Supplementary Materials

Characteristics and Sources of Selected Halocarbon and Hydrocarbon Volatile Organic Compounds in Surface Water of the Han River Basin

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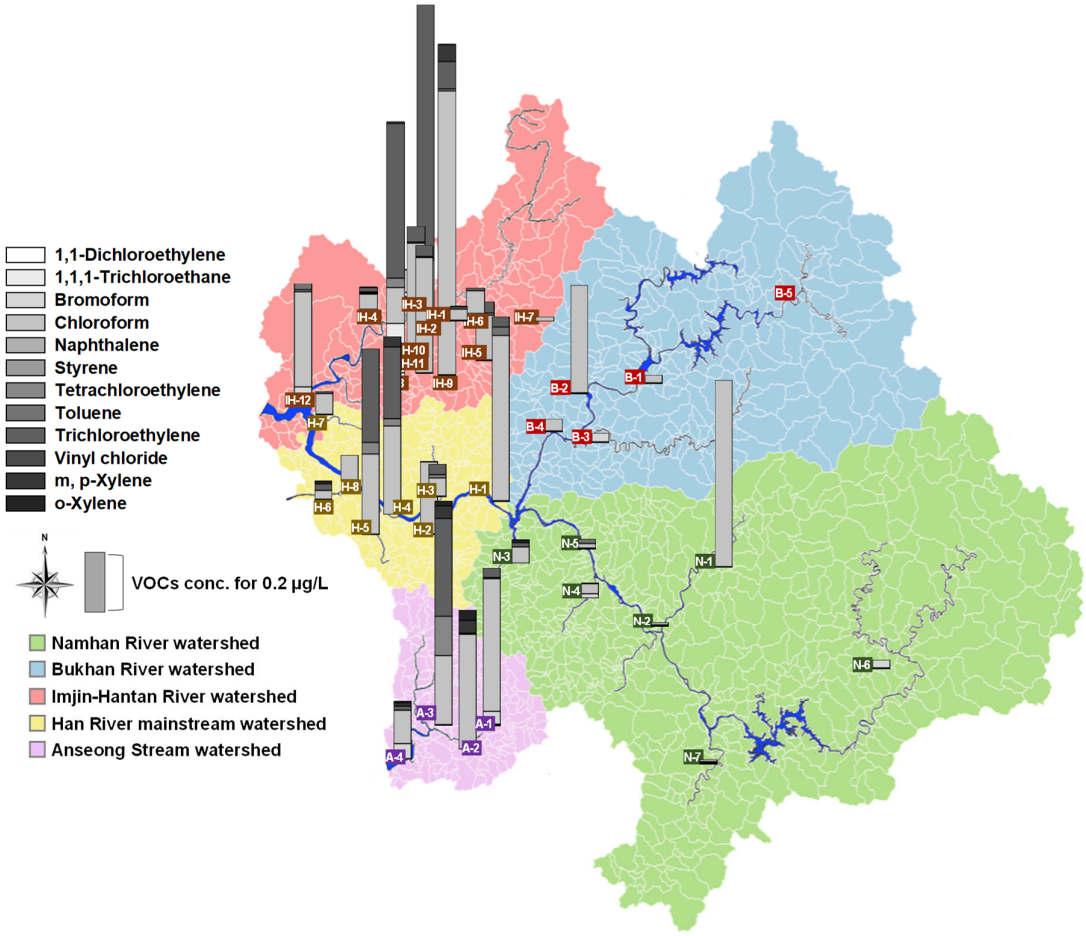
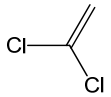
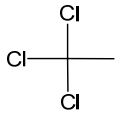
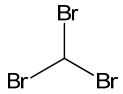
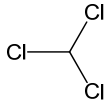
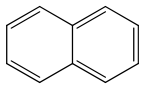
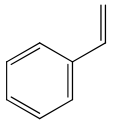
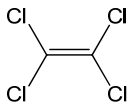
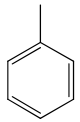
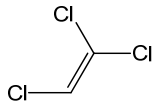
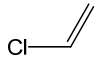
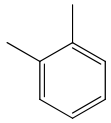
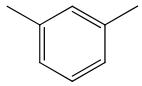
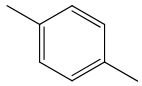


Figure S1. Spatial trends for cumulative VOC concentrations at different sites.

Table S1. Physical and chemical properties of VOCs.

