

Supplementary Information for

Industrial influence on atmospheric VOCs and associated health risks in small residential areas near industrial complexes in Ulsan, South Korea

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Site 1



Site 2



Site 3



Site 4



Site 5



Site 6



Site 7



Figure S1. Photographs of individual sampling sites (Sites 1–7).

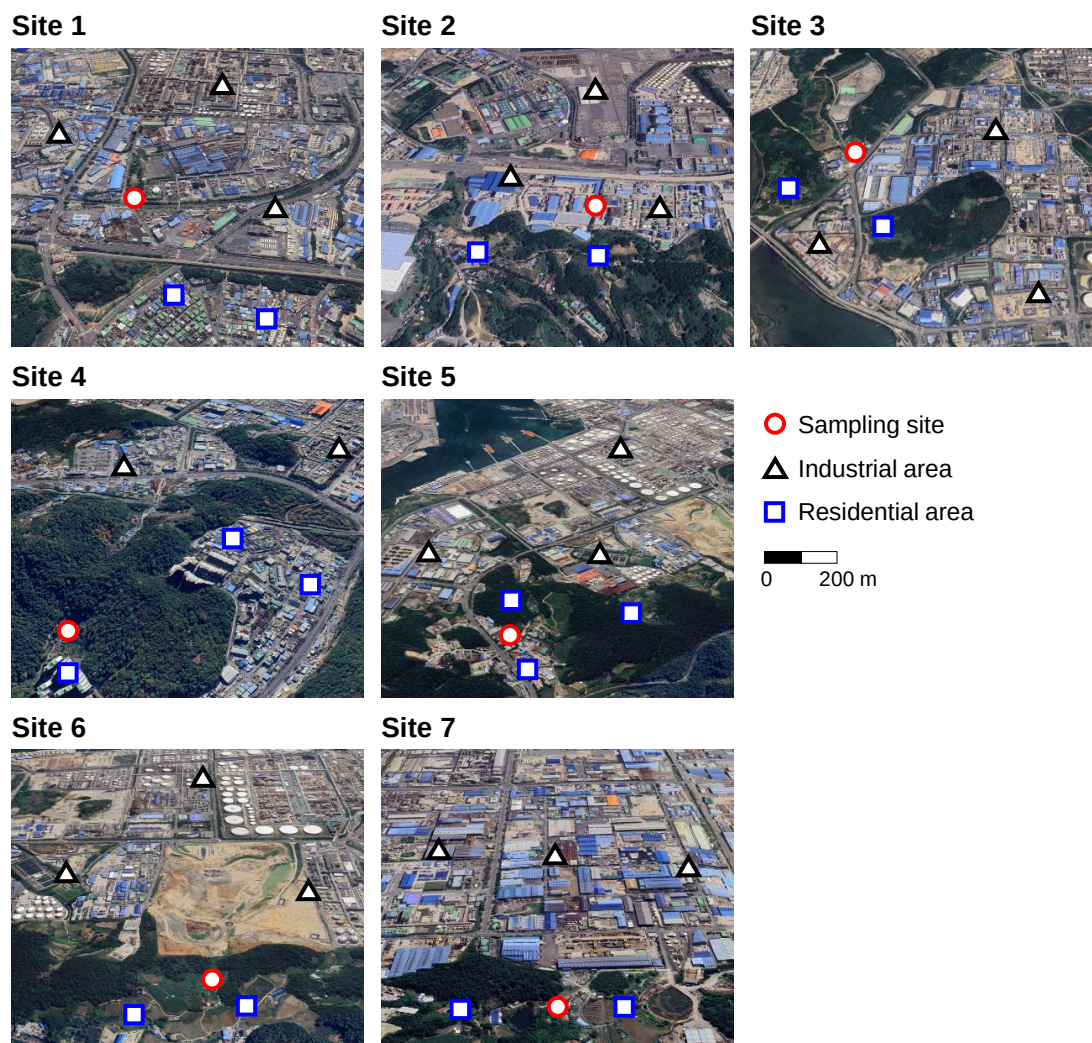


Figure S2. Satellite images of sampling sites and their proximity to industrial and residential areas.

Table S1. Calibration curve details for VOC analysis.

VOCs		CS 1	CS 2	CS 3	CS 4	CS 5
Final amount (μg)		0.025	0.05	0.1	0.3	0.5
Native standard (1 ppm)	Dilution rate	1:24	1:12	1:6	1:6	1:6
	Injection time (min)	1	1	1	3	5
Internal standard (1 ppm)	Dilution rate	1:6	1:6	1:6	1:6	1:6
	Injection time (min)	1	1	1	1	1

Table S2. Concentrations (mean $\pm$ standard deviation (SD), $\mu\text{g}/\text{m}^3$), method detection limits (MDLs, $\mu\text{g}/\text{m}^3$), unit risks (URs, $\mu\text{g}/\text{m}^3$)⁻¹), health guideline values (HGVs) for chronic (mg/m^3) and acute (ppm) exposure, and endpoints for individual VOCs based on ATSDR classifications.

