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S1: Supplementary tables

Table S1. Locations and descriptions of the sampling sites. Two samples that were used in the second incubation experiment are indicated by asterisks.

Site	Local name	Description	Coordinates		Elev. (m)	Distance to mouth (km)	River width (m)
			Latitude	Longitude			
Up 1	Haean forest	Forested headwater stream	38°15'N	128°70'E	582	299	< 1
Up 2	Inbuk Stream	Agricultural stream	38°60'N	128°11'E	220	255	60
Up 3	Soyang River	A major tributary to North Han River	38°00'N	128°60'E	183	234	600
Mid 1	Lake Uiam	A reservoir along the North Han River	37°52'N	127°41'E	75	172	1400
Mid 2	North Han River	Inflow to Lake Paldang	37°36'N	127°20'E	30	108	430
Mid 3	Lake Paldang	The most downstream reservoir receiving the North and South Han River	37°30'N	127°18'E	30	97	830
Mainstem*	Amsa	Han River upstream of Down 1	37°33'N	127°70'E	9	76	700
Down 1	Jamwon	Han River	37°31'N	127°10'E	7	63	910
Down 2	Bamseom	Han River	37°32'N	126°55'E	5	53	860
Down 3	Gimpo	Han River	37°41'N	126°39'E	2	23	875
Urban 1	Tan Stream	Urban stream	37°30'N	127° 40'E	10	78	80
Urban 2 (Tributary*)	Jungnang Stream	Urban stream	37°33'N	127° 20'E	11	67	80
Urban 3	Anyang Stream	Urban stream	37°32'N	126°53'E	8	60	60

Table S2. Summary of optical indices.

Parameter	Calculation	Description
Humification Index	Determined by dividing the peak area under Em 435-480 nm divided by the peak area under Em 300-345 nm at Ex 254 nm (Zsolnay et al., 1999).	Indicator of level of humic substance in OM or extent of humification. Usual value for terrestrial and microbially derived DOM is >16 and <4 respectively (Huguet et al., 2009).
Fluorescence Index	Measured as the ratio of Em intensity between 450 nm and 500 nm at Ex 370 nm (McKnight et al., 2001).	Indicator of the source of DOM from terrestrial (1.4) or microbial (1.9) sources (McKnight et al., 2001).
Biological Index	Measured as the ratio between Em intensity at 380 nm and maximum Em intensity observed between 420-435 nm at Ex 310 nm (Parlanti et al., 2000; Wilson and Xenopoulos, 2009).	Indicator of extent of recently produced DOM from biological activities. Values >1 and <0.6 indicates DOM from microbial and terrestrial origin respectively (Huguet et al., 2009).
Humic-like component	Measured as Em intensity at 467 nm at Ex 325 nm (Fellman et al., 2010).	High molecular weight and aromatic humic substance, common in terrestrial environments (Fellman et al., 2010).
Microbial humic-like component	Measured as Em intensity at 404 nm at Ex 315 nm (Fellman et al., 2010).	Low molecular weight humic substance associated with biological activities, common in marine, agricultural, wastewater, and wetland environment (Fellman et al., 2010).

Protein-like component	Measured at Em intensity at 354 nm at Ex 275 nm (Fellman et al., 2010).	Amino acids, proteins and peptides associated with biological activity, indicator of water quality and DOM cycling rate (Fellman et al., 2010).
a_{254}, a_{350}, $SUVA_{254}$, $SUVA_{350}$	UV absorption coefficients (a_{254}, a_{350}) are calculated by: $a = 2.303A/l$, where A = absorbance and l = path length in meters (Helms et al., 2008). Specific UV absorbance is determined by dividing the absorption coefficients at 254 and 350 nm by DOC concentration (Weishaar et al., 2003).	a_{350} can be used as a proxy for DOC concentration and lignin phenol contents of OM (Spencer et al., 2012) and $SUVA_{254}$ is an indicator of the aromaticity and reactivity of OM in aquatic environment (Weishaar et al., 2003).
$S_{275-295}$, $S_{350-450}$, S_R	Calculated using linear regression of the log transformed absorbance coefficients (a) at the intervals of 275-295 nm and 350-400 nm spectra (Helms et al., 2008).	Indicator of source, molecular weight, aromaticity of OM in the aquatic environment. Higher slope ratios indicate high molecular weight, aromatic terrestrial DOM (Spencer et al., 2012).

