Source investigation and risk assessment of air toxics in an environmental justice community

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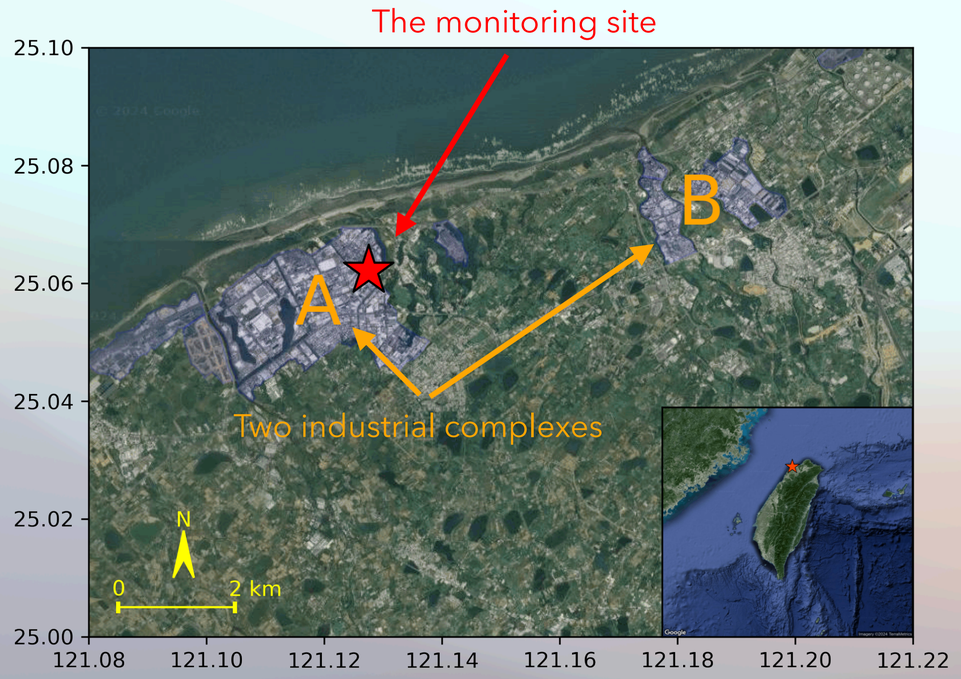
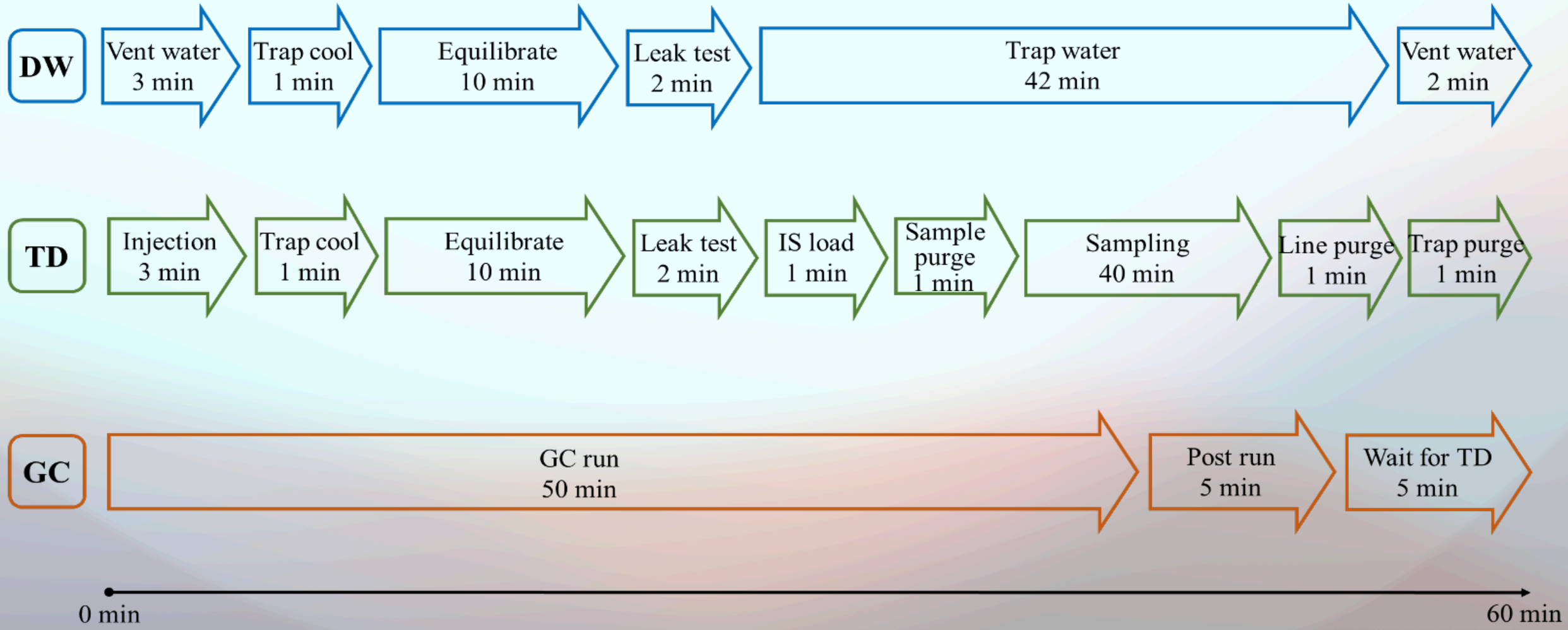
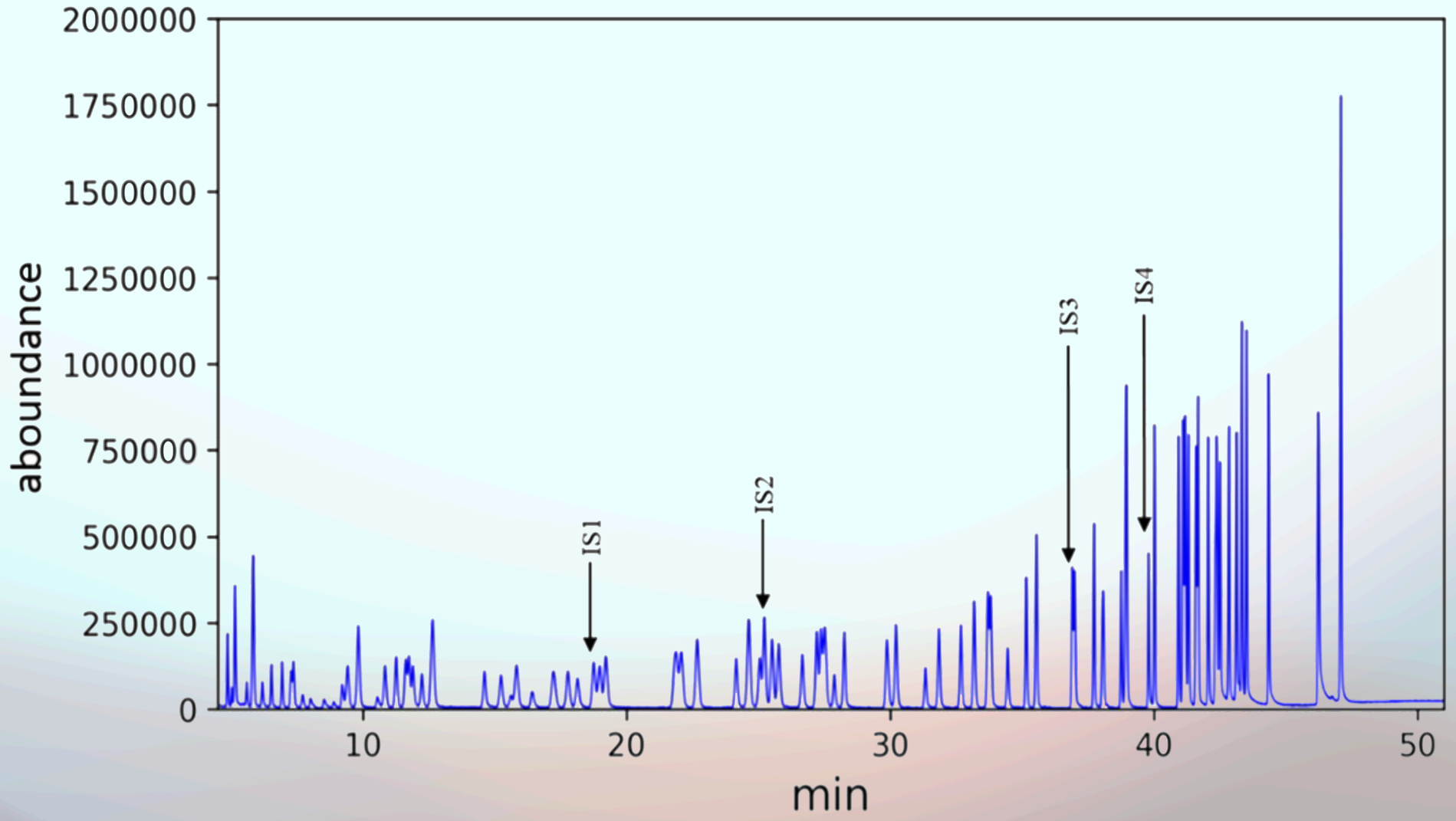
Site Description & Instruments



