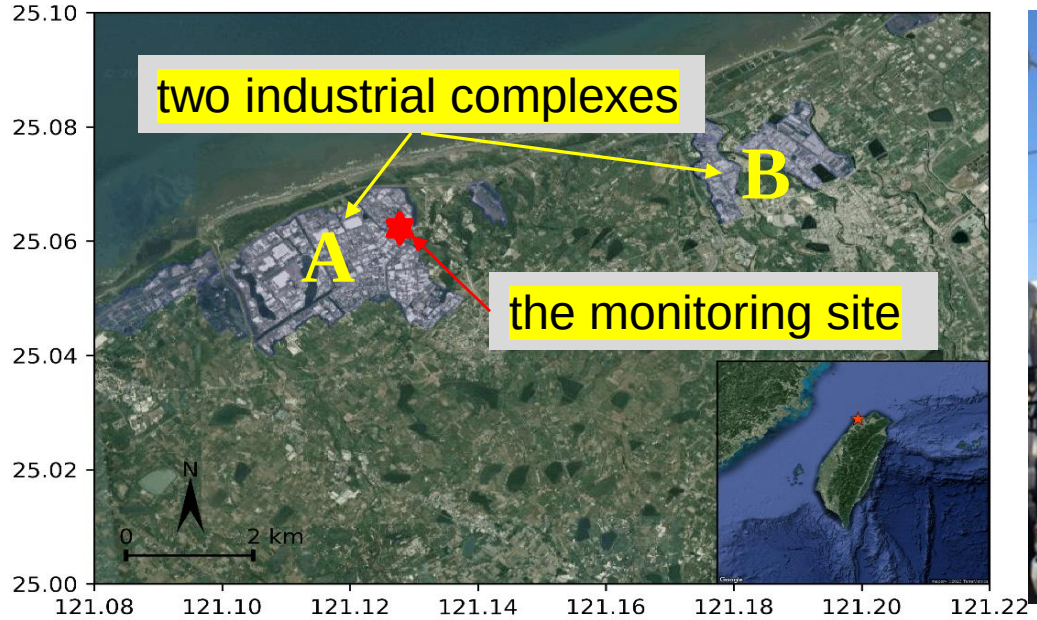
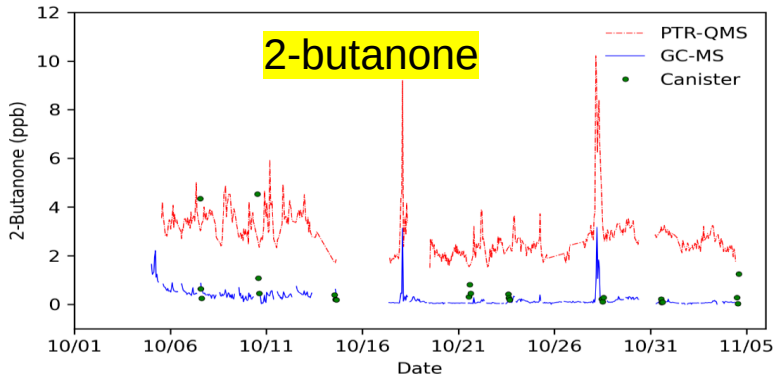
Online measurement of ambient toxic volatile organic compounds using thermal desorption gas chromatography-mass spectrometry (TD-GC/MS)

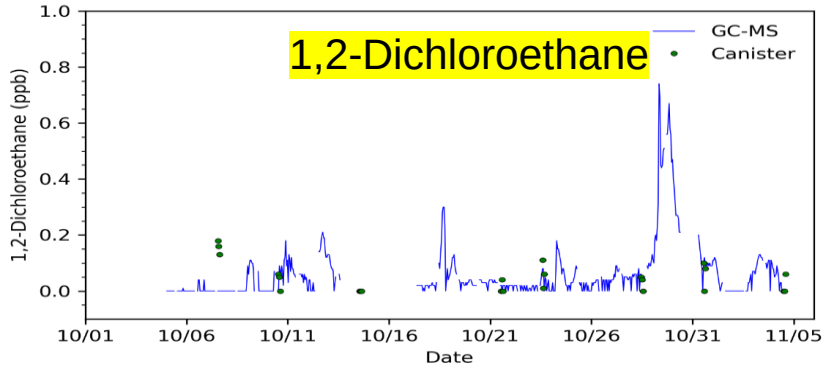
Jia-Lin Wang[1*], Chieh-Heng Wang[2], Hsin-Cheng Hsieh[1], Chen-Hsuan Chu[1], Mei-Hui Tseng[1], KuanChun Lee[1], and Po-Sheng Tseng[1]