Table S3a. Summary of the concentrations and fluorescence characteristics of DOM in the filtered samples from the Han River watershed before and after 7-day incubation. Values are mean of three sites in up-, mid-, and downstream mainstem sites, and three urban stream tributaries followed by standard deviations in parentheses.

Sample Name		DOC (mg L^{-1})	BDOC (mg L^{-1})	C1 (Ex/Em: 325/467)	C2 (Ex/Em: 315/404)	C3 (Ex/Em: 275/354)	C2:C1	C3:C1	C3:C2	%C1	%C2	%C3	FI	HIX	BIX
Initial	Up	1.06 (0.12)		0.84 (0.09)	1.05 (0.07)	1.23 (0.47)	1.26 (0.13)	1.43 (0.40)	1.17 (0.46)	27.22 (2.19)	29.90 (2.86)	30.66 (5.85)	1.29 (0.06)	5.11 (2.60)	0.77 (0.07)
	Mid	1.65 (0.20)		0.76 (0.13)	1.20 (0.21)	1.52 (0.38)	1.58 (0.01)	1.97 (0.30)	1.25 (0.20)	22.03 (1.38)	27.95 (2.13)	29.62 (4.24)	1.39 (0.05)	2.35 (0.31)	0.97 (0.05)
	Down	2.31 (0.09)		1.76 (0.06)	3.01 (0.15)	5.09 (1.47)	1.71 (0.08)	2.91 (0.87)	1.69 (0.42)	18.11 (2.79)	31.05 (3.78)	52.14 (1.98)	1.54 (0.04)	1.33 (0.52)	1.13 (0.07)
	Urban	5.34 (0.77)		5.73 (0.99)	10.05 (1.82)	17.02 (5.51)	1.76 (0.12)	3.00 (1.04)	1.69 (0.47)	17.85 (3.57)	35.56 (5.77)	77.68 (3.25)	1.65 (0.10)	1.67 (0.71)	1.18 (0.13)
Post-incubation	Up	0.99 (0.06)	0.07 (0.06)	0.85 (0.08)	1.09 (0.10)	0.69 (0.20)	1.28 (0.15)	0.82 (0.25)	0.63 (0.13)	32.67 (4.61)	35.74 (2.68)	24.58 (2.36)	1.28 (0.06)	5.54 (1.84)	0.76 (0.09)
	Mid	1.47 (0.15)	0.19 (0.05)	0.79 (0.12)	1.29 (0.19)	1.29 (0.15)	1.63 (0.04)	1.64 (0.17)	1.00 (0.08)	23.49 (1.12)	30.60 (2.45)	28.28 (2.60)	1.40 (0.05)	2.63 (0.46)	0.99 (0.06)
	Down	2.16 (0.05)	0.15 (0.13)	1.77 (0.05)	3.05 (0.18)	4.57 (1.44)	1.72 (0.06)	2.57 (0.75)	1.49 (0.38)	19.16 (2.70)	33.06 (3.76)	51.07 (2.84)	1.53 (0.04)	1.50 (0.59)	1.13 (0.06)
	Urban	4.52 (0.69)	0.82 (0.18)	5.69 (1.17)	10.04 (2.06)	14.72 (5.15)	1.77 (0.13)	2.59 (0.89)	1.45 (0.39)	19.11 (3.48)	38.58 (5.44)	76.41 (4.33)	1.67 (0.09)	1.94 (0.75)	1.16 (0.11)

Table S3b. Summary of the concentrations and absorption indices of DOM in the unfiltered samples before and after 7-day incubation. Values are mean of three sites in up-, mid-, and downstream, and three urban stream tributaries followed by standard deviations in parentheses.