Synergic actions between DW, TD, and GC of TD-GCMS



A typical TIC chromatogram from analysis of 86 target compounds.



Internal Standards: (IS1) bromochloromethane, (IS2) 1,4-difluorobenzene, (IS3) chlorobenzene-d5, (IS4) p-bromofluorobenzene.

Calibration Curve & Method Detection Limit

No.	Compound	R^2	RSD (%)	MDL (ppb)
1	Propane	0.997	14.76	0.67
2	Isopentane	0.998	24.41	0.50
3	Pentane	0.999	17.08	0.14
4	2-Methylpentane	1.000	2.93	0.12
5	3-Methylpentane	0.995	7.59	0.11
6	Hexane	0.994	7.58	0.14
7	2,4-Dimethylpentane	0.999	6.76	0.23
8	Methylcyclopentane	0.999	4.70	0.93
9	2-Methylhexane	0.999	8.53	0.20
10	Cyclohexane	0.999	4.42	1.18
11	2,3-Dimethylpentane	0.999	4.67	0.17
12	2,2,4-Trimethylpentane	0.999	2.14	1.09
13	Heptane	0.998	5.67	0.31
14	Methylcyclohexane	0.997	4.88	1.03
15	2-Methylheptane	0.996	6.06	1.13
16	3-Methylheptane	0.995	7.45	1.09
17	Octane	0.998	4.71	0.99
18	n-Undecane	0.998	5.21	0.91
19	n-Dodecane	0.979	17.74	0.82
20	1,3-Butadiene	0.997	13.35	0.28
21	trans-2-Butene	0.998	16.77	0.25
22	cis-2-Butene	0.996	19.03	0.16
23	trans-2-Pentene	0.999	14.78	0.09
24	cis-2-Pentene	0.998	16.18	0.12
25	Benzene	0.999	3.73	0.44
26	Toluene	0.995	7.33	0.22
27	Ethylbenzene	0.999	2.56	0.65
28	m,p-Xylene	0.999	3.89	0.24
29	o-Xylene	0.998	4.57	0.69
30	Styrene	0.998	5.65	0.28
31	Isopropylbenzene	0.997	4.48	0.19
32	n-Propylbenzene	0.996	4.27	0.98
33	m-Ethyltoluene	0.997	3.15	0.17
34	p-Ethyltoluene	0.999	5.22	0.21
35	1,3,5-Trimethylbenzene	0.998	2.89	1.10
36	o-Ethyltoluene	0.998	2.61	0.17
37	alpha-Methylstyrene	0.995	5.04	0.75
38	1,2,4-Trimethylbenzene	0.998	2.59	0.18
39	1,2,3-Trimethylbenzene	0.996	4.00	0.90
40	m-Diethylbenzene	0.996	3.85	0.21
41	p-Diethylbenzene	0.998	3.54	0.16

No.	Compound	R^2	RSD (%)	MDL (ppb)
42	Acrolein	0.998	13.21	2.46
43	Acetone	0.993	26.98	1.76
44	Acetonitrile	0.999	19.01	0.60
45	Acrylonitrile	0.999	3.50	0.32
46	Vinyl acetate	0.996	4.96	1.87
47	2-Butanone	0.986	8.71	0.32
48	Methyl methacrylate	0.996	8.17	0.62
49	Methyl isobutyl ketone	0.995	7.64	0.21
50	CFC-12	0.999	7.09	0.65
51	CFC-22	1.000	13.78	0.78
52	CFC-114	0.999	11.11	0.22
53	Chloromethane	0.990	23.69	0.50
54	Vinyl chloride	1.000	13.40	0.29
55	Bromomethane	1.000	11.81	0.62
56	Chloroethane	1.000	14.18	0.72
57	CFC-11	1.000	12.76	0.14
58	1,1-Dichloroethene	0.999	15.55	0.11
59	CFC-113	0.904	25.62	0.17
60	3-Chloro-1-propene	0.999	24.15	0.13
61	Methylene chloride	0.999	15.95	0.39
62	1,1-Dichloroethane	0.999	4.13	0.13
63	cis-1,2-Dichloroethene	1.000	6.17	0.88
64	Chloroform	0.995	6.89	0.18
65	1,1,1-Trichloroethane	0.998	5.82	0.30
66	Carbon tetrachloride	0.998	4.31	0.32
67	1,2-Dichloroethane	0.998	3.93	0.70
68	Trichloroethene	0.999	3.70	0.13
69	1,2-Dichloropropane	0.999	3.90	0.20
70	Bromodichloromethane	0.999	2.64	0.26
71	cis-1,3-Dichloro-1-propene	0.996	5.05	0.97
72	1,1,2-Trichloroethane	0.997	6.33	0.14
73	Tetrachloroethylene	0.997	6.60	0.15
74	Dibromochloromethane	0.994	6.47	1.16
75	1,2-Dibromoethane	0.994	6.35	0.15
76	Chlorobenzene	0.997	3.20	0.85
77	1,1,2,2-Tetrachloroethane	0.997	3.97	0.30
78	1,3-Dichlorobenzene	0.997	4.54	0.19
79	1,4-Dichlorobenzene	0.997	4.58	0.20
80	1,2-Dichlorobenzene	0.997	3.63	0.20
81	1,2,4-Trichlorobenzene	0.996	9.75	0.24
82	Hexachlorobutadiene	0.996	12.62	0.24

Health Risk Assessment

Hazard Index Acute, HI_A

$$HI_A = \frac{C_1}{Acute\_REL_1} + \frac{C_2}{Acute\_REL_2} + \cdots\cdots + \frac{C_i}{Acute\_REL_i}$$