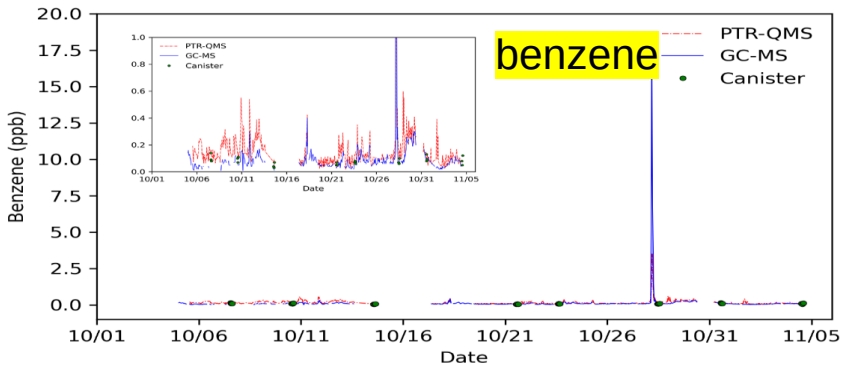
[1]Department of Chemistry, National Central University, Taoyuan 320, Taiwan (cwang@cc.ncu.edu.tw)
[2]Center for Environmental Studies, National Central University, Taoyuan 320, Taiwan (chwang1110@gmail.com)