Group	Compound	Mean ± SD	MDL	UR	HGV		Endpoint ^e
				Chronic		Acute ^e	
				Cancer	Non-cancer	Non-cancer	
Aromatic	1,2,4-Trimethylbenzene (TMB)	3.77 ± 2.73	0.26	- ^b	6.0E-2 ^c	-	-
	1,3,5-Trimethylbenzene (TMB)	0.68 ± 0.54	0.14	-	6.0E-2 ^c	-	-
	4-Ethyltoluene	0.83 ± 0.65	0.15	-	-	-	-
	Benzene	1.98 ± 0.57	0.05	7.8E-6 ^c	3.0E-2 ^c	9.0E-3	Immunological
	Benzyl chloride	0.03 ± 0.01	0.06	4.9E-5 ^d	-	-	-
	Ethylbenzene	5.93 ± 3.98	0.11	-	1.0E+0 ^c	5.0E+0	Neurological
	m,p-Xylenes	9.11 ± 5.99	0.22	-	1.0E-1 ^c	2.0E+0	Neurological
	Naphthalene	0.66 ± 0.32	0.20	3.4E-5 ^d	3.0E-3 ^c	6.0E-5	Respiratory
	o-Xylene	4.51 ± 2.62	0.11	-	1.0E-1 ^c	2.0E+0	Neurological
	Styrene	1.45 ± 2.17	0.09	-	1.0E+0 ^c	5.0E+0	Neurological
Toluene	11.7 ± 11.9	0.28	-	5.0E+0 ^c	2.0E+0	Neurological	
Halogenated	1,1,1-Trichloroethane	0.01 ± 0.00 ^a	0.06	-	5.0E+0 ^c	1.0E+0	Neurological
	1,1,2,2-Tetrachloroethane	0.00 ± 0.00	0.10	5.8E-5 ^d	-	-	-
	1,1,2-Trichloroethane	0.02 ± 0.01	0.06	-	-	3.0E-2	Respiratory
	1,1-Dichloroethane	0.00 ± 0.00	0.11	-	-	-	-
	1,1-Dichloroethene	0.00 ± 0.00	0.16	-	2.0E-1 ^c	-	-
	1,2,4-Trichlorobenzene	0.03 ± 0.00	0.01	-	-	-	-
	1,2-Dibromoethane	0.00 ± 0.00	0.10	6.0E-4 ^c	9.0E-3 ^c	-	-
	1,2-Dichlorobenzene	0.05 ± 0.04	0.14	-	-	-	-
	1,2-Dichloroethane	0.15 ± 0.19	0.03	2.6E-5 ^c	-	1.0E-1	Respiratory
	1,2-Dichloropropane	0.61 ± 1.07	0.04	-	4.0E-3 ^c	2.0E-2	Respiratory
	1,3-Dichlorobenzene	0.01 ± 0.01	0.10	-	-	-	-
	1,4-Dichlorobenzene	0.02 ± 0.01	0.08	-	8.0E-1 ^c	2.0E+0	Respiratory
	Bromodichloromethane	0.01 ± 0.01	0.19	-	-	-	-
	Bromoform	0.04 ± 0.02	0.13	1.1E-6 ^c	-	-	-
	Bromomethane	0.00 ± 0.00	0.02	-	5.0E-3 ^c	2.0E-2	Neurological
	Carbon tetrachloride (CTC)	0.34 ± 0.04	0.07	6.0E-6 ^c	1.0E-1 ^c	-	-
	Chlorobenzene	0.04 ± 0.01	0.10	-	1.0E+0 ^d	-	-
	Chloroethane	0.00 ± 0.00	0.03	-	1.0E+1 ^c	1.3E+1	Developmental
	Chloroform	0.11 ± 0.11	0.07	2.3E-5 ^c	3.0E-1 ^d	1.0E-3	Respiratory
	Chloromethane	0.00 ± 0.01	0.02	-	9.0E-2 ^c	5.0E-1	Neurological
	cis-1,2-Dichloroethene	0.00 ±0.00	0.03	-	-	-	-
	cis-1,3-Dichloropropene	0.01 ± 0.01	0.03	-	-	-	-
	Dibromochloromethane	0.02 ± 0.00	0.37	-	-	-	-
	Freon11	0.04 ± 0.01	0.15	-	-	-	-
	Freon113	0.15 ± 0.03	0.26	-	-	-	-
	Freon114	0.00 ± 0.00	0.10	-	-	-	-
	Freon12	0.00 ± 0.00	0.04	-	-	-	-
	Tetrachloroethene (PCE)	0.16 ± 0.05	0.13	2.6E-7 ^c	4.0E-2 ^c	6.0E-3	Neurological
	trans-1,2-Dichloroethene	0.02 ± 0.04	0.10	-	-	3.0E+0	Ocular
	trans-1,3-Dichloropropene	0.00 ± 0.00	0.02	-	-	-	-
Trichloroethylene (TCE)	0.25 ± 0.17	0.12	4.1E-6 ^c	2.0E-3 ^c	-	-	
Vinyl chloride	0.00 ± 0.00	0.02	8.8E-6 ^c	1.0E-1 ^c	5.0E-1	Developmental	
Other	1,3-Butadiene	0.07 ± 0.10	0.24	3.0E-5 ^c	2.0E-3 ^c	-	-
	1,4-Dioxane	0.03 ± 0.01	0.04	5.0E-6 ^c	3.0E-2 ^c	2.0E+0	Ocular
	Acrolein	0.96 ± 0.73	0.09	-	2.0E-5 ^c	3.0E-3	Respiratory
	Cyclohexane	0.54 ± 0.24	0.04	-	6.0E+0 ^c	-	-
	Ethyl acetate	2.39 ± 0.71	0.02	-	-	-	-
	n-Heptane	0.70 ± 0.46	0.06	-	-	-	-
	Hexachlorobutadiene	0.07 ± 0.03	0.19	-	-	-	-
	Isopropyl alcohol	0.93 ± 0.82	0.29	-	7.0E+0 ^d	-	-
	Methyl butyl ketone (MBK)	0.11 ± 0.02	0.05	-	3.0E-2 ^c	-	-

Methyl ethyl ketone (MEK)	3.29 ± 2.34	0.06	-	5.0E+0 ^c	1.0E+0	Neurological
Methyl methacrylate (MMA)	0.53 ± 0.82	0.04	-	7.0E-1 ^c	-	-
Methyl isobutyl ketone (MIBK)	1.03 ± 0.78	0.06	-	3.0E+0 ^c	-	-
Methyl tert-butyl ether (MTBE)	1.41 ± 0.51	0.08	-	3.0E+0 ^c	2.0E+0	Neurological
Propylene	0.17 ± 0.12	0.11	-	3.0E+0 ^d	-	-
Tetrahydrofuran	0.02 ± 0.01	0.03	-	2.0E+0 ^c	-	-
Vinyl acetate	1.82 ± 0.73	0.01	-	2.0E-1 ^c	1.0E+0	Respiratory

^a A value of 0.00 indicates that the concentration is more than three decimal places.