Sample Name		TSS (mg L^{-1})	pCO_2 (µatm)	DOC (mg L^{-1})	BDOC (mg L^{-1})	$S_{275\text{-}295}$ (nm^{-1})	$S_{350\text{-}400}$ (nm^{-1})	S_R	a_{254} (m^{-1})	a_{350} (m^{-1})	$SUVA_{254}$ (L (mg C)$^{-1}$ m^{-1})	$SUVA_{350}$ (L (mg C)$^{-1}$ m^{-1})
Initial	Up	2.00 (1.06)	516 (338)	1.06 (0.12)		0.011 (0.001)	0.011 (0.000)	1.00 (0.133)	7.28 (0.93)	2.47 (0.32)	6.96 (1.40)	2.36 (0.46)
	Mid	3.40 (0.60)	376 (342)	1.65 (0.20)		0.014 (0.001)	0.009 (0.001)	1.54 (0.107)	7.69 (0.63)	2.19 (0.15)	4.66 (0.19)	1.33 (0.09)
	Down	120.73 (197.86)	1946 (449)	2.31 (0.09)		0.016 (0.000)	0.017 (0.001)	1.00 (0.100)	10.59 (0.33)	2.47 (0.24)	4.58 (0.23)	1.07 (0.08)
	Urban	21.27 (19.90)	7895 (5025)	5.34 (0.77)		0.014 (0.001)	0.015 (0.001)	0.97 (0.023)	24.85 (2.37)	6.58 (1.28)	4.75 (1.12)	1.27 (0.43)
Post-incubation	Up	0.00 (3.31)		0.99 (0.06)	0.07 (0.06)	0.019 (0.003)	0.027 (0.026)	1.50 (1.483)	5.96 (0.24)	0.47 (0.17)	6.05 (0.61)	0.48 (0.19)
	Mid	1.25 (1.25)		1.47 (0.15)	0.19 (0.05)	0.017 (0.004)	0.013 (0.005)	1.22 (0.288)	6.96 (1.29)	1.34 (1.01)	4.74 (0.56)	0.91 (0.64)
	Down	7.92 (11.55)		2.16 (0.05)	0.15 (0.13)	0.012 (0.000)	0.010 (0.001)	1.25 (0.090)	11.30 (0.21)	3.33 (0.09)	5.23 (0.03)	1.54 (0.07)
	Urban	0.83 (1.91)		4.52 (0.69)	0.82 (0.18)	0.013 (0.000)	0.013 (0.002)	0.98 (0.122)	23.12 (0.89)	6.91 (0.43)	5.18 (0.69)	1.54 (0.17)

Table S4a. Changes in the mean concentrations and fluorescence characteristics of DOM in mainstem, tributary and mixture sample during the 5-day incubation.

Sample name		DOC (mg L^{-1})	BDOC (mg L^{-1})	C1 (Ex/Em: 325/467)	C2 (Ex/Em: 315/404)	C3 (Ex/Em: 275/354)	C2:C1	C3:C1	C3:C2	FI	HIX	BIX
Mainstem	0 h	2.01	0.00	1.00	1.71	3.21	1.72	3.22	1.87	1.41	1.00	1.14
	1 h	1.98	0.03	1.00	1.68	3.10	1.67	3.09	1.85	1.42	1.03	1.11
	1 day	1.92	0.09	1.01	1.72	3.05	1.71	3.03	1.77	1.43	1.03	1.11
	3 day	1.86	0.15	1.01	1.72	2.93	1.70	2.89	1.71	1.45	1.05	1.10
	5 day	1.81	0.20	1.03	1.77	2.99	1.72	2.90	1.69	1.44	1.07	1.12
Tributary	0 h	4.65	0.00	6.35	11.41	17.68	1.80	2.79	1.55	1.76	1.51	1.27
	1 h	4.60	0.06	6.41	11.58	17.54	1.81	2.74	1.51	1.76	1.53	1.26
	1 day	4.56	0.10	6.75	12.09	18.46	1.79	2.74	1.53	1.77	1.53	1.26
	3 day	4.45	0.20	6.52	11.65	17.28	1.79	2.65	1.48	1.77	1.56	1.26
	5 day	4.19	0.46	6.60	11.72	16.97	1.78	2.57	1.45	1.81	1.60	1.26
Mixture	0 h	3.25	0.00	3.82	6.85	10.85	1.79	2.84	1.58	1.73	1.38	1.24
	1 h	3.26	-0.01	3.72	6.65	10.43	1.78	2.80	1.57	1.72	1.41	1.24
	1 day	3.25	0.00	3.84	6.84	10.71	1.78	2.79	1.57	1.74	1.40	1.26

	3 day	3.10	0.15	3.77	6.70	10.10	1.78	2.68	1.51	1.73	1.47	1.24
	5 day	2.95	0.30	3.87	6.89	10.18	1.78	2.63	1.48	1.75	1.50	1.24

Table S4b. Changes in the concentrations and absorbance indices of DOM in mainstem, tributary and mixture sample during the 5-day incubation.