Hazard Index Chronic, HI_C

$$HI_C = \frac{C_{avg_1}}{Chronic\_REL_1} + \frac{C_{avg_2}}{Chronic\_REL_2} + \cdots\cdots + \frac{C_{avg_i}}{Chronic\_REL_i}$$

Lifetime Cancer Risk, LCR

$$LCR_i = C_i \times URF_i$$

Reference Exposure Level, REL: μg/m^3

Unite Risk Factor, URF: m^3/μg

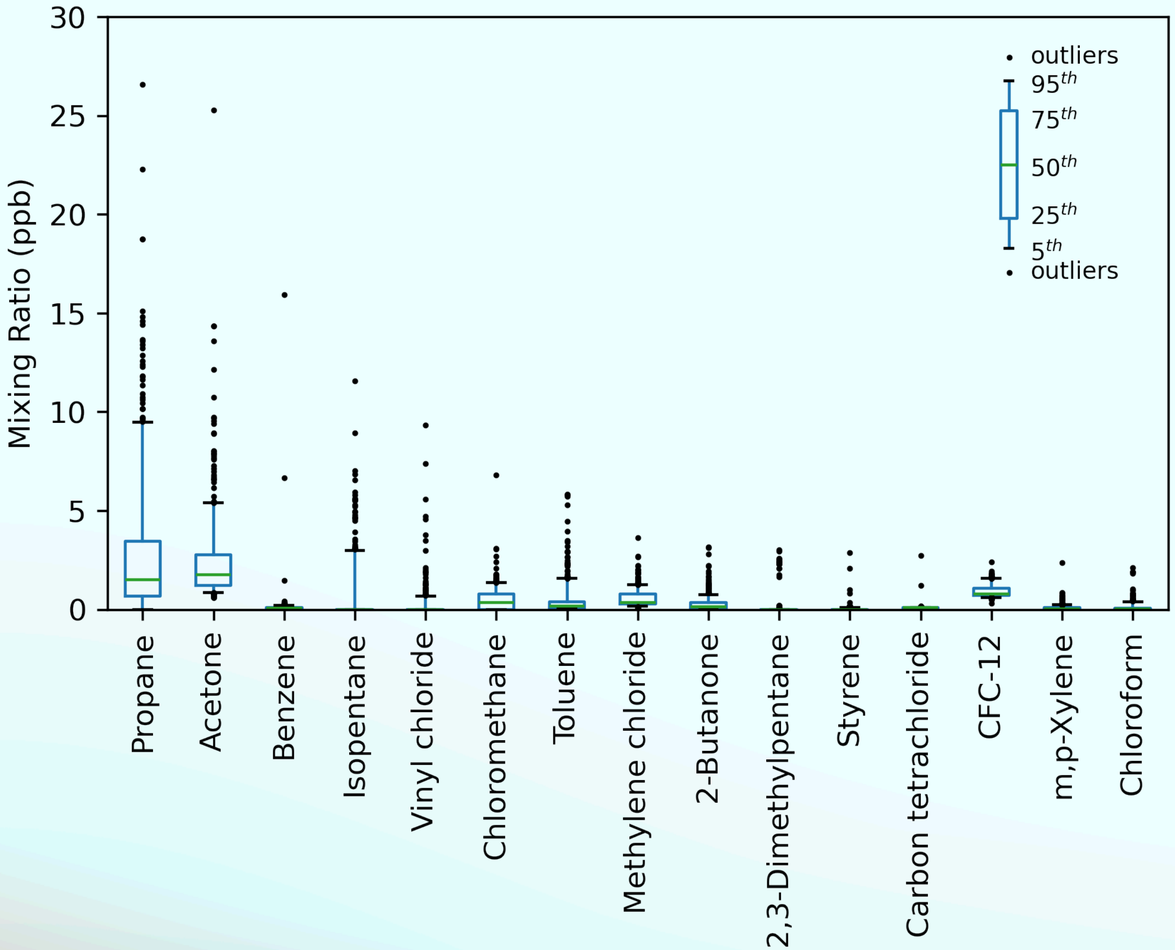
HI_A or HI_C Threshold ≥ 1

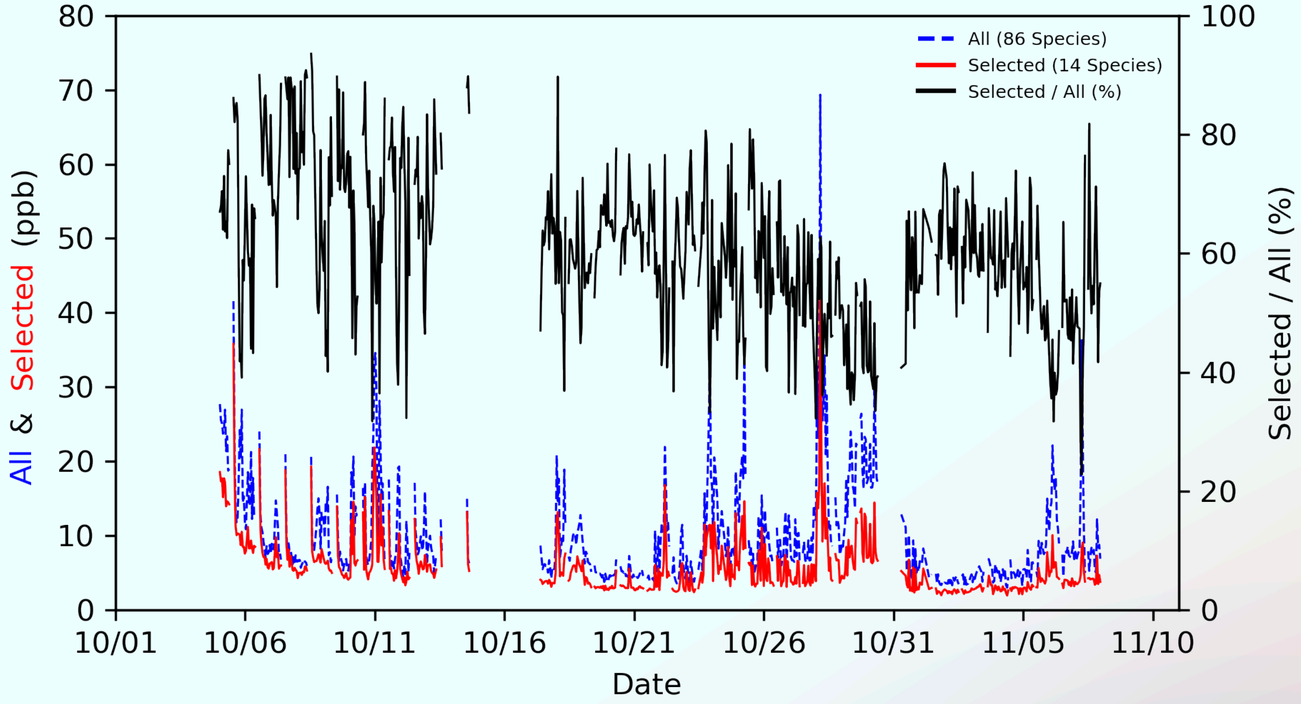
LCR Threshold ≥ 1×10^{-6}

OEHHA Reference Exposure Level Summary

No.	Compound	Macular Weight	Acute	Non-carcinogenic	Carcinogenic
1	Propane	44.10			
2	Isopentane	72.15			
3	Pentane	72.15			
4	2-Methylpentane	86.18			
5	3-Methylpentane	86.18			
6	Hexane	86.18		7000	
7	2,4-Dimethylpentane	100.20			
8	Methylcyclopentane	84.16			
9	2-Methylhexane	100.20			
10	Cyclohexane	84.16			
11	2,3-Dimethylpentane	100.20			
12	2,2,4-Trimethylpentane	114.23			
13	Heptane	100.20			
14	Methylcyclohexane	98.19			
15	2-Methylheptane	114.23			
16	3-Methylheptane	114.23			
17	Octane	114.23			
18	n-Undecane	156.31			
19	n-Dodecane	170.34			
20	1,3-Butadiene	54.09	660	2	1.70E-04
21	trans-2-Butene	56.11			
22	cis-2-Butene	56.11			
23	trans-2-Pentene	70.13			
24	cis-2-Pentene	70.13			
25	Benzene	78.11	27	3	2.90E-05
26	Toluene	92.14	5000	420	
27	Ethylbenzene	106.17		2000	2.50E-06
28	m,p-Xylene	106.17	22000	700	
29	o-Xylene	106.17	22000	700	
30	Styrene	104.15	21000	900	
31	Isopropylbenzene	120.19			
32	n-Propylbenzene	120.19			
33	m-Ethyltoluene	120.19			
34	p-Ethyltoluene	120.19			
35	1,3,5-Trimethylbenzene	120.19	2400	4	
36	o-Ethyltoluene	120.19			
37	alpha-Methylstyrene	118.18			
38	1,2,4-Trimethylbenzene	120.19	2400	4	
