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

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S1: Supplementary tables

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})	TA (µeq L^{-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	112	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)	(55)	(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	591	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)	(189)	(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	367	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)	(112)	(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	542	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)	(125)	(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	897	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)	(207)	(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	1406	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)	(303)	(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	1039	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)	(179)	(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 ($\mu S\ cm^{-1}$)	TA ($\mu eq\ L^{-1}$)	DOC ($mg\ L^{-1}$)	HIX	FI	$SUVA_{254}$ ($L\ mg\text{-}C^{-1}\ m^{-1}$)	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* ($\mu g\ L^{-1}$)
HR1	6.80	8.85	40	73	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	463	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	187	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	418	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	343	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	552	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	532	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	556	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	1166	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	1287	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	912	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	1025	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	1057	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	1021	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	1023	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 ($\mu S\ cm^{-1}$)	TA ($\mu eq\ L^{-1}$)	DOC ($mg\ L^{-1}$)	HIX	FI	$SUVA_{254}$ ($L\ mg\text{-}C^{-1}\ m^{-1}$)	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* ($\mu g\ L^{-1}$)
HR1	6.98	9.94	39	83	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	631	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	360	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	346	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	342	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	502	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	523	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	481	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	1231	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	896	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	823	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	1754	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	1106	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	1116	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	1483	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
EC	0.20	-0.21	-0.03	**0.42**	0.12	0.03	**0.36**	-0.08	**0.56**
Water Temp.	0.10	**-0.24**	**0.40**	0.28	**0.34**	**0.30**	-0.14	-0.13	**-0.28**
TA	**0.33**	**-0.24**	-0.08	**0.51**	0.29	0.00	**0.40**	-0.01	**0.66**
TSS	0.16	-0.13	**0.24**	**0.52**	0.15	0.08	0.24	0.11	0.12
DOC	-0.05	-0.13	0.10	0.15	**0.31**	0.17	0.05	0.00	**0.56**
HIX	-0.07	**0.31**	**0.23**	-0.29	-0.10	0.04	-0.10	0.05	**-0.49**
FI	**0.26**	-0.13	-0.07	**0.53**	0.25	0.11	**0.41**	**0.34**	**0.67**
$SUVA_{254}$	-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**
NH_4^+-N	0.16	0.25	0.13	0.27	0.16	0.21	0.32	0.14	**0.73**
NO_3^--N	0.18	0.08	**-0.23**	0.28	0.15	0.01	**0.42**	0.14	**0.49**
PO_4^{3-}	NA	NA	**0.47**	NA	NA	**0.36**	NA	NA	0.13
Chl *a*	-0.16	-0.11	**-0.27**	0.19	0.25	0.05	-0.05	-0.03	0.21
Na^+	0.23	**-0.41**	-0.06	**0.52**	**0.33**	0.10	0.22	-0.07	**0.61**
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
SO_4^{2-}	0.03	**-0.24**	0.07	**0.45**	0.26	-0.05	0.05	-0.10	**0.51**

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. NA indicates that correlation analysis results were not available for PO_4^{3-} in the upper and middle reaches due to many values below detection limit.

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})	TA (μeq L-1)	DOC (mg L^{-1})	HIX	FI	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	112	0.97	3.41	1.33	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	735	2.12	4.73	1.37	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	1267	2.07	3.99	1.48	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	1449	3.82	2.02	1.55	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	1308	3.15	2.43	1.67	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	1277	3.67	1.82	1.63	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	1408	2.47	2.30	1.65	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	1806	5.03	1.42	1.77	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	1524	4.21	1.46	1.74	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	106	0.56	5.88	1.36	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	543	1.14	4.71	1.31	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	1145	1.66	3.52	1.49	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	1399	2.08	2.57	1.53	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	1239	2.69	1.82	1.63	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	1239	2.50	1.97	1.56	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	1169	2.42	2.02	1.60	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	1843	4.64	1.21	1.71	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	1496	3.90	1.16	1.72	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.