Sample name		TSS	DOC (mg L^{-1})	BDOC (mg L^{-1})	% BDOC	$S_{275\text{-}295}$ (nm^{-1})	$S_{350\text{-}400}$ (nm^{-1})	S_R	a_{254} (m^{-1})	a_{350} (m^{-1})	$SUVA_{254}$ (L (mg C)$^{-1}$ m^{-1})	$SUVA_{350}$ (L (mg C)$^{-1}$ m^{-1})
	0 h	0.00	2.01			0.031	0.038	0.79	7.55	0.02	3.76	0.01
	1 h	0.00	1.98	0.03	1.56	0.027	0.012	2.43	7.50	0.12	3.79	0.06
Mainstem	1 day	3.33	1.92	0.09	4.66	0.018	0.014	1.30	8.49	1.85	4.43	0.96
	3 day	0.00	1.86	0.15	7.55	0.066			5.68		3.06	
	5 day	3.33	1.81	0.20	10.09	0.018	0.012	1.49	8.43	1.67	4.66	0.92
	0 h	1.67	4.65			0.016	0.017	0.95	21.00	4.10	4.52	0.88
	1 h	5.00	4.60	0.06	1.33	0.014	0.012	1.18	22.62	5.23	4.92	1.14
Tributary	1 day	13.33	4.56	0.10	2.08	0.013	0.014	0.87	22.47	6.53	4.93	1.43
	3 day	15.00	4.45	0.20	4.24	0.018	0.029	0.63	19.22	2.73	4.32	0.61
	5 day	1.67	4.19	0.46	9.90	0.012	0.017	0.68	21.95	6.93	5.24	1.66
	0 h	3.33	3.25			0.018	0.013	1.35	14.04	2.21	4.32	0.68
Mixture	1 h	5.00	3.26			0.017	0.010	1.66	14.48	2.54	4.45	0.78
	1 day	6.67	3.25			0.014	0.015	0.96	15.29	4.20	4.70	1.29

	3 day	16.67	3.10	0.15	4.70	0.026	0.000	0.00	11.90	0.15	3.84	0.05
	5 day	10.00	2.95	0.30	9.28	0.013	0.016	0.83	14.90	4.29	5.06	1.45

S2: Supplementary figures

Fig. S1a. Changes and spatial pattern of optical parameters of DOM in the Han River before and after the biodegradation assay. Significant differences between initial and final values during 7-day incubation are indicated by asterisks.

Fig. S1b. Changes and spatial pattern of absorption indices and dissolved nutrients at different reaches of Han River watershed. Significant differences between the initial and final values during 7-day incubation are indicated by asterisks.

Fig. S2. Initial, final and differential (final – initial) fluorescence EEMs from 7-day incubation of filtered water samples from up-, mid-, and downstream and urban tributaries of the Han River. Positive and negative values indicate the production and consumption of OM respectively.

Fig. S3. Changes in optical characteristics of the mainstem, tributary and mixture samples during 5-day incubation.

Fig. S4. Van Krevelen diagrams of identified molecular formulas showing 2-fold changes in the peak intensity relative to the initial value during a 5-day incubation of unfiltered water samples from (a) a mainstem and (b) a tributary site of the Han River. Red and blue symbols represent peaks that increased in intensity more than two fold relative to the initial value or newly identified peaks (termed “production”) and peaks that decreased in intensity more than two fold or disappeared peaks (termed “consumption”) following the 5 day incubation, respectively.