39	1,2,3-Trimethylbenzene	120.19	2400	4	
40	m-Diethylbenzene	134.22			
41	p-Diethylbenzene	134.22			

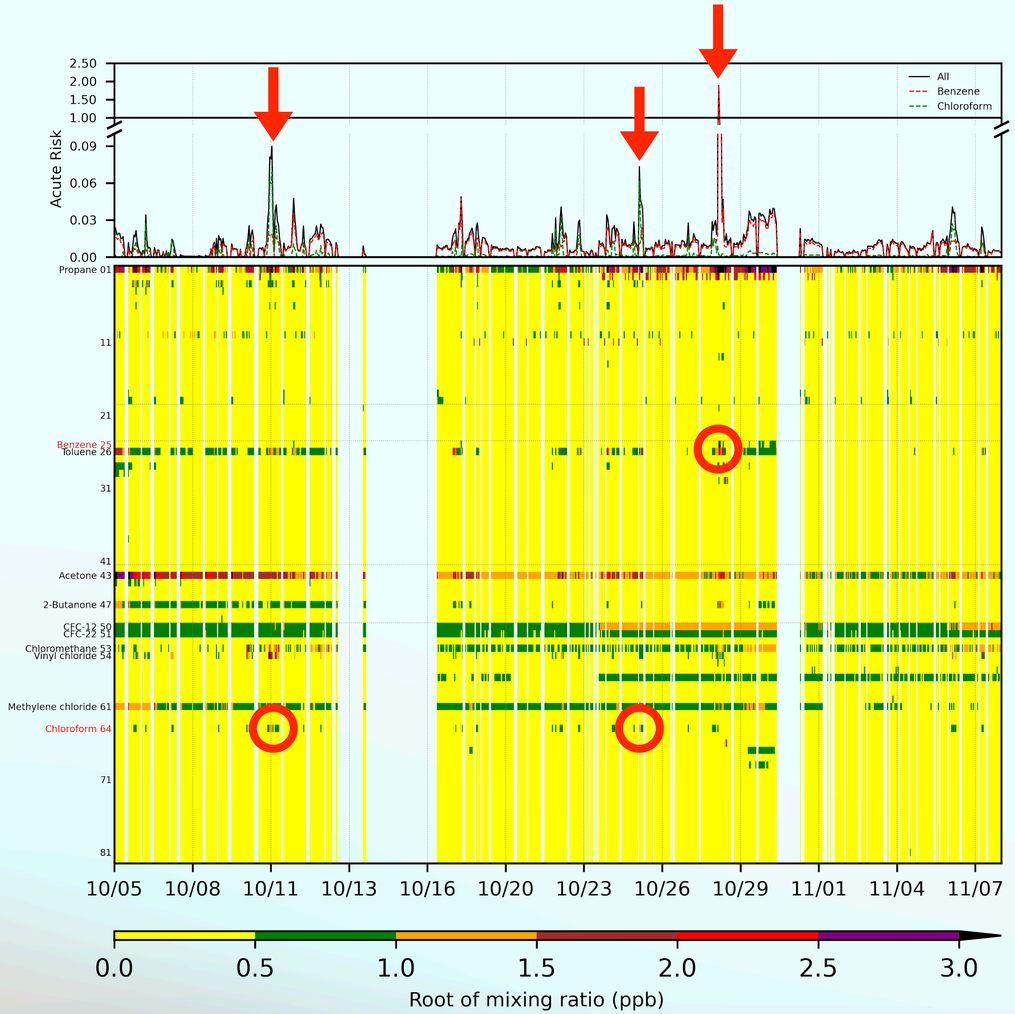
No.	Compound	Macular Weight	Acute	Non-carcinogenic	Carcinogenic
42	Acrolein	56.06	2.5	0.35	
43	Acetone	58.08			
44	Acetonitrile	41.05			
45	Acrylonitrile	53.06		5	2.90E-04
46	Vinyl acetate	86.09		200	
47	2-Butanone	72.11	13000		
48	Methyl methacrylate	100.12			
49	Methyl isobutyl ketone	100.16			
50	CFC-12	120.91			
51	CFC-22	86.47			
52	CFC-114	170.92			
53	Chloromethane	50.49			
54	Vinyl chloride	62.50	180000		7.80E-05
55	Bromomethane	94.94	3900	5	
56	Chloroethane	64.51		30000	
57	CFC-11	137.37			
58	1,1-Dichloroethene	96.94		70	
59	CFC-113	187.38			
60	3-Chloro-1-propene	76.53			6.00E-06
61	Methylene chloride	84.93	14000	400	1.00E-06
62	1,1-Dichloroethane	98.96			1.60E-06
63	cis-1,2-Dichloroethene	96.94			
64	Chloroform	119.38	150	300	5.30E-06
65	1,1,1-Trichloroethane	133.40	68000	1000	
66	Carbon tetrachloride	153.82	1900	40	4.20E-05
67	1,2-Dichloroethane	98.96		400	2.10E-05
68	Trichloroethene	131.39		600	2.00E-06
69	1,2-Dichloropropane	112.99			1.00E-05
70	Bromodichloromethane	163.83			3.70E-05
71	cis-1,3-Dichloro-1-propene	110.97			
72	1,1,2-Trichloroethane	133.40			1.60E-05
73	Tetrachloroethylene	165.83	20000	35	6.10E-06
74	Dibromochloromethane	208.28			
75	1,2-Dibromoethane	187.86		0.8	7.10E-05
76	Chlorobenzene	112.56		1000	
77	1,1,2,2-Tetrachloroethane	167.85			8.50E-05
78	1,3-Dichlorobenzene	147.00			
79	1,4-Dichlorobenzene	147.00		800	1.10E-05
80	1,2-Dichlorobenzene	147.00			
81	1,2,4-Trichlorobenzene	181.45			
82	Hexachlorobutadiene	260.76			