Compound (Abb.)	CAS no.	Molecular formula	Molecular weight (g/mol)	Structure	Density at 20°C (g/cm^3)	Solubility in water at 25°C (mg/L)	Vapor pressure at 25°C (mmHg)	Henrys law constant ($atm\text{-}m^3/mol$)	log Kow	log Kaw *	log Koa *
1,1-Dichloroethylene (1,1-DCE)	75-35-4	$C_2H_2Cl_2$	96.9		1.213	2420	600	0.03	2.13	0.089	2.04
1,1,1-Trichloroethane (1,1,1-TCA)	71-55-6	$C_2H_3Cl_3$	133.4		1.338	1290	124	0.02	2.49	−0.087	2.58
Bromoform	75-25-2	$CHBr_3$	252.7		2.891	3100	5.4	0.00054	2.40	−1.656	4.06
Chloroform	67-66-3	$CHCl_3$	119.4		1.483	7950	197	0.00	1.97	−0.824	2.79
Naphthalene	91-20-3	$C_{10}H_8$	128.2		1.162	31	0.085	0.00044	3.30	−1.745	5.05
Styrene	100-42-5	C_8H_8	104.2		0.906	300	6.4	0.00	2.95	−0.949	3.90
Tetrachloroethylene (PCE)	127-18-4	C_2Cl_4	165.8		1.623	206	18.5	0.02	3.40	−0.087	3.49

Toluene	108-88-3	C_7H_8	92.1		0.862	526	28.4	0.01	2.73	−0.388	3.12
Trichloroethylene (TCE)	79-01-6	C_2HCl_3	131.4		1.464	1280	69	0.01	2.61	−0.388	3.00
Vinyl chloride	75-01-4	C_2H_3Cl	62.5		0.911	2700	2980	0.03	1.46	0.089	1.37
o-Xylene	95-47-6	C_8H_{10}	106.2		0.880	180	6.7	0.01	3.12	−0.388	3.51
m-Xylene	108-38-3	C_8H_{10}	106.2		0.870	160	8.3	0.01	3.20	−0.388	3.59
p-Xylene	106-42-3	C_8H_{10}	106.2		0.861	165	8.8	0.01	3.15	−0.388	3.54

Kow: Octanol-water partition coefficient; Kaw: Air-water partition coefficient; Koa: Octanol-air partition coefficient. * Values estimated using EPI Suite™ ver. 4.11 (https://www.epa.gov/tsca-screening-tools/download-epi-suitetm-estimation-program-interface-v411). **Source:** PubChem (https://pubchem.ncbi.nlm.nih.gov).

Table S2. Water quality data measured at the sampling sites.

Sampling Sites	Water Temp. (°C)	pH	DO (mg/L)	Cond. (μS/cm)
N-1	21.5 ± 3.5	7.1 ± 0.4	6.2 ± 0.3	480 ± 135
N-2	23.7 ± 4.8	8.7 ± 0.8	11.7 ± 3.0	264 ± 130
N-3	22.4 ± 3.3	7.8 ± 0.3	9.7 ± 2.8	333 ± 189
N-4	23.8 ± 3.8	7.7 ± 0.2	8.5 ± 1.5	974 ± 550
N-5	22.2 ± 5.1	8.4 ± 0.6	10.8 ± 1.6	168 ± 78
N-6	22.5 ± 7.3	8.6 ± 0.6	10.6 ± 1.6	208 ± 31
N-7	24.3 ± 5.0	8.1 ± 0.7	9.3 ± 2.1	217 ± 57
B-1	20.4 ± 5.7	8.1 ± 0.8	10.9 ± 2.2	172 ± 12
B-2	19.2 ± 5.4	7.8 ± 0.3	10.6 ± 1.3	111 ± 62
B-3	22.3 ± 6.1	8.1 ± 0.3	9.5 ± 0.8	167 ± 87
B-4	20.6 ± 5.7	8.0 ± 0.3	10.3 ± 0.8	163 ± 59
B-5	16.9 ± 6.7	7.7 ± 0.8	10.0 ± 1.2	86 ± 38
IH-1	22.5 ± 6.4	8.7 ± 1.1	12.2 ± 3.5	524 ± 383
IH-2	24.0 ± 5.1	8.1 ± 0.4	9.9 ± 1.2	1820 ± 1503
IH-3	24.4 ± 5.7	8.6 ± 1.1	11.8 ± 3.1	173 ± 20
IH-4	22.3 ± 5.8	8.8 ± 1.3	13.5 ± 4.6	589 ± 413
IH-5	24.5 ± 7.3	7.9 ± 0.4	10.7 ± 1.8	898 ± 951
IH-6	23.3 ± 8.3	8.1 ± 0.5	11.0 ± 1.8	831 ± 932
IH-7	21.7 ± 7.0	8.4 ± 0.6	10.9 ± 1.8	193 ± 87
IH-8	21.9 ± 6.2	7.9 ± 0.4	7.2 ± 0.4	1936 ± 1390
IH-9	22.8 ± 6.1	7.7 ± 0.2	6.3 ± 0.8	2035 ± 1429
IH-10	24.9 ± 5.9	7.8 ± 0.4	9.5 ± 2.9	2030 ± 1250
IH-11	24.4 ± 4.5	7.6 ± 0.1	7.8 ± 1.2	2695 ± 1354
IH-12	28.0 ± 2.0	8.0 ± 0.8	8.3 ± 0.7	1351 ± 89
H-1	21.4 ± 4.9	7.2 ± 0.1	7.0 ± 1.4	496 ± 139
H-2	21.5 ± 4.6	7.1 ± 0.1	5.8 ± 2.5	447 ± 183
H-3	20.2 ± 5.2	7.6 ± 0.4	7.7 ± 2.2	211 ± 65
H-4	21.6 ± 4.5	7.2 ± 0.1	6.7 ± 1.7	417 ± 217
H-5	21.5 ± 4.7	7.4 ± 0.2	6.1 ± 0.2	501 ± 216
H-6	20.5 ± 5.0	7.5 ± 0.3	6.1 ± 3.1	221 ± 40
H-7	22.5 ± 4.9	7.9 ± 0.5	9.2 ± 3.0	564 ± 303
H-8	19.2 ± 7.1	7.4 ± 0.2	6.2 ± 1.3	391 ± 90
A-1	22.3 ± 1.8	7.7 ± 0.4	8.6 ± 2.9	520 ± 409
A-2	26.0 ± 6.6	7.8 ± 0.5	9.7 ± 2.4	1157 ± 782
A-3	22.2 ± 2.4	7.7 ± 0.2	6.4 ± 1.9	517 ± 288
A-4	22.6 ± 6.1	8.1 ± 0.7	9.7 ± 3.0	1024 ± 547