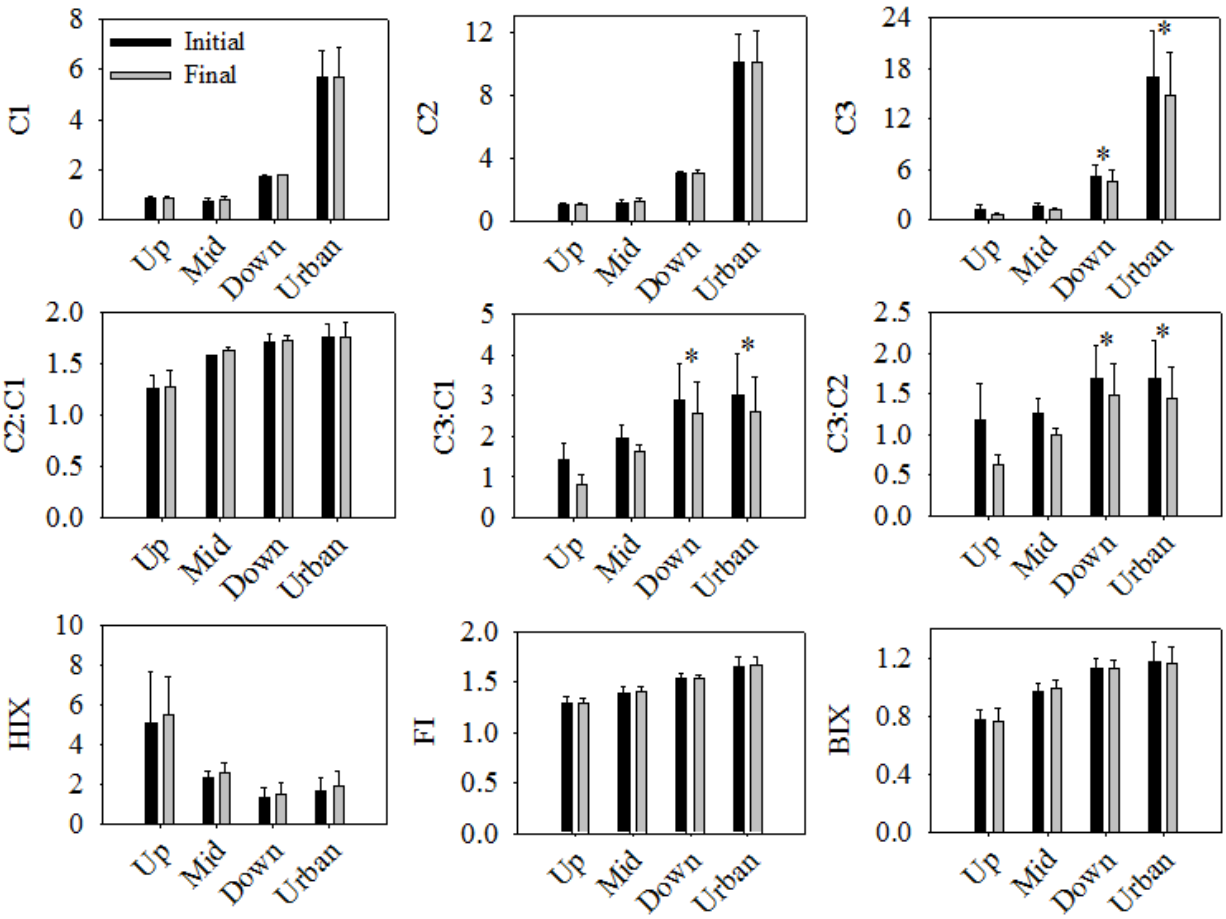

Initial
Final
C1
C2
C3
C2:C1
C3:C1
C3:C2
HIX
FI
BIX
Up
Mid
Down
Urban

Fig. S1a

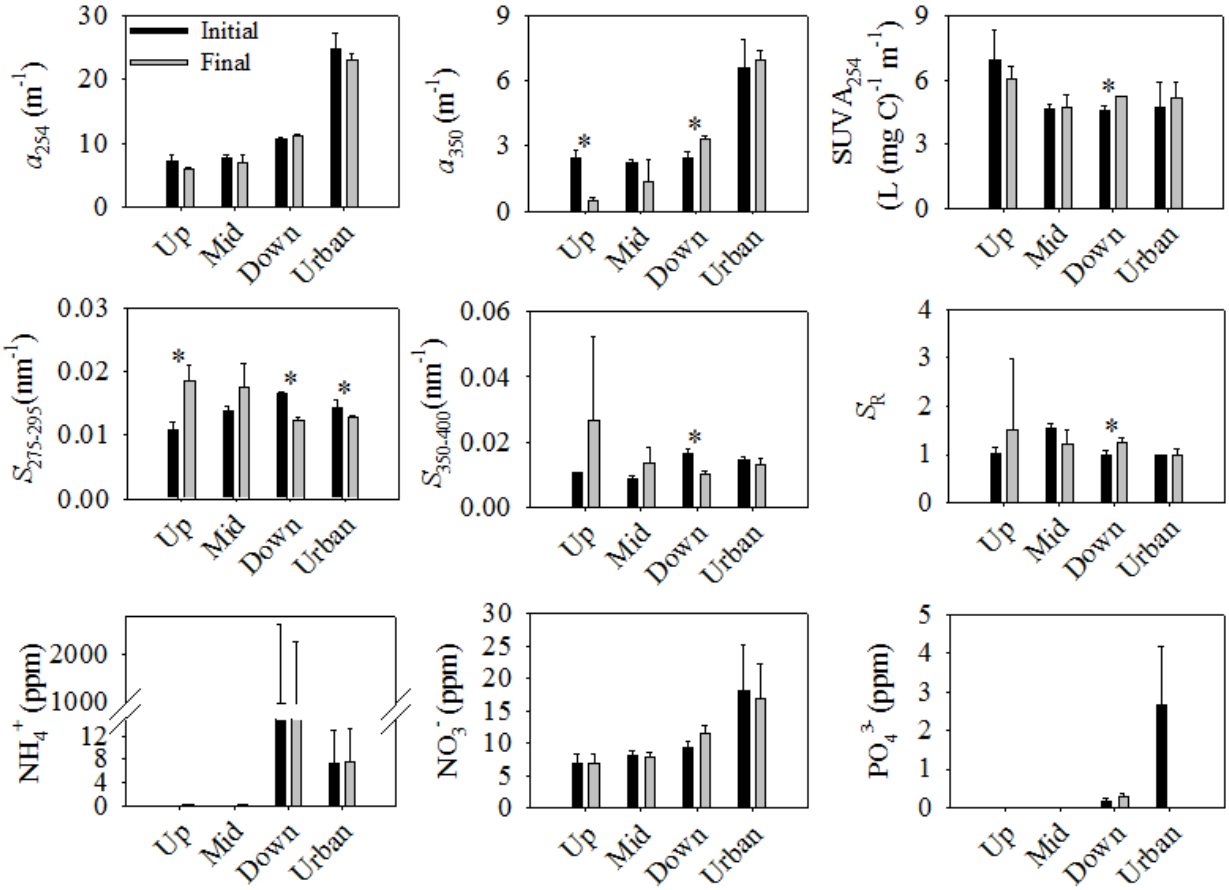

Initial
Final
a_{254} (m^{-1})
a_{350} (m^{-1})
SUVA$_{254}$ (L (mg C)$^{-1}$ m^{-1})
$S_{275\text{-}295}$(nm^{-1})
$S_{350\text{-}400}$(nm^{-1})
S_R
NH_4^+ (ppm)
NO_3^- (ppm)
PO_4^{3-} (ppm)
Up
Mid
Down
Urban