^b Not available.

^c United States Environmental Protection Agency (US EPA)'s Integrated Risk Information System (IRIS).

^d California EPA (CalEPA)'s Office of Environmental Health Hazard Assessment (OEHHA).

^e Department of Health and Human Services (DHHS)'s Agency for Toxic Substances and Disease Registry (ATSDR).

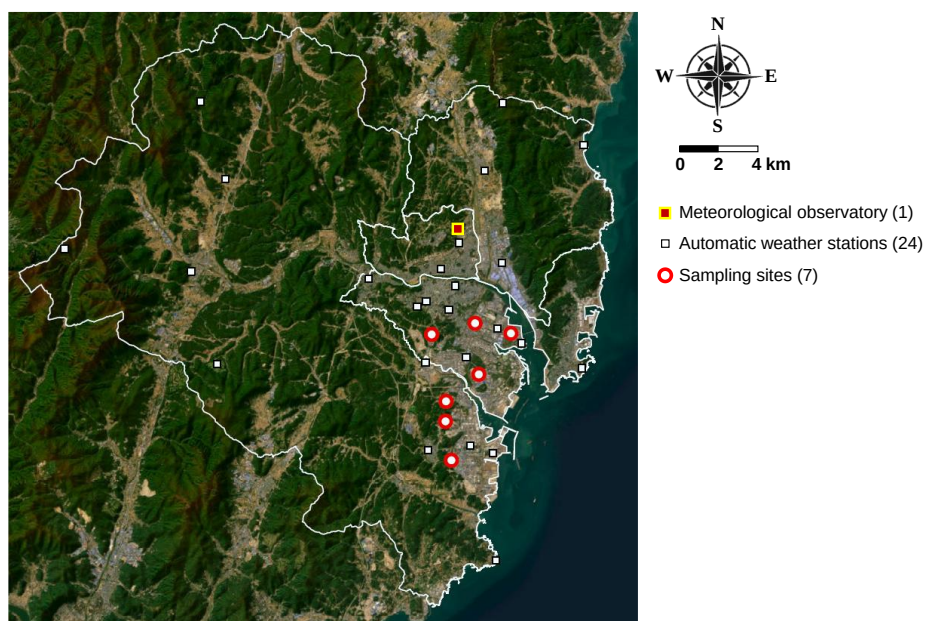


Figure S3. Locations of the meteorological observatory (MO), automatic weather stations (AWSs), and VOC sampling sites.

Table S3. Hourly mean meteorological parameters (temperature, wind speed, and relative humidity) and total precipitation during the four seasons of 2020 and during the sampling period (October 13–20, 2020) at an MO in Ulsan.

	Spring	Summer	Fall	Winter	Study period
Temperature (°C)	13.3 ± 4.4	24.2 ± 3.0	16.0 ± 5.1	4.88 ± 1.4	15.3 ± 3.0
Wind speed (m/s)	2.2 ± 0.3	1.8 ± 0.3	2.3 ± 0.2	2.4 ± 0.1	2.0 ± 0.9
Relative humidity (%)	61.6 ± 8.9	83.0 ± 7.9	68.7 ± 11.1	55.6 ± 7.9	64.8 ± 18.3
Total precipitation (mm)	166.3	854.0	299.6	238.0	0.0