Sampling date: April 07–08, 11; June 23–25; August 20, 26–27.

Table S3. Purge-and-trap gas chromatography/mass spectrometry analytical conditions and parameters [39].

P&T Conditions	
Valve oven temperature	150 ºC
Transfer line temperature	150 ºC
Syringe fill volume	25 mL
Sample mount temperature	90 ºC
Purge	He, 40 mL/min, 0 ºC for 11 min
Desorb	200 mL/min, 250 ºC for 2 min (preheat temp. 245 ºC)
Bake	400 mL/min, 260 ºC for 10 min

GC/MS conditions

GC	Column	Agilent DB-624 column (60 m × 0.32 mm × 1.8 μm)
	Carrier gas flow	He at 1.0 mL/min constant flow
	Injector	temperature 250ºC, Splitless mode
	Oven temperature	30 ºC for 2 min 8 ºC/min to 140 ºC, hold 10 min 30 ºC/min to 220 ºC, hold 4 min
MS	Ionization mode	Electron Ionization (EI)
	Electron Energy	70 eV
	Source temperature	200 ºC
	Transfer line temperature	250 ºC
	Data Acquisition	Selected Ions Monitoring (SIM)

Table S4. Measured VOC concentrations during the sampling periods.

Compound	MDL	Min	Max	Average ± std	Median	75%	95%	DF (n=108)
1,1-Dichloroethylene (1,1-DCE)	0.06	0.000	0.062	0.001 ± 0.006	0.000	0.000	0.000	1
1,1,1-Trichloroethane (1,1,1-TCA)	0.011	0.000	0.498	0.005 ± 0.048	0.000	0.000	0.000	3
Bromoform	0.010	0.000	0.093	0.006 ± 0.018	0.000	0.000	0.056	13
Chloroform	0.012	0.000	2.659	0.187 ± 0.330	0.069	0.252	0.560	81
Naphthalene	0.007	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0
Styrene	0.005	0.000	0.010	0.000 ± 0.001	0.000	0.000	0.000	3
Tetrachloroethylene (PCE)	0.010	0.000	0.264	0.008 ± 0.031	0.000	0.000	0.030	16
Toluene	0.009	0.000	0.085	0.002 ± 0.010	0.000	0.000	0.019	7
Trichloroethylene (TCE)	0.005	0.000	2.450	0.075 ± 0.289	0.000	0.028	0.380	47
Vinyl chloride	0.009	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0
m, p-Xylene	0.007	0.000	0.150	0.006 ± 0.025	0.000	0.000	0.021	13
o-Xylene	0.005	0.000	0.111	0.002 ± 0.012	0.000	0.000	0.006	8
total VOCs				0.291 ± 0.469				

MDL: method detection limit. n.d.: Not detected; DF: Detection frequency. total VOCs: Sum of individual VOC (such as ΣVOC).