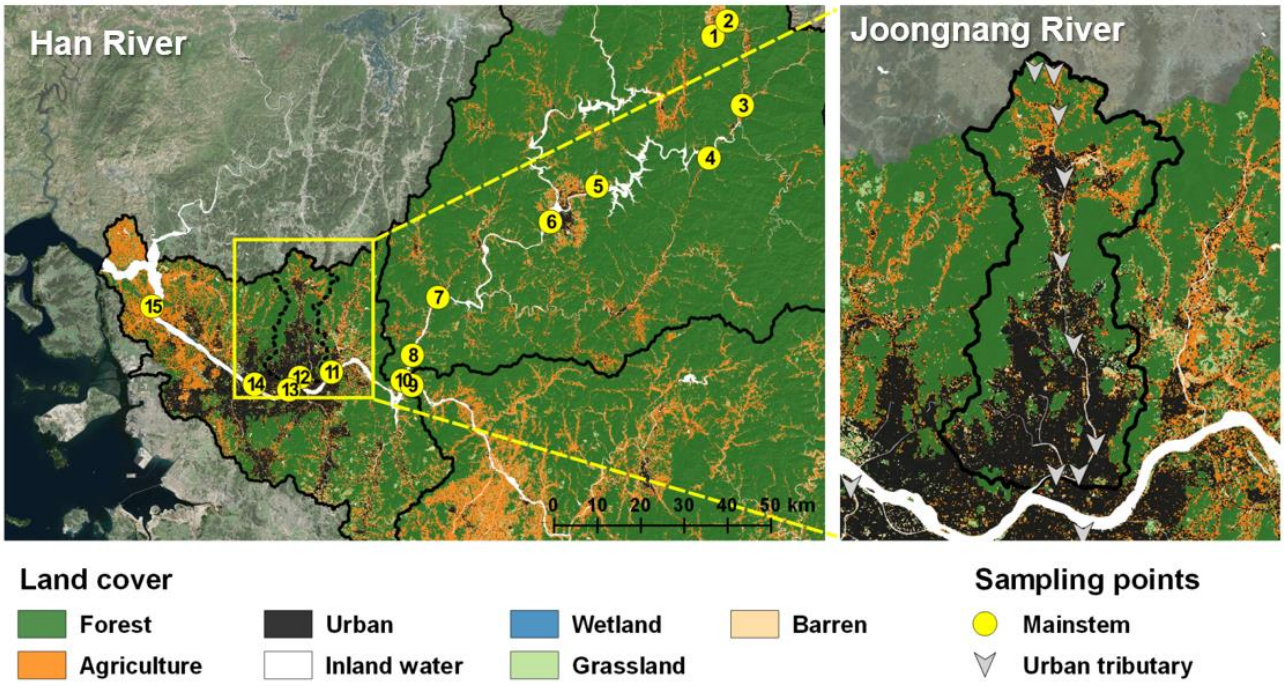
Coordinates	Distance to mouth (km)	pCO_2 (μatm)	CH_4 (nmol L^{-1})	N_2O (nmol L^{-1})	pH	DO (mg L^{-1})	EC (μS cm^{-1})	TA (μeq L^{-1})	DOC (mg L^{-1})	HIX	FI	C1/ DOC	C2/ DOC	C3/ DOC	NO_3^--N (mg L^{-1})	NH_4^+-N (mg L^{-1})	PO_4^{3-} (mg L^{-1})	Chl a (μg L^{-1})
Mainstem																		
37°33'N, 127°7'E	76	289	870.2	16.6	7.80	ND	149	813	1.88	2.43	1.39	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	706	1.92	2.09	1.44	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	904	1.99	1.97	1.53	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	7.01	5.87	556	ND	4.16	1.23	1.75	1.16	2.20	3.70	5.43	7.30	0.31	ND
37°31'N, 127°0'E	63	1661	ND	ND	7.02	8.59	224	989	2.07	1.65	1.58	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	7.20	7.67	243	1002	2.03	1.63	1.56	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	7.17	7.15	253	1013	2.11	1.81	1.56	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	1016	2.08	1.88	1.57	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	1664	3.79	1.68	1.67	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	1654	3.86	1.24	1.79	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	1279	4.74	0.94	1.72	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.