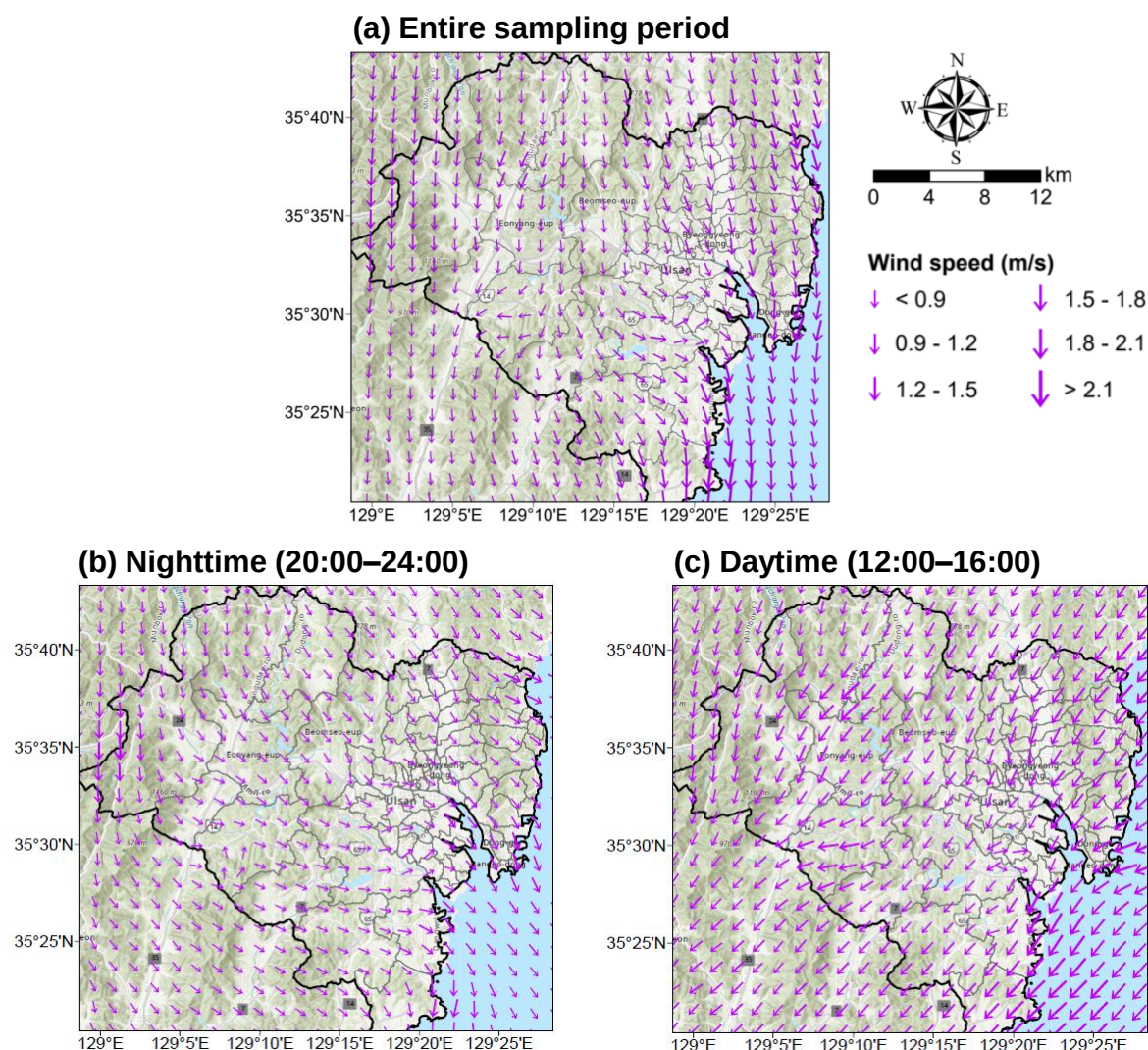


Figure S4. Average wind fields in Ulsan during (a) the entire sampling period (October 13–20, 2020), (b) nighttime (20:00–24:00), and (c) daytime (12:00–16:00).

Table S4. Concentrations of 10 major VOCs in 9 South Korean cities, as reported by national monitoring projects, compared with those measured in this study.

Name	Seoul ^a	Incheon ^b	Busan ^c	Daegu ^d	Gwangju ^e	Yeosu·Gwangyang ^f	Daesan ^g	Pohang ^h	Ulsan ⁱ	This study
Category	M ^j	M	M	M	M	I ^k	I	I	I	I
Year	2013 – 2014	2014 – 2015	2015 – 2016	2016 – 2017	2018	2008 – 2009	2011	2012 – 2013	2019 – 2020	2020
Benzene	1.53	1.95	1.60	1.28	1.05	4.86	3.16	1.34	1.47	1.85
Toluene	18.1	18.4	21.2	34.4	5.28	5.65	6.56	3.88	4.90	9.61
Ethylbenzene	3.26	2.69	3.30	4.17	1.78	2.39	2.17	0.96	3.21	4.46
m,p-Xylenes	3.65	3.86	5.17	4.78	1.48	4.17	3.08	1.78	2.65	7.34
o-Xylene	1.35	1.39	1.87	1.56	1.22	1.04	1.09	0.65	2.34	3.60
Naphthalene	0.21	0.10	0.16	0.10	1.42	0.21	0.26	0.16	1.57	0.66
Ethyl acetate	5.59	12.6	4.40	7.31	3.86	0.58	5.22	1.30	1.44	2.81
1,2,4-TMB	0.54	0.39	0.05	0.59	1.03	0.59	0.44	0.29	1.72	2.86
MEK	2.06	1.78	4.48	5.28	2.60	6.90	3.19	1.14	1.47	3.10
Acrolein	0.02	0.00	0.39	0.50	0.02	0.28	0.02	0.00	0.14	1.35

^a NIER (2014), ^b NIER (2015), ^c NIER (2016), ^d NIER (2017), ^e NIER (2018), ^f NIER (2009), ^g NIER (2012), ^h NIER (2013), ⁱ NIER (2020).

^j Metropolitan city, ^k Industrial city.