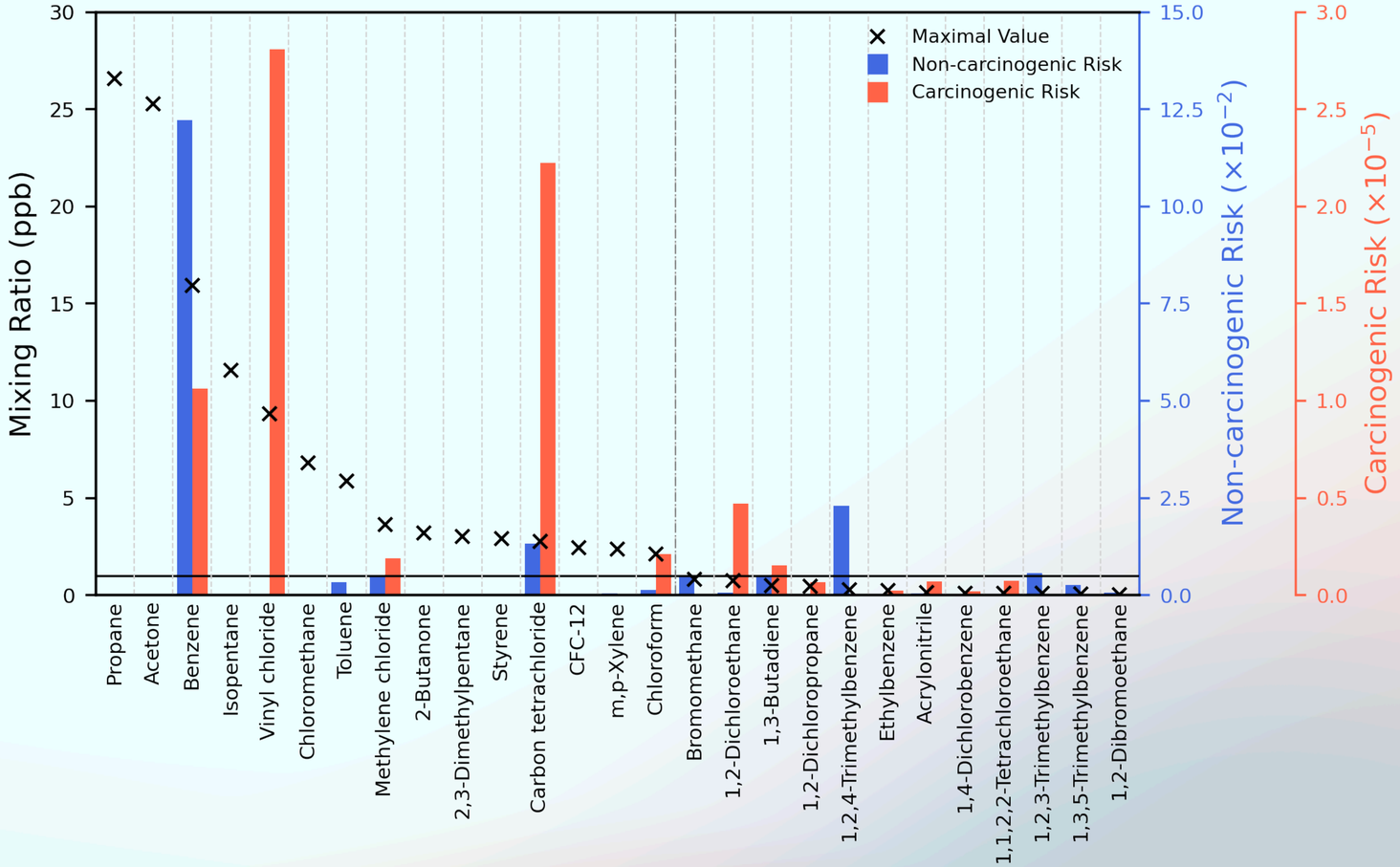




⬅️: Box plots for the 15 most variable species of the 86 target VOCs measured over a month-long period with hourly resolution at an industrial site near an EJ community. The large variability suggests significant emissions.

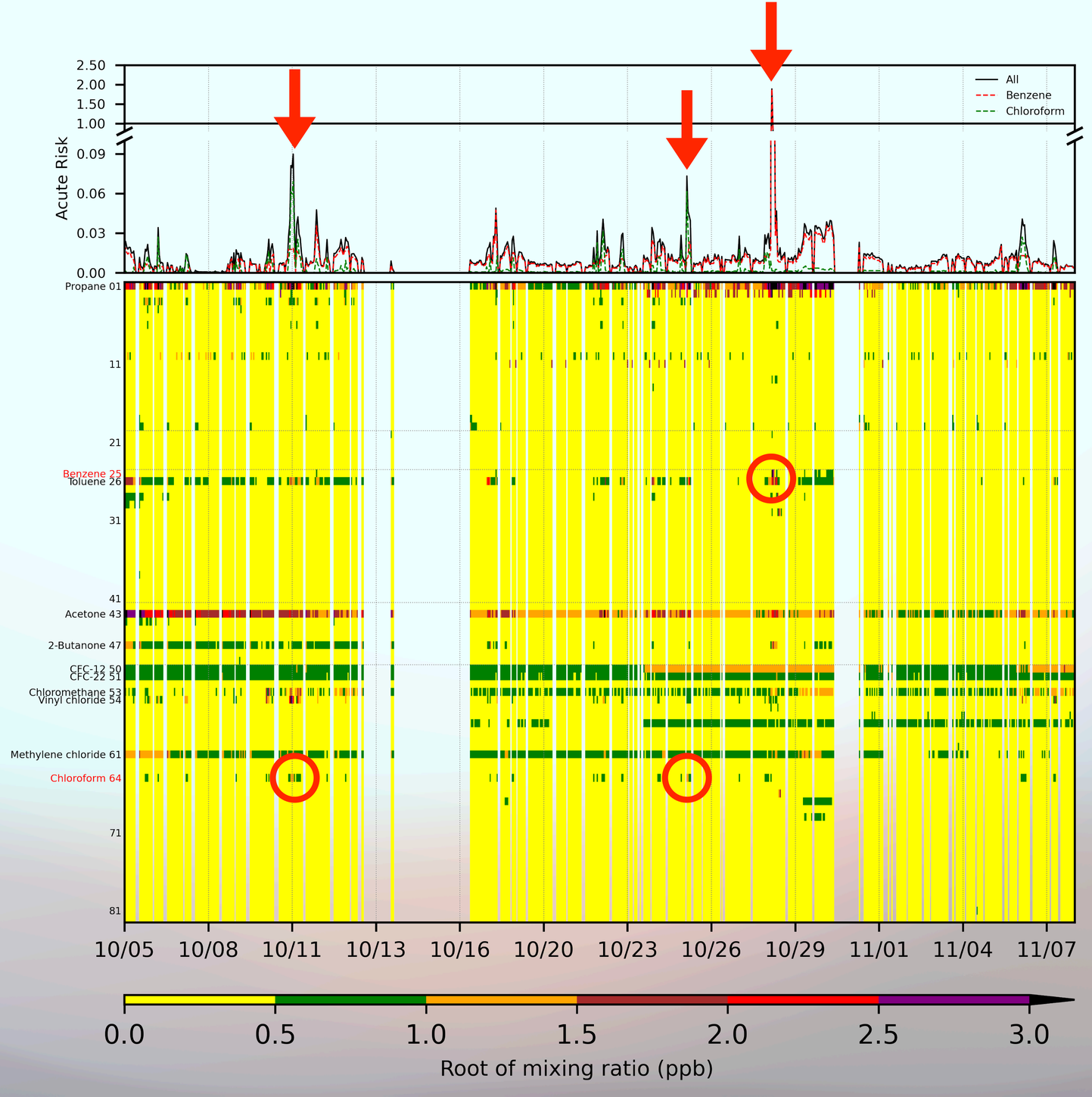
➡️: The chart displays the total abundance of 86 toxic VOCs (blue dashed line) and the 14 most variable, yet more toxic species without propane (red line), both measured against the left Y-axis. The contribution of these 14 species to the total is shown by a dark line on the right Y-axis. Propane was excluded due to its lower toxicity but high abundance. Despite its removal, these 14 species still make up 40% to 85% of the total VOCs.