Table S5. Water quality guidelines for VOCs [39].

Compound	Ambient Water (μg/L) *					Drinking Water (μg/L) **				
	EU		South Korea	USA		EU	South Korea	USA		WHO
	AA-EQS[1)]	MAC-EQS[2)]		W+O[3)]	O only[4)]	DWQS	DWQS	MCLG[5)]	MCL[6)]	HBGV
1,1-Dichloroethylene (1,1-DCE)	-	-	-	300	20000	-	30	7	7	-
1,1,1-Trichloroethane (1,1,1-TCA)	-	-	-	10000	200000	-	100	200	200	-
Bromoform	-	-	-	7	120	-	100(R)	0	-	100
Chloroform	2.5	not applicable	80	60	2000	-	80	70	-	300
Naphthalene	2	130	-	-	-	-	-	-	-	-
Styrene	-	-	-	-	-	-	20(R)	100	100	20
Tetrachloroethylene (PCE)	10	not applicable	40	10	29	10(S)	10	0	5	40
Toluene	-	-	-	57	520	-	700	1000	1000	700
Trichloroethylene (TCE)	10	not applicable	-	0.6	7	10(S)	30	0	5	20(P)
Vinyl chloride	-	-	-	0.022	1.6	0.5	2(R)	0	2	0.3
Xylenes-total	-	-	-	-	-	-	500	10000	10000	500

AA-EQS: Annual Average-Environmental Quality Standards; MAC-EQS: Maximum Allowable Concentration-Environmental Quality Standards; DWQS: Drinking water quality standards; MCLG: Maximum contaminant level goal; MCL: Maximum contaminant level; HBGV: Health-based guideline value. (S) Sum of PCE and TCE; (R) Recommendation criteria for drinking water quality; (P) Provisional guideline value because of uncertainties in the health database. [1)] Unless otherwise specified, applies to the total concentration of all isomers. [2)] Where the MAC-EQS are marked as 'not applicable', AA-EQS values are considered protective against short-term pollution peaks in continuous discharges since they are significantly lower than the values derived on the basis of acute toxicity. [3)] Human Health for the consumption of water and organism. [4)] Human Health for the consumption of organism only. [5)] The level of a contaminant in drinking water below which there is no known or expected risk to health. MCLGs allow for a margin of safety and are non-enforceable public health goals. [6)] The highest level of a contaminant that is allowed in drinking water. MCLs are set as close to MCLGs as feasible using the best available treatment technology and taking cost into consideration. MCLs are enforceable standards. * **Source:** - EU: Environmental quality standards (https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=CELEX:32013L0039). - South Korea: Water Quality Standards (Water Environment Conservation Act (Act No. 16605) > Administrative Rules: Ministry of Environment (MoE) Notice No. 2018-6 (https://www.law.go.kr/LSW/admRulInfoP.do?admRulSeq=2100000111712). - USA: Water Quality Criteria (https://www.epa.gov/wqc/national-recommended-water-quality-criteria-human-health-criteria-table). ** **Source:** - EU: Drinking water directive (https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:01998L0083-20151027). - South Korea: Drinking Water Quality Standards. (a) Water Supply and Waterworks Installation Act (Act No. 17178) > Enforcement Rule: Ministry of Environment (MoE) Decree No. 833, [Attached Table 1] (https://www.law.go.kr/LSW/lsInfoP.do?lsiSeq=212567&lsId=007134&efYd=20191220&chrClsCd=010102&viewCls=lsInfoP&ancYnChk=#J8823815). (b) Drinking Water Management Act (Act No. 17326) > Administrative Rules: Ministry of Environment (MoE) Notice No. 2019-81, [Attached Table 1] (https://law.go.kr/LSW/admRulLsInfoP.do?chrClsCd=&admRulSeq=2100000178074#J1996368). - USA: National primary drinking water regulations (https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations#one). - WHO: Drinking water quality guidelines (https://www.who.int/teams/environment-climate-change-and-health/water-sanitation-and-health/water-safety-and-quality/drinking-water-quality-guidelines).

Table S6. ANOVA analysis of VOC concentration by sampling time and site.

Compound	Sampling Time (3 months)	Sampling Site (36 sites)
1,1-Dichloroethylene (1,1-DCE)	0.379	0.743
1,1,1-Trichloroethane (1,1,1-TCA)	0.411	0.764
Bromoform	**0.020**	**0.003**
Chloroform	**0.016**	0.313
Styrene	0.244	0.371
Tetrachloroethylene (PCE)	0.174	**0.015**
Toluene	0.305	0.721
Trichloroethylene (TCE)	**0.047**	0.384
Xylenes	0.198	**0.013**