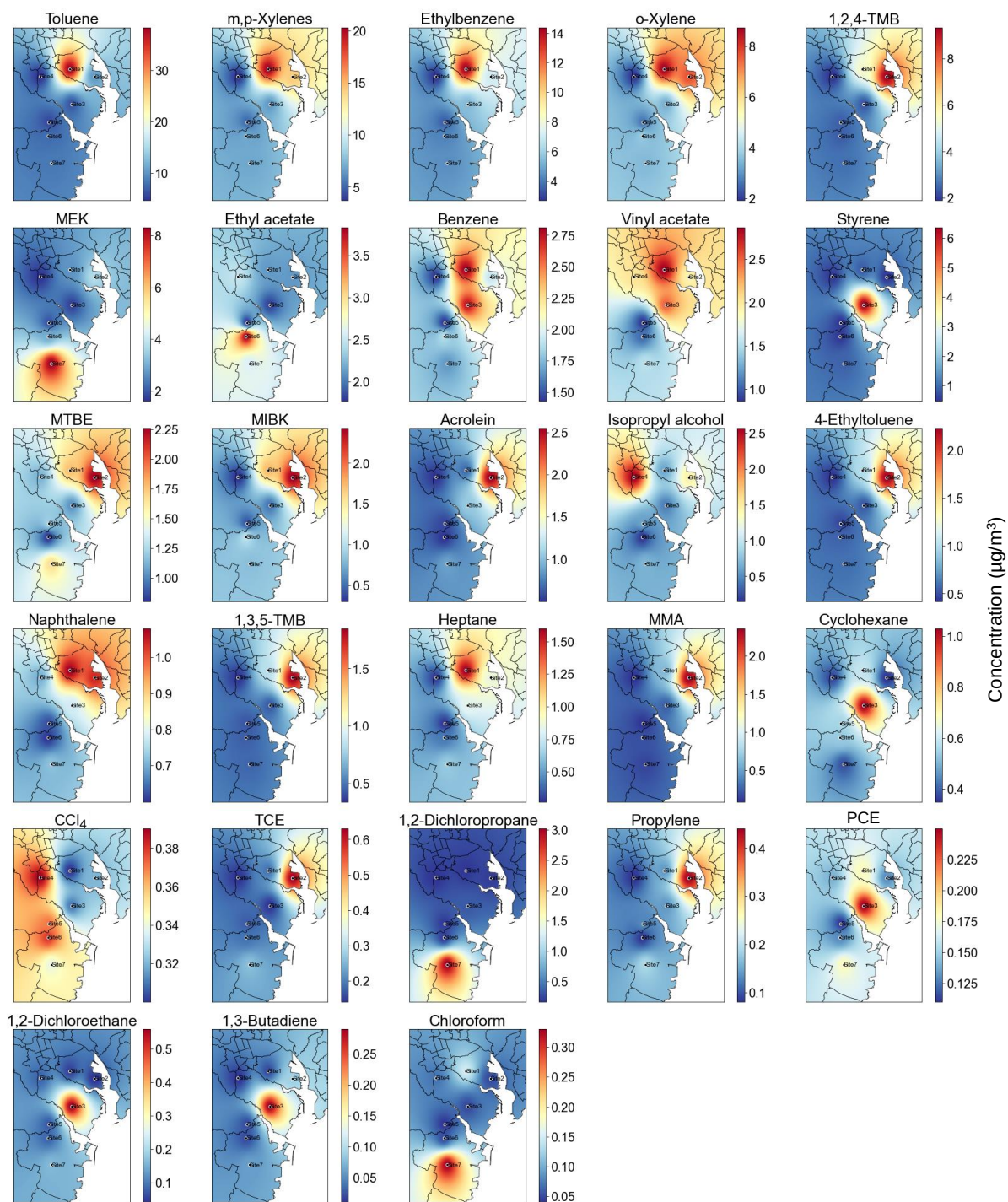


Figure S5. Spatial distributions for concentrations (µg/m³) for the top 28 species among the 59 target VOCs.