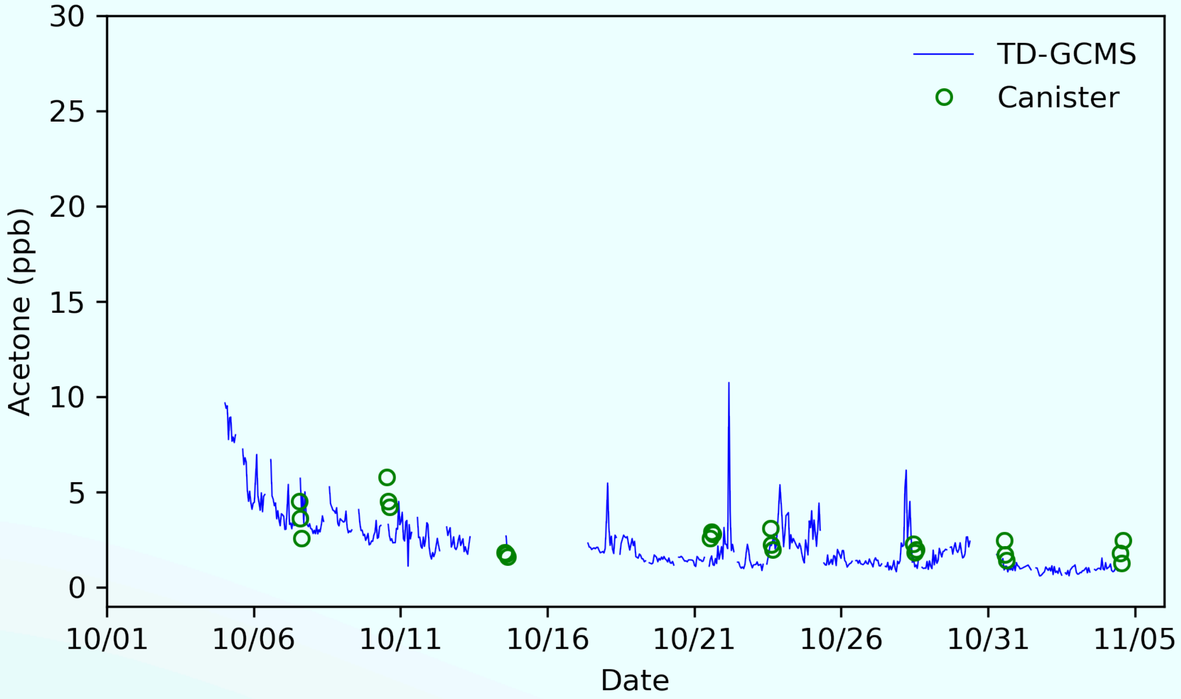


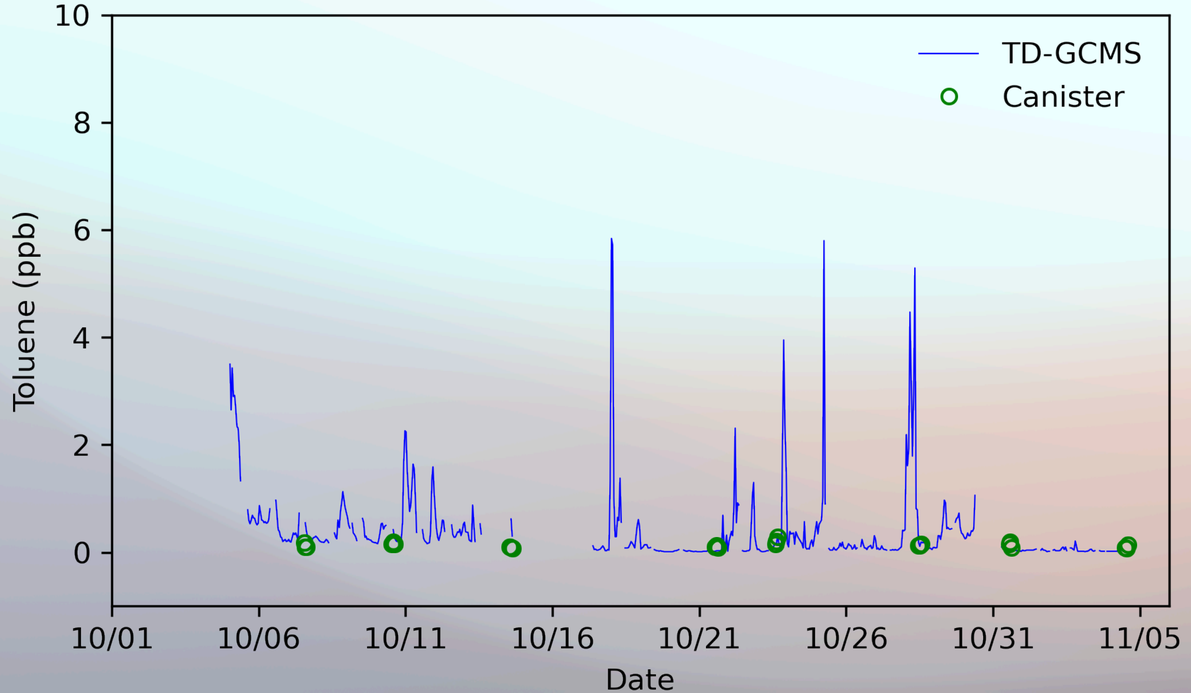


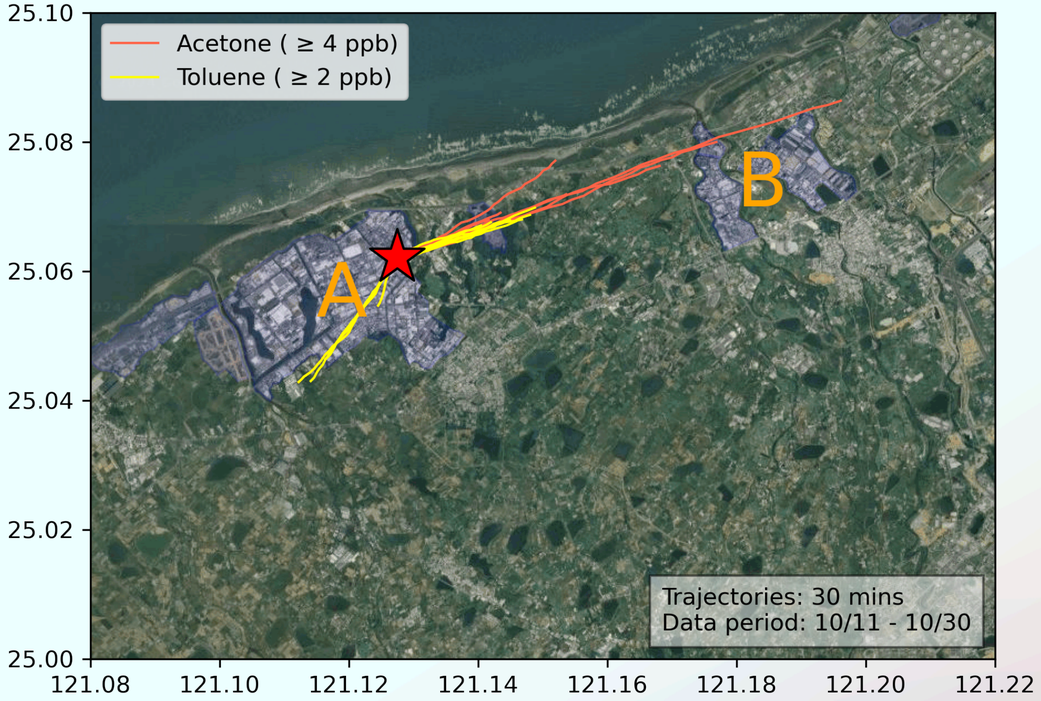
The heatmap reveals the relationship between mixing ratio and time for target VOCs. The relatively high chloroform and benzene mixing ratio (red circle) correspond to the abrupt surges in acute risk, as seen in the hourly risk chart above indicated by arrows.

