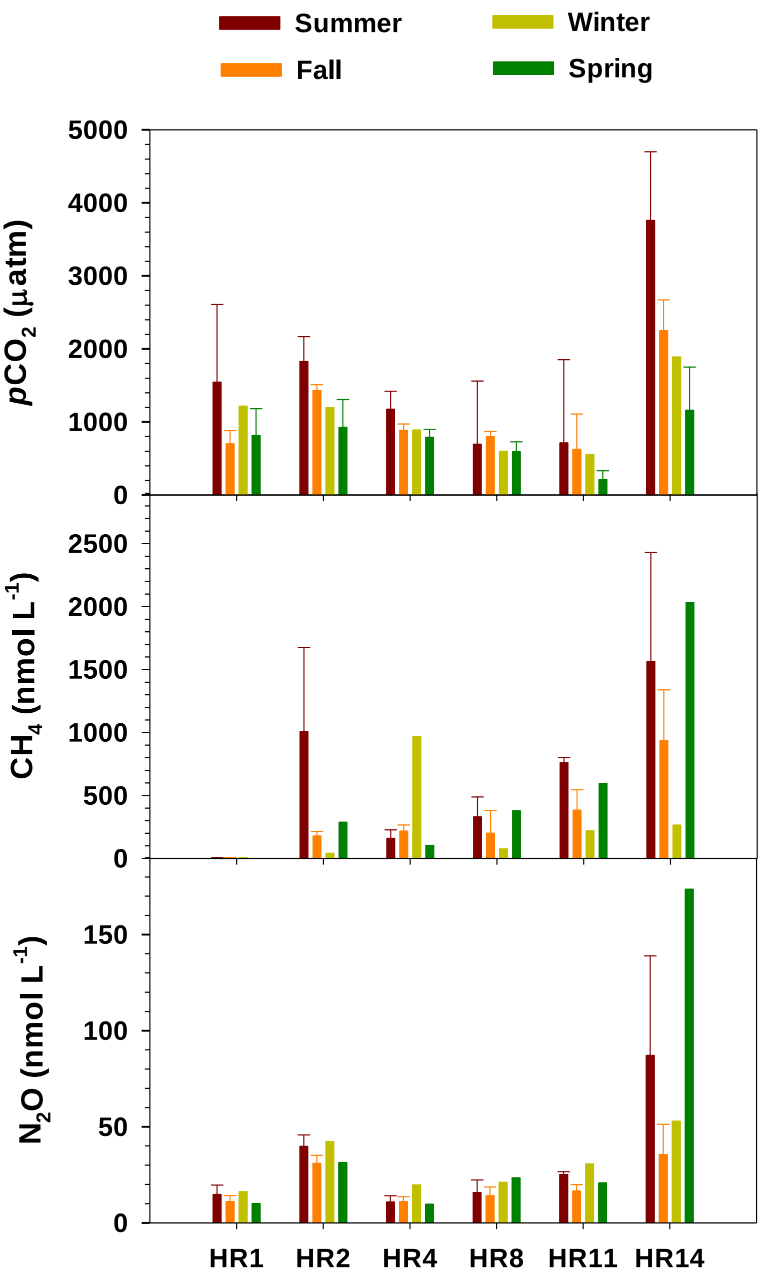
Summer
Winter
Fall
Spring
5000
4000
3000
2000
1000
0
pCO2 (µatm)
2500
2000
1500
1000
500
0
CH4 (nmol L-1)
150
100
50
0
N2O (nmol L-1)
HR1
HR2
HR4
HR8
HR11
HR14

Fig. **S1**