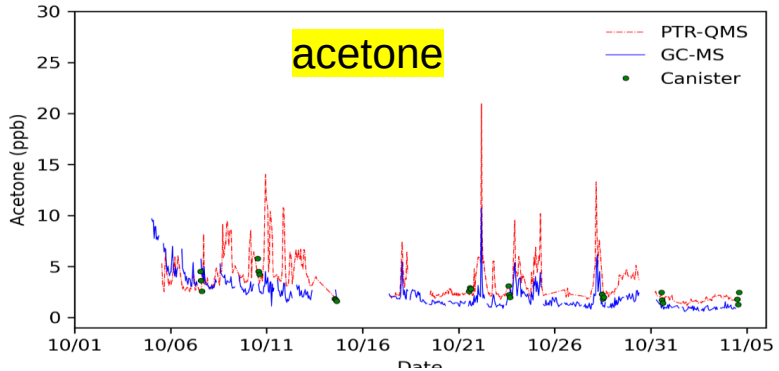


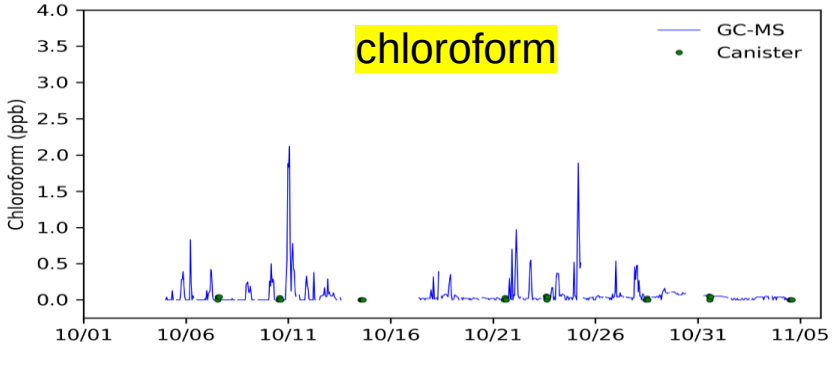
Study area & Instruments

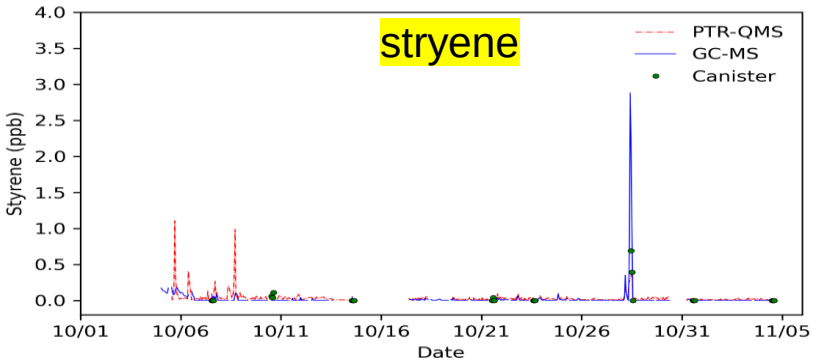


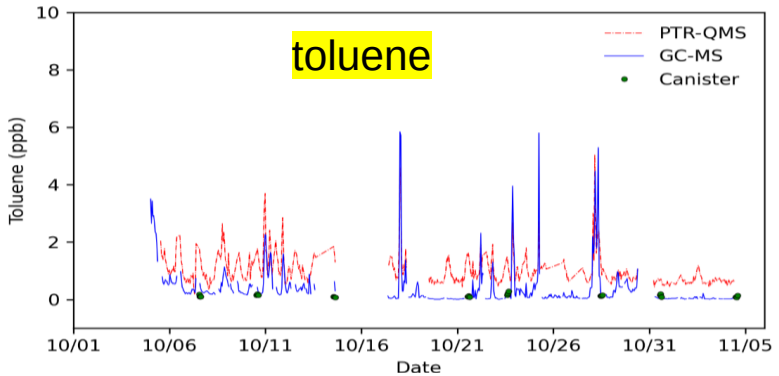


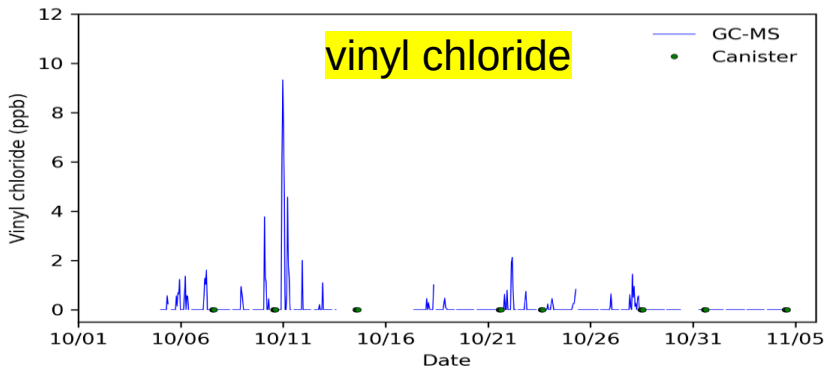


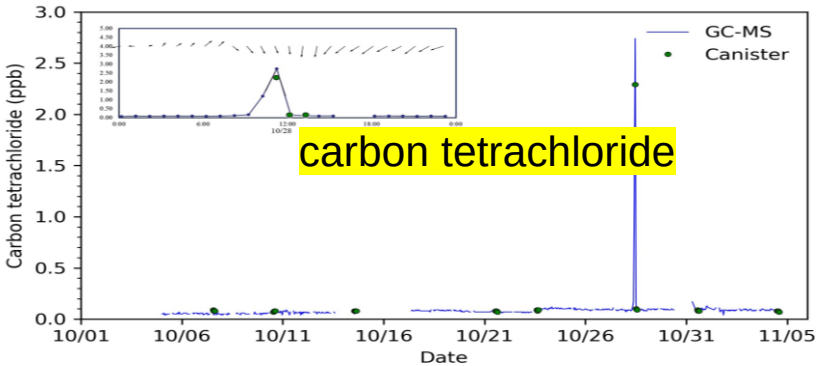






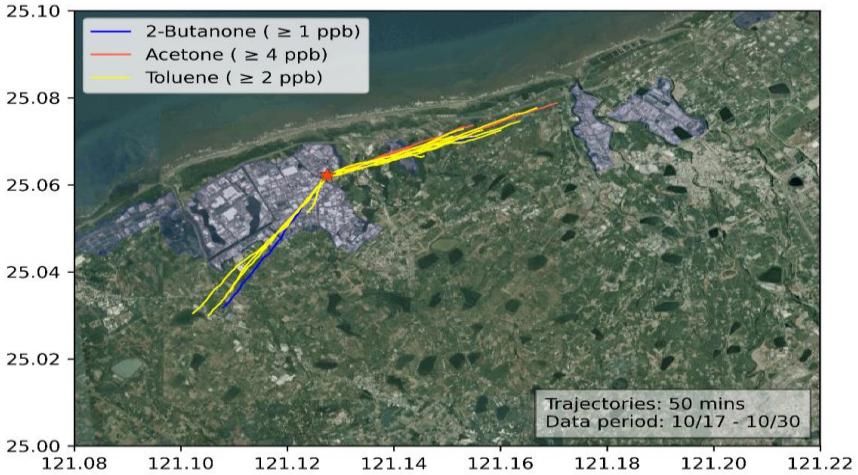