Despite the relatively high concentrations of propane and acetone, they pose no chronic or carcinogenic risks. Both benzene and chloroform are strongly linked to carcinogenic risks, but benzene alone carries both acute and carcinogenic risks, with the acute threshold at 1, and the carcinogenic threshold at 10^{-6}, as indicated by the dark line.

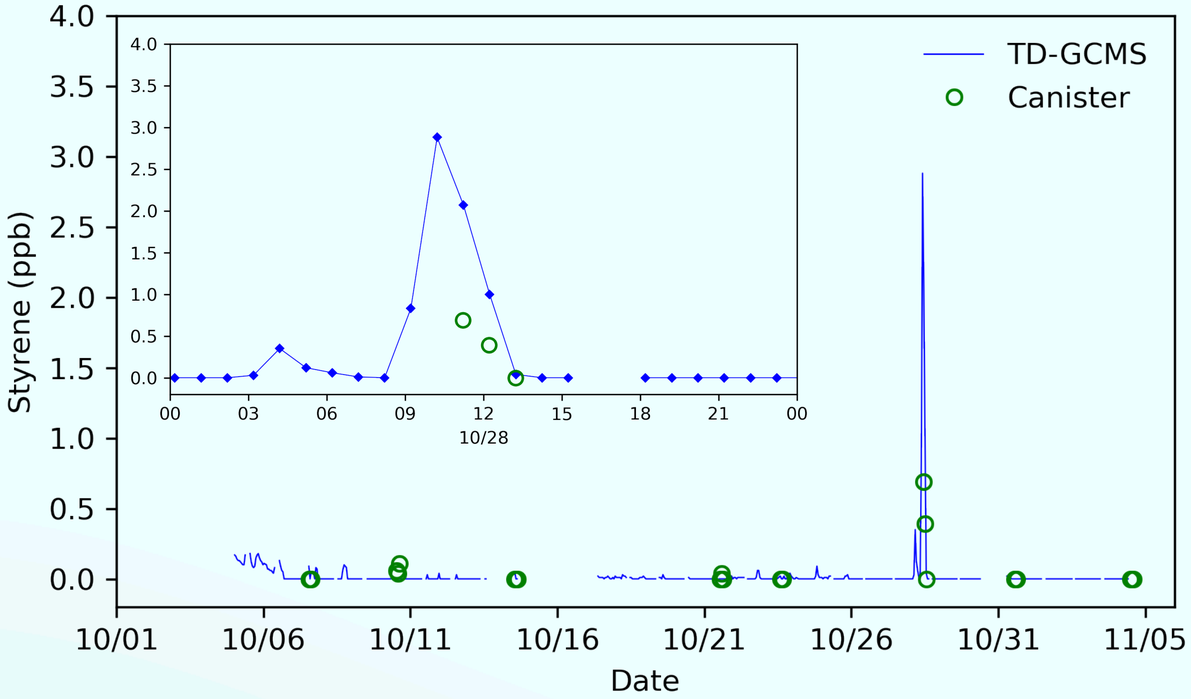

Acute Risk
2.50
2.00
1.50
1.00
0.09
0.06
0.03
0.00
All
Benzene
Chloroform
Propane 01
11
21
Benzene 25
Toluene 26
31
41
Acetone 43
2-Butanone 47
CFC-12 50
CFC-22 51
Chloromethane 53
Vinyl chloride 54
Methylene chloride 61
Chloroform 64
71
81
10/05
10/08
10/11
10/13
10/16
10/20
10/23
10/26
10/29
11/01
11/04
11/07
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Root of mixing ratio (ppb)