Fig. S1b

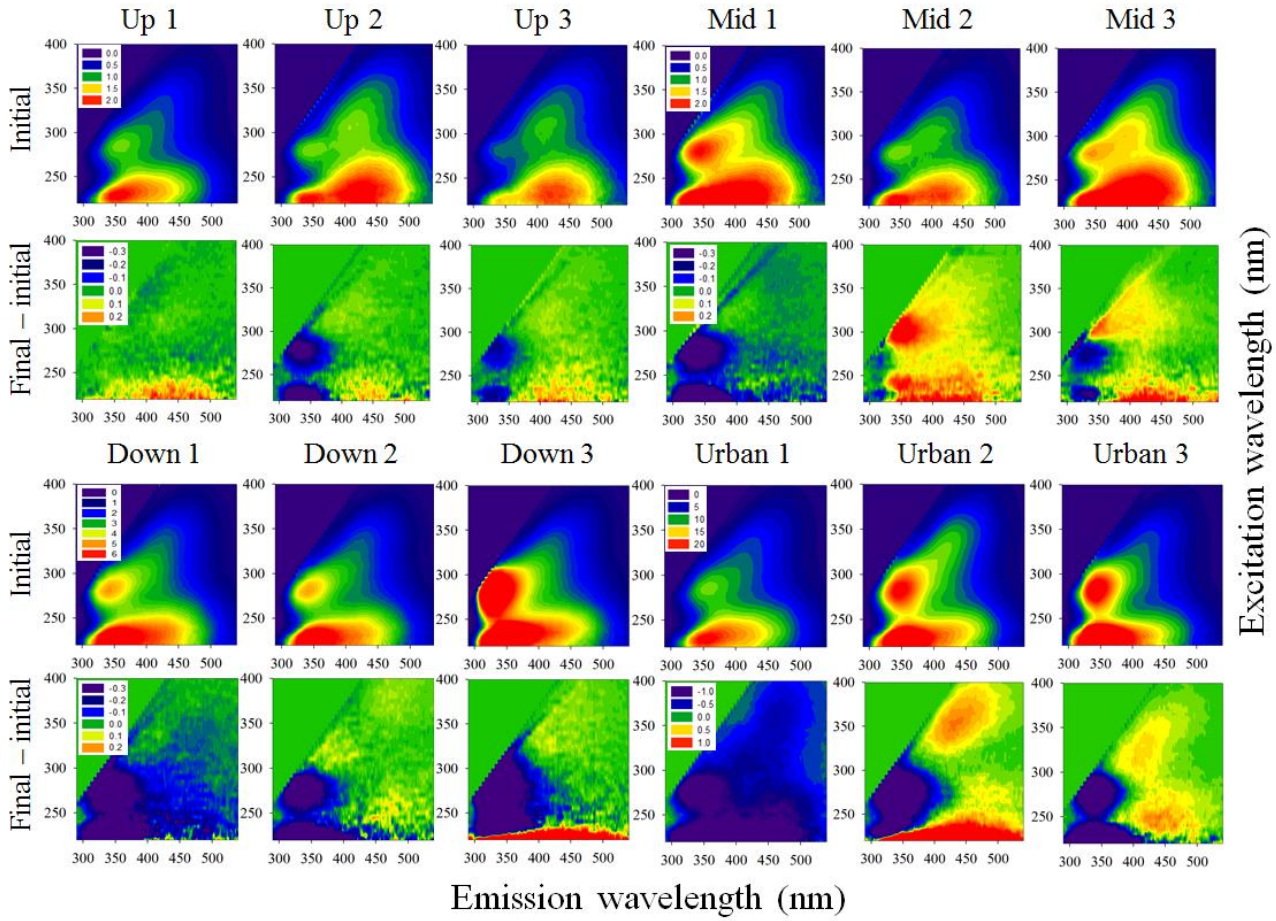

Up 1
Up 2
Up 3
Mid 1
Mid 2
Mid 3
Down 1
Down 2
Down 3
Urban 1
Urban 2
Urban 3
Initial
Final – initial
Excitation wavelength (nm)
Emission wavelength (nm)