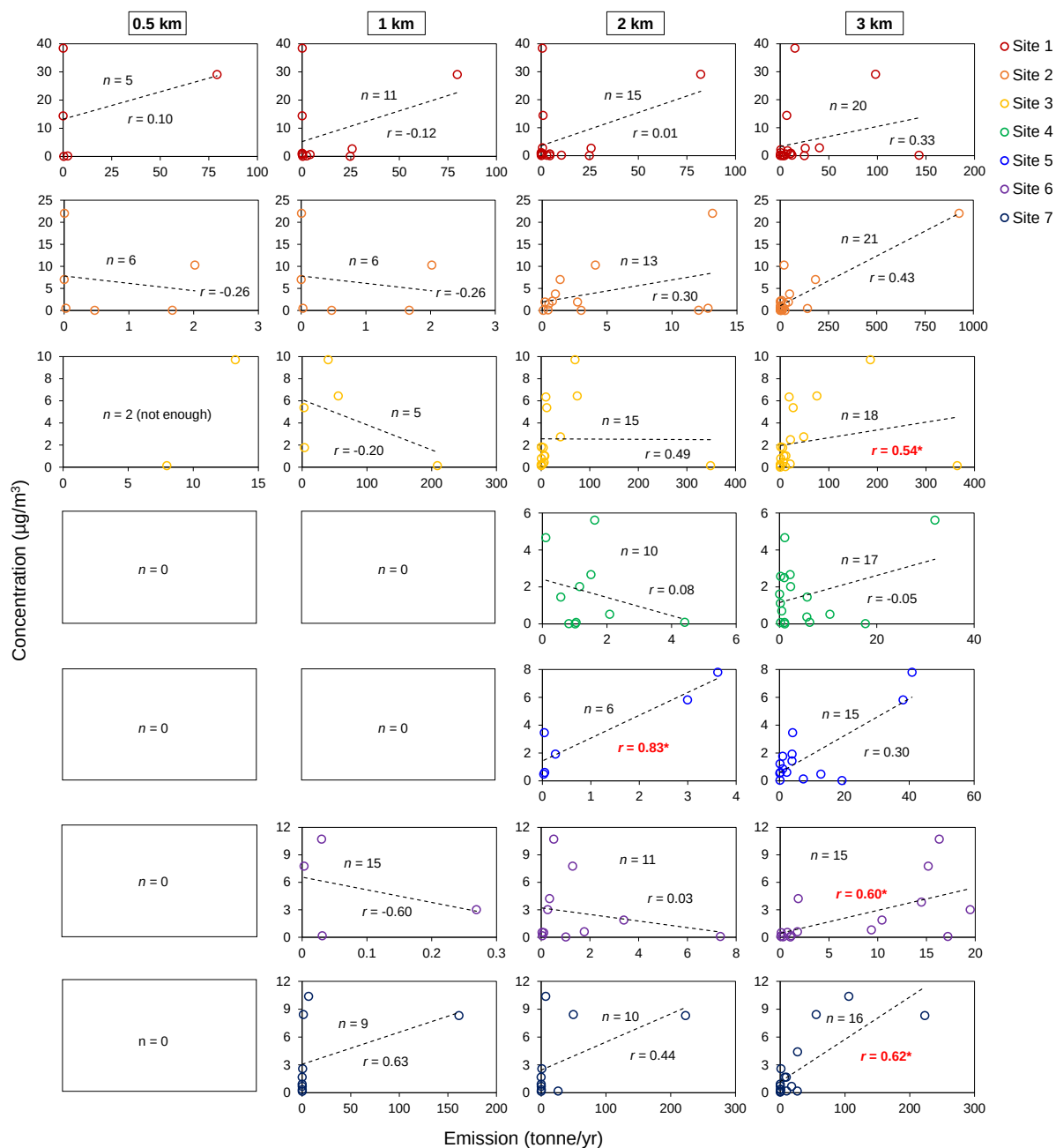


Figure S6. Scatter plots of Spearman's correlations between measured VOC concentrations ($\mu\text{g}/\text{m}^3$) at each sampling site and toxic chemical emissions (tonne/yr) from industrial facilities, as reported in the PRTR system for the year 2020, within radii of 0.5, 1, 2, and 3 km from each site.

Table S5. Detailed factor loadings from PCA of VOCs measured at all passive air sampling sites.

Compound	PC		
	1	2	3
Acrolein	0.54	0.55	0.57
MTBE	0.03	0.81	-0.22
Vinyl acetate	-0.56	0.48	0.29
MEK	-0.08	0.37	-0.60
Ethyl acetate	-0.33	0.64	-0.36
1,2-Dichloroethane	-0.63	0.11	0.69
Benzene	-0.72	0.48	0.37
CTC	-0.39	0.76	-0.21
Cyclohexane	-0.67	0.33	0.47
1,2-Dichloropropane	-0.17	0.18	-0.48
TCE	0.73	0.68	0.00
MMA	0.90	0.04	0.39
n-Heptane	-0.39	-0.51	0.60
MIBK	0.89	-0.03	0.02
Toluene	-0.09	-0.84	-0.38
MBK	-0.54	0.72	-0.17
Ethylbenzene	-0.31	-0.78	0.25
m,p-Xylenes	0.75	-0.53	-0.01
Styrene	-0.56	0.00	0.78
o-Xylene	0.86	-0.07	0.14
4-Ethyltoluene	0.86	0.41	0.28
1,3,5-TMB	0.87	0.38	0.29
1,2,4-TMB	0.88	0.35	0.24
% of Variance	38.4	25.9	15.8
Cumulative %	38.4	64.3	80.1

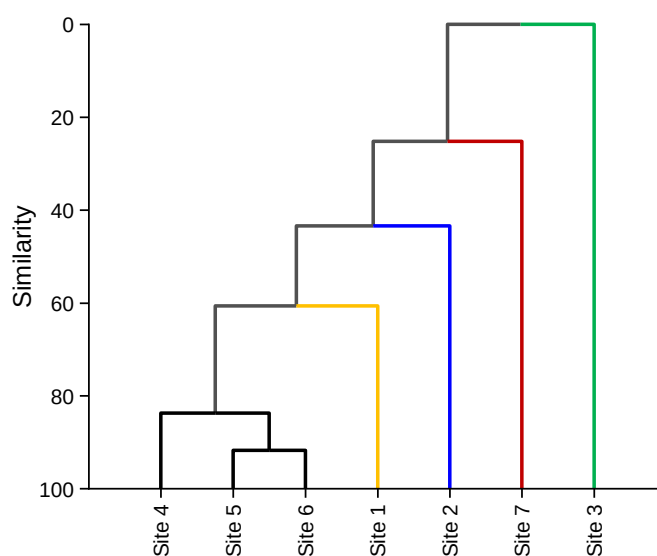


Figure S7. Hierarchical clustering dendrogram for Groups 1 (yellow), 2 (blue), 3 (green), 4 (red), and 5 (black) from the PCA score plot.

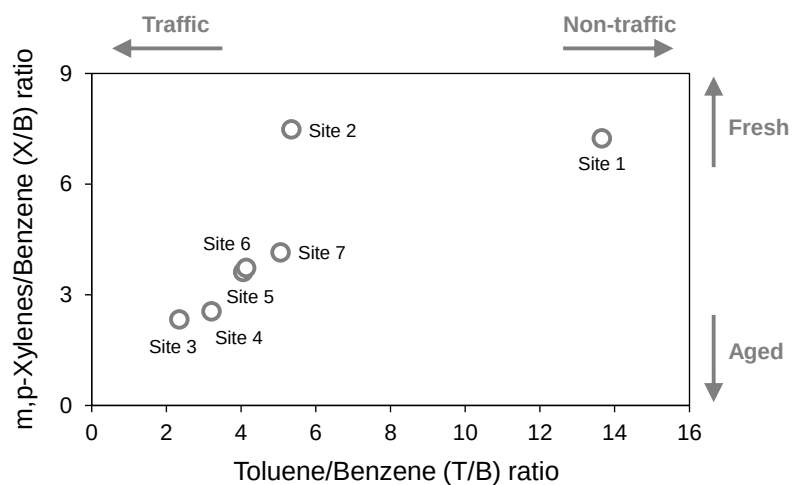


Figure S8. Diagnostic ratios, including toluene/benzene (T/B) and m,p-xylenes/benzene (X/B), for all passive air samples in this study.

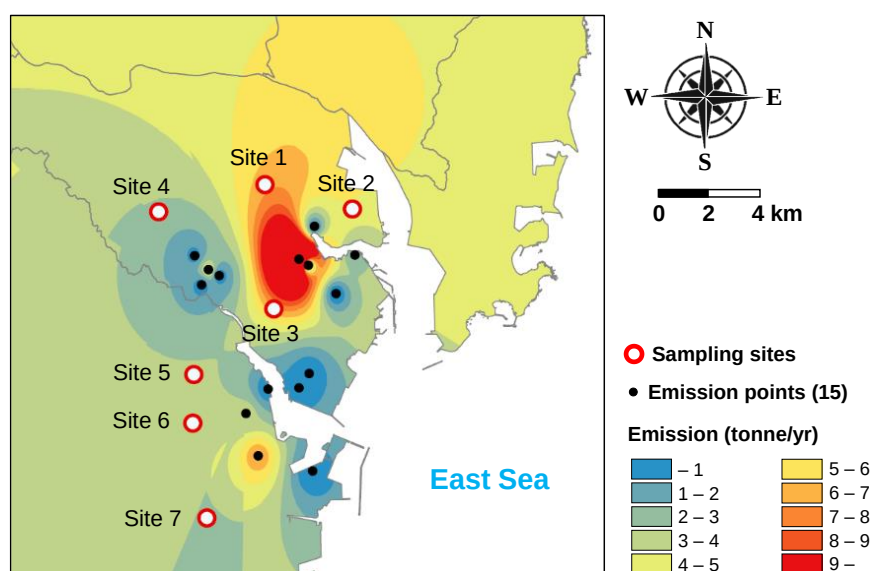


Figure S9. Spatial distribution of benzene emissions reported in the PRTR system for the year 2020.

Table S6. Cancer risks of 14 VOCs from chronic exposure at each passive sampling site.

No.	Compound	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Mean
1	Naphthalene	1.2E-6	1.2E-6	8.2E-7	4.2E-7	2.9E-7	5.4E-7	7.4E-7	7.4E-7
2	Benzene	7.2E-7	4.9E-7	7.0E-7	3.7E-7	3.7E-7	4.8E-7	4.3E-7	5.1E-7
3	Chloroform	3.9E-8	3.0E-8	4.8E-7	6.6E-8	5.7E-8	7.1E-8	1.3E-7	1.3E-7
4	Benzyl chloride	1.2E-7	4.1E-8	3.9E-8	5.5E-8	3.2E-8	3.5E-8	2.5E-7	8.1E-8
5	CTC	2.0E-8	9.0E-8	2.9E-7	1.2E-8	2.1E-8	2.4E-8	6.3E-8	7.4E-8
6	1,2-Dichloroethane	5.9E-8	6.4E-8	6.1E-8	7.8E-8	7.4E-8	7.4E-8	6.7E-8	6.8E-8
7	1,2-Dibromoethane	8.1E-8	3.6E-8	4.4E-8	4.9E-8	3.0E-8	3.3E-8	3.7E-8	4.4E-8
8	TCE	2.5E-8	8.5E-8	1.9E-8	1.9E-8	2.3E-8	2.6E-8	3.5E-8	3.3E-8
9	1,3-Butadiene	3.2E-8	2.6E-8	1.1E-8	3.0E-8	8.7E-9	7.5E-9	9.8E-9	1.8E-8
10	1,1,2,2-Tetrachloroethane	6.0E-9	4.4E-9	5.4E-9	1.0E-8	2.1E-9	3.9E-9	9.0E-9	5.9E-9
11	1,4-Dioxane	4.3E-9	4.5E-9	8.1E-9	3.7E-9	4.2E-9	4.8E-9	8.6E-9	5.4E-9
12	PCE	1.4E-9	3.0E-9	1.4E-9	1.5E-9	1.2E-9	1.3E-9	1.5E-9	1.6E-9
13	Bromoform	1.5E-9	1.1E-9	1.2E-9	1.2E-9	9.4E-10	1.1E-9	1.5E-9	1.4E-9
14	Vinyl chloride	7.1E-12	2.1E-10	3.6E-11	- ^a	-	-	1.5E-10	1.0E-10

^a Not detected in duplicated passive air samples at the site.

Table S7. Non-cancer risks of 36 VOCs from chronic exposure at each passive sampling site.

No.	Compound	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Mean
1	Acrolein	6.7E-2	2.5E-1	1.0E-1	5.0E-2	5.6E-2	5.0E-2	8.7E-2	9.5E-2
2	Naphthalene	3.3E-2	3.2E-2	2.2E-2	1.1E-2	8.0E-3	1.5E-2	2.0E-2	2.0E-2
3	1,2-Dichloropropane	3.9E-3	4.6E-3	7.4E-3	3.5E-3	4.0E-3	4.3E-3	6.9E-2	1.4E-2
4	TCE	8.5E-3	2.9E-2	6.3E-3	6.4E-3	7.9E-3	8.7E-3	1.2E-2	1.1E-2
5	m,p-Xylenes	1.8E-2	1.3E-2	5.8E-3	3.4E-3	4.7E-3	6.3E-3	6.2E-3	8.3E-3
6	Benzene	8.5E-3	5.8E-3	8.3E-3	4.4E-3	4.3E-3	5.7E-3	5.0E-3	6.0E-3
7	1,2,4-TMB	8.3E-3	1.4E-2	3.4E-3	2.9E-3	3.6E-3	3.6E-3	4.0E-3	5.7E-3
8	o-Xylene	7.9E-3	7.0E-3	3.0E-3	1.7E-3	2.4E-3	3.4E-3	3.2E-3	4.1E-3
9	1,3-Butadiene	9.2E-4	4.1E-3	1.3E-2	5.3E-4	9.5E-4	1.1E-3	2.9E-3	3.4E-3
10	1,3,5-TMB	1.3E-3	2.8E-3	6.5E-4	5.1E-4	6.3E-4	6.7E-4	7.0E-4	1.0E-3
11	Vinyl acetate	1.3E-3	8.7E-4	1.1E-3	9.2E-4	3.9E-4	4.7E-4	6.9E-4	8.2E-4
12	Ethylbenzene	1.3E-3	6.4E-4	4.9E-4	2.4E-4	3.1E-4	3.8E-4	4.0E-4	5.4E-4
13	PCE	4.1E-4	2.8E-4	5.6E-4	3.1E-4	2.5E-4	3.0E-4	4.0E-4	3.6E-4
14	MBK	4.7E-4	3.6E-4	3.3E-4	2.8E-4	2.3E-4	3.5E-4	3.4E-4	3.4E-4
15	CTC	2.7E-4	2.9E-4	2.8E-4	3.6E-4	3.4E-4	3.4E-4	3.1E-4	3.1E-4
16	Toluene	7.0E-4	1.9E-4	1.2E-4	8.5E-5	1.1E-4	1.4E-4	1.5E-4	2.1E-4
17	Styrene	7.6E-5	4.6E-5	5.8E-4	4.7E-5	4.4E-5	4.5E-5	8.4E-5	1.3E-4
18	1,4-Dioxane	7.9E-5	8.2E-5	1.5E-4	6.7E-5	7.6E-5	8.8E-5	1.6E-4	1.0E-4
19	MMA	7.9E-5	3.1E-4	3.1E-5	1.2E-5	1.1E-5	2.4E-5	2.0E-5	6.9E-5
20	MEK	4.8E-5	6.8E-5	3.2E-5	2.9E-5	3.5E-5	5.5E-5	1.5E-4	6.0E-5
21	MTBE	5.3E-5	6.8E-5	3.1E-5	3.4E-5	3.7E-5	2.4E-5	5.1E-5	4.3E-5
22	Chloroform	4.6E-5	1.6E-5	1.5E-5	2.2E-5	1.3E-5	1.4E-5	1.0E-4	3.2E-5
23	MIBK	5.3E-5	7.4E-5	1.6E-5	9.1E-6	1.2E-5	3.1E-5	2.5E-5	3.1E-5
24	Bromomethane	3.6E-5	1.6E-5	1.4E-5	1.3E-5	2.4E-5	-	2.7E-6	1.8E-5
25	Isopropyl alcohol	7.9E-6	1.9E-5	5.7E-6	3.3E-5	7.8E-6	2.0E-6	8.9E-6	1.2E-5
26	1,2-Dibromoethane	1.6E-5	1.3E-5	5.6E-6	1.6E-5	4.4E-6	3.8E-6	5.0E-6	9.1E-6
27	Cyclohexane	8.9E-6	5.2E-6	1.6E-5	5.6E-6	8.4E-6	8.1E-6	5.8E-6	8.2E-6
28	Propylene	4.2E-6	1.3E-5	4.2E-6	2.5E-6	4.0E-6	2.4E-6	5.7E-6	5.2E-6
29	Chloromethane	1.6E-6	1.8E-5	2.5E-6	1.1E-6	1.2E-6	-	1.6E-6	4.3E-6
30	Chlorobenzene	3.9E-6	4.1E-6	4.2E-6	3.2E-6	2.7E-6	3.6E-6	4.4E-6	3.7E-6
31	1,4-Dichlorobenzene	2.6E-6	2.4E-6	1.8E-6	3.4E-6	1.8E-6	1.7E-6	3.6E-6	2.5E-6
32	Tetrahydrofuran	1.1E-6	6.1E-7	1.7E-6	1.3E-6	6.3E-7	7.2E-7	8.1E-7	9.7E-7
33	1,1-Dichloroethene	- ^a	1.5E-6	1.4E-7	-	7.3E-8	-	-	5.9E-7
34	Vinyl chloride	2.2E-8	6.6E-7	1.1E-7	-	-	-	4.8E-7	3.2E-7
35	1,1,1-Trichloroethane	1.0E-7	1.2E-7	1.7E-7	1.2E-7	1.1E-7	1.9E-7	1.3E-7	1.3E-7
36	Chloroethane	2.8E-8	1.0E-7	4.4E-8	6.3E-9	-	1.1E-8	5.2E-8	4.1E-8

^a Not detected in duplicated passive air samples at the site.

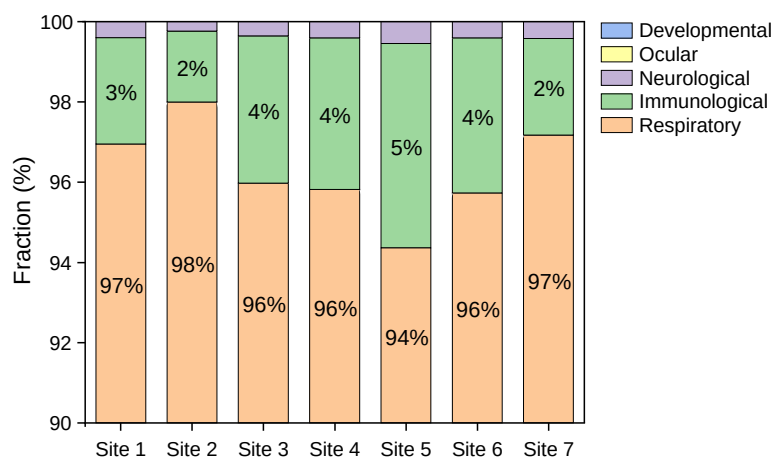


Figure S10. Fractional contributions (%) of hazard indices for each organ system, including developmental, ocular, neurological, immunological, and respiratory.

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