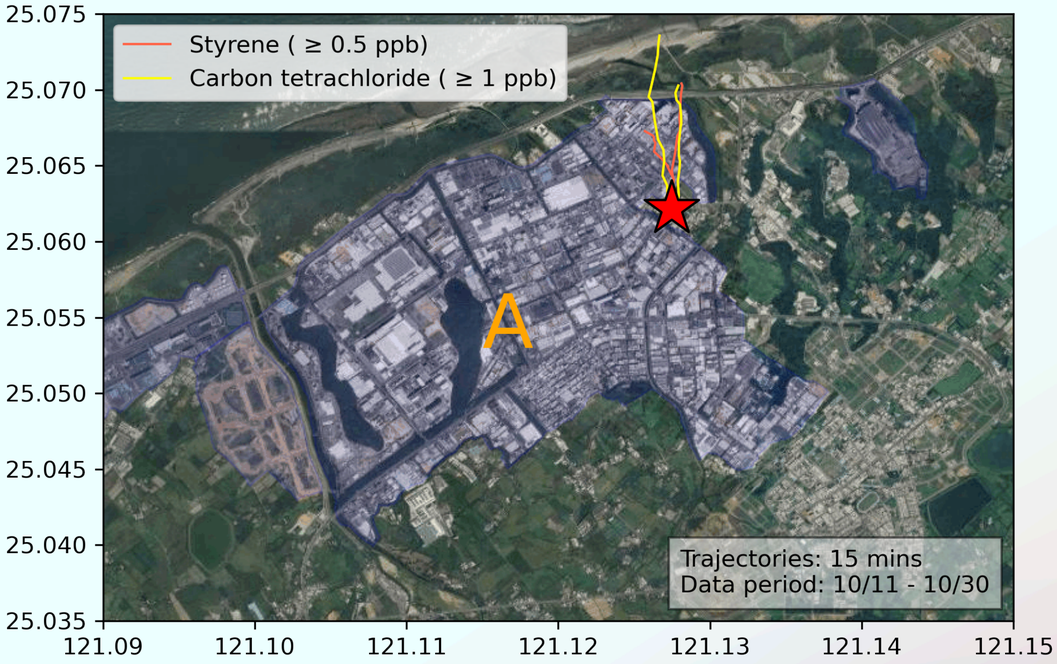


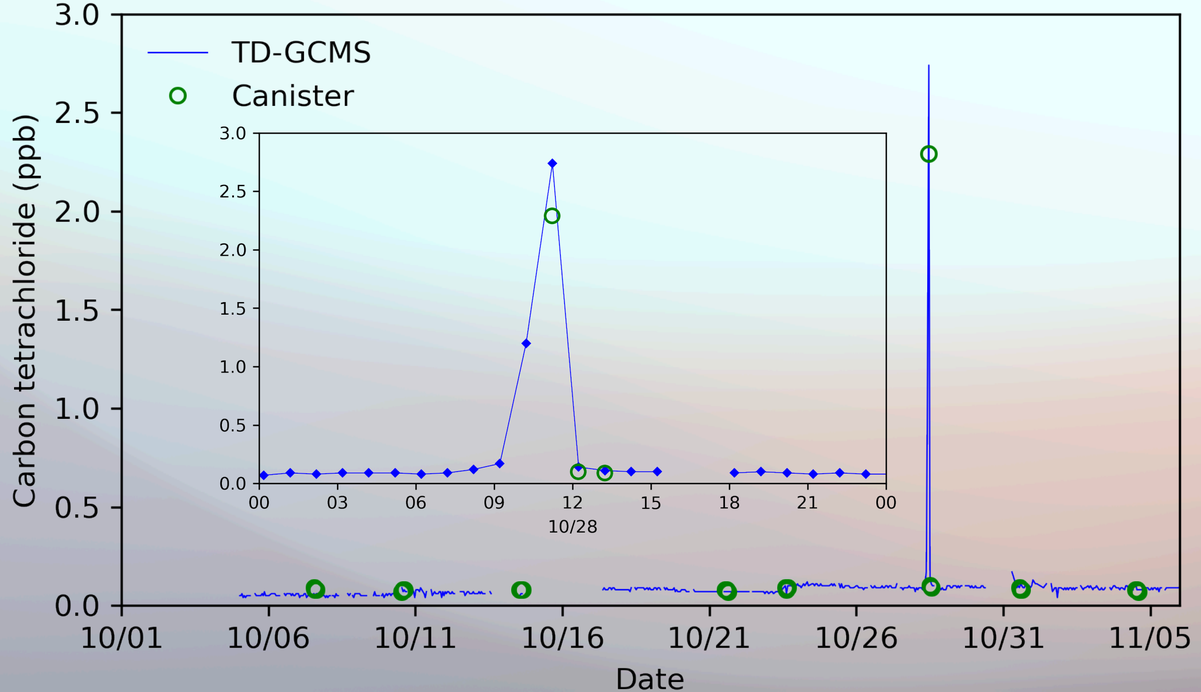




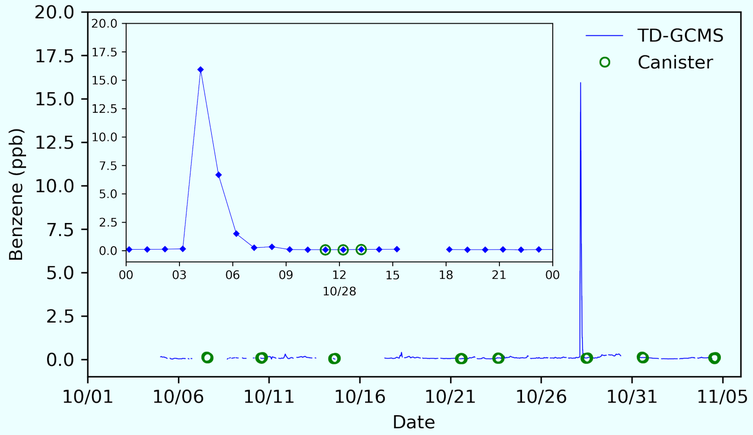
Back trajectories for acetone and toluene. The concentration threshold for identifying spikes and calculating trajectories for each compound is indicated in the legend. Acetone and toluene appeared to come from complexes A and B since they are pervasively used in the industry.

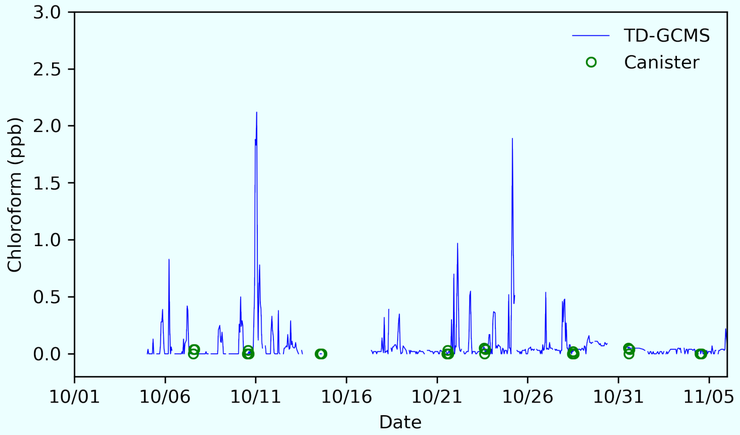


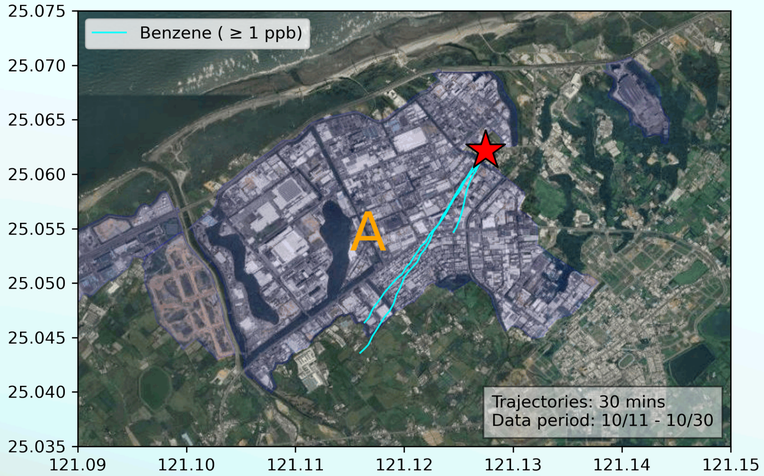


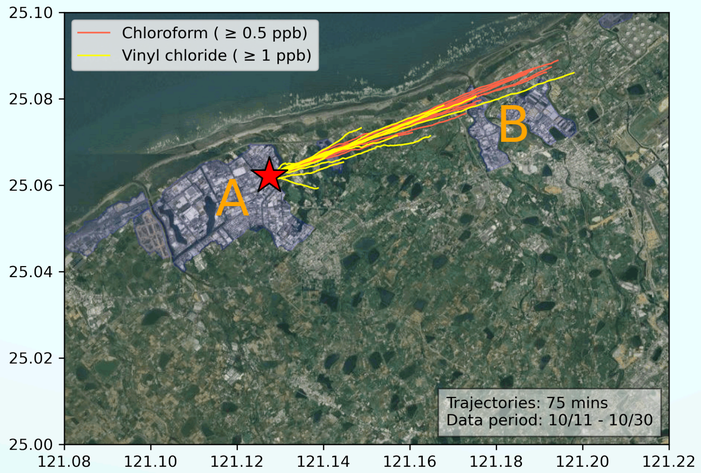


Blowups of styrene and carbon tetrachloride spikes. Hourly data points of the online TD-GCMS are also shown. We noticed that carbon tetrachloride was found in one canister sample and two canisters captured styrene. A sudden shift in wind direction can quickly change the relationship between the source and receptor, potentially causing confusion in investigating the source if online results are not available.









The offline method of Flask sampling (green circle) failed to detect pollution plumes in a timely manner. Backward trajectory analysis traced benzene spikes to the southwest and vinyl chloride and chloroform to the northeast, beyond the monitoring site's industrial park. This analysis pointed to Complex B, where textile and plastic factories use chlorinated solvents, as the likely source of these emissions.

Conclusion

TD-GCMS gathering hourly data was deemed the most suitable online device for source investigation and health risk assessment due to its superior accuracy, species coverage, and data continuity. It proved to be more versatile in detecting both chlorinated and non-chlorinated air toxics with irreplaceable accuracy pivotal for robust hazard assessment resulting from the acute effects, chronic effects, and carcinogenic risks induced by long-term exposure to ambient air toxics.