Fig. S2

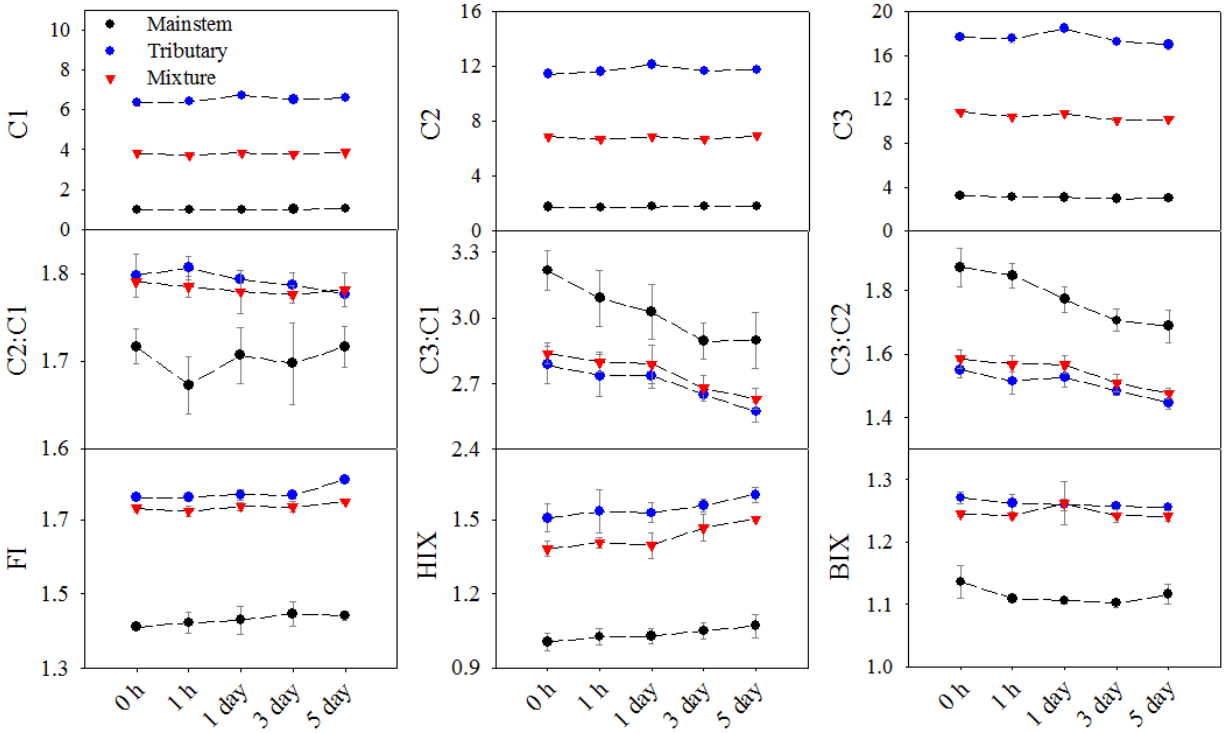
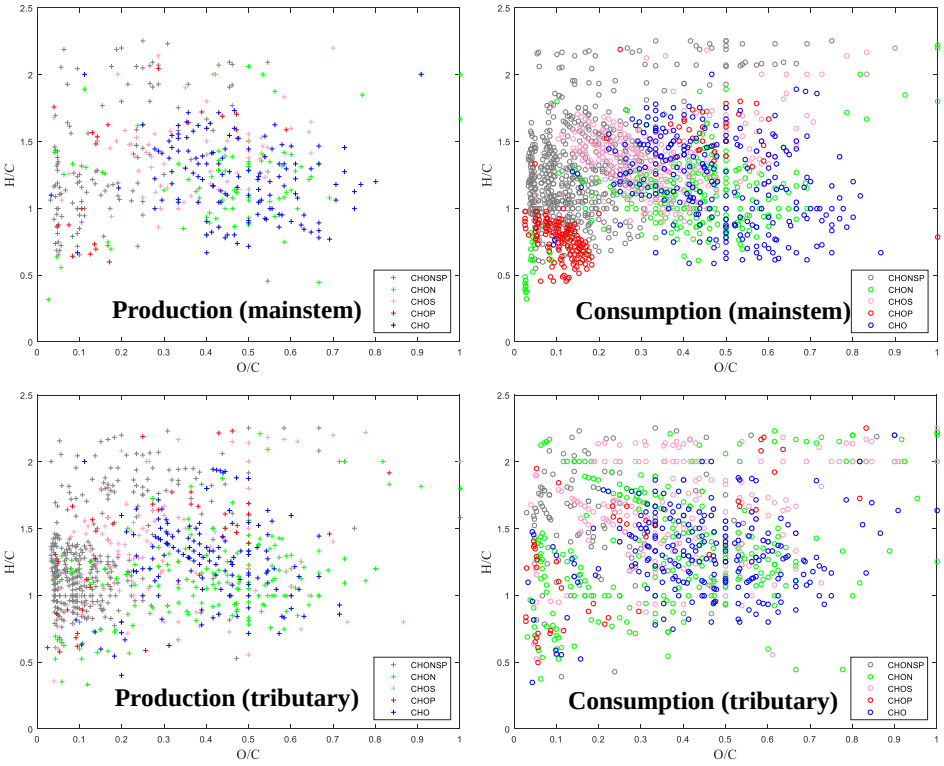

Mainstem
Tributary
Mixture
C1
C2
C3
C2:C1
C3:C1
C3:C2
FI
HIX
BIX
0 h
1 h
1 day
3 day
5 day

Fig. S3



Mainstem
- **Total (all peaks): 4775**
- **Subtotal (>2-fold): 2904**
- **Production: 601**
- **Consumption: 2303**

Tributary
- **Total (all peaks): 4286**
- **Subtotal (>2-fold): 2730**
- **Production: 1592**
- **Consumption: 1138**

Fig. S4