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49 **Fig S1**. Site map showing 7 major land cover types in the Han River basin and the sub-catchment of the urban tributary

50 (Joongnang).

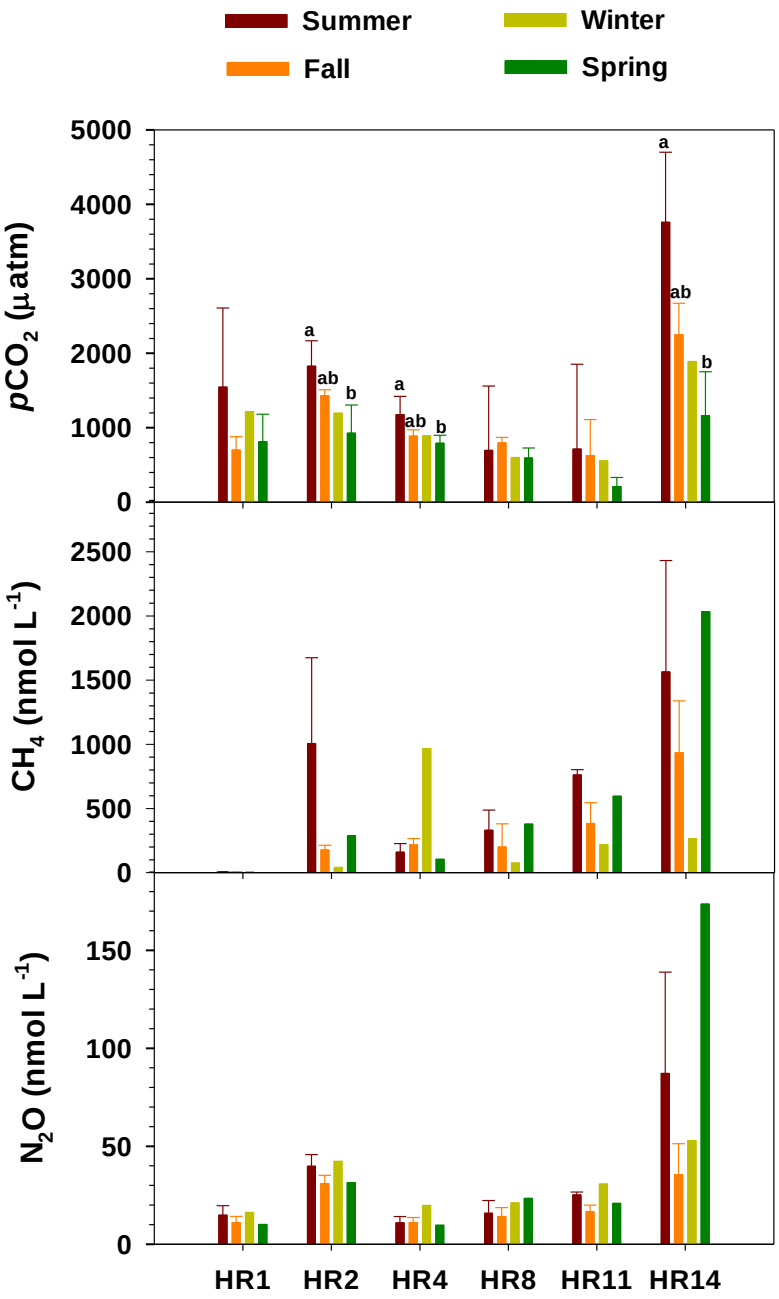
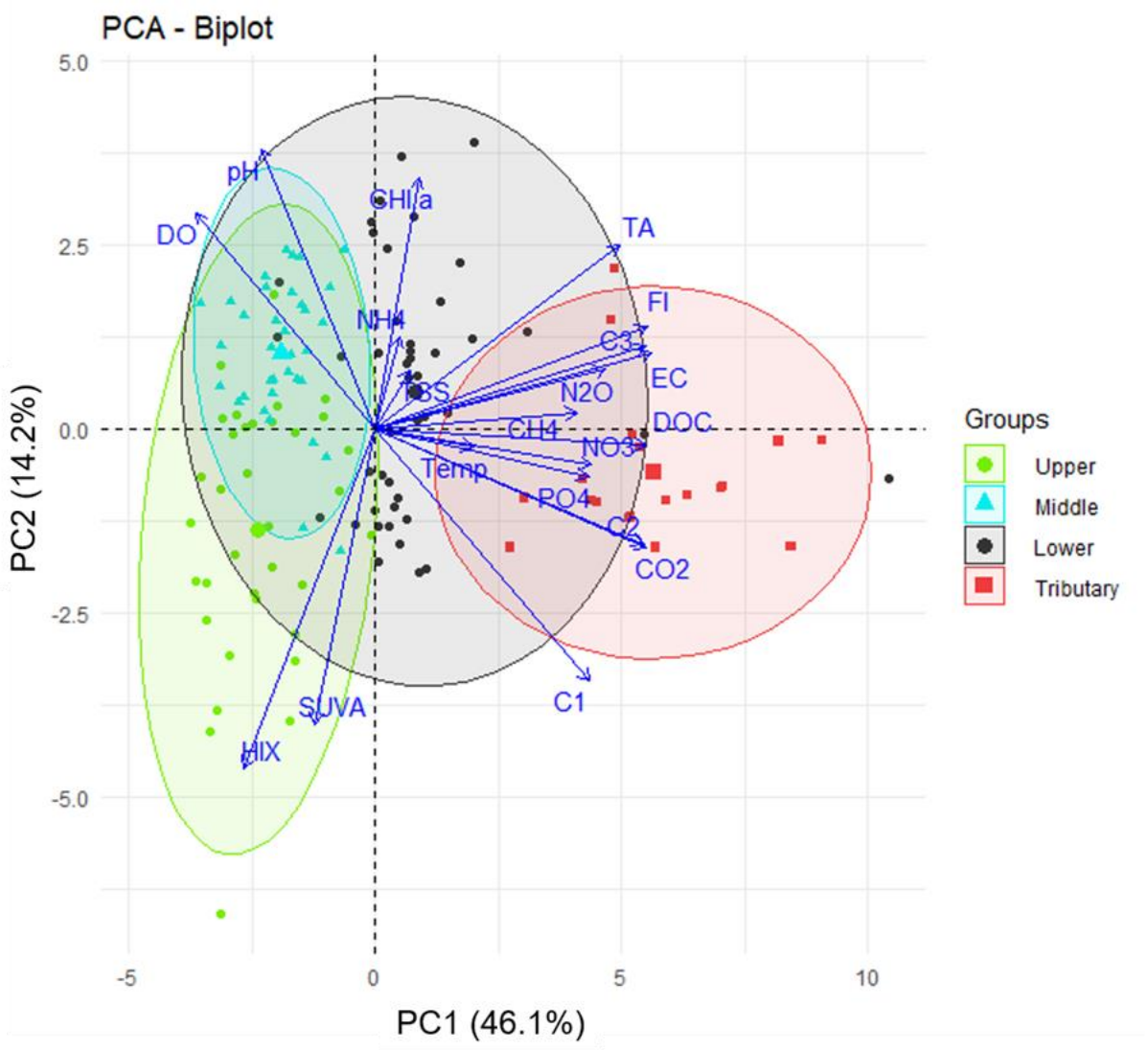


Fig. **S2.** Comparison of seasonal mean pCO_2,CH_4, and N_2O. Error bars indicate one standard deviation, except for one-time measurement in winter (pCO_2, CH_4, and N_2O) and and spring (CH_4, and N_2O). Seasoanl mean was calculate from two-year measurements in summer (July 2014, August 2014, June 2015), and one-year measurements in fall (September, October, and November 2014) and spring (March, April, and May 2015). Significant seasonal differences in pCO_2 were analyzed by the non-parametric Kruskal-Wallis analysis of variance follwed by Dunn's multiple comparisons.



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60 **Fig. S3.** Reach-based grouping of all measurements in the upper, middle, and lower reaches of the Han River and three

61 urban tributaries (TC, JN, and AY) along two major components identified by principal component analysis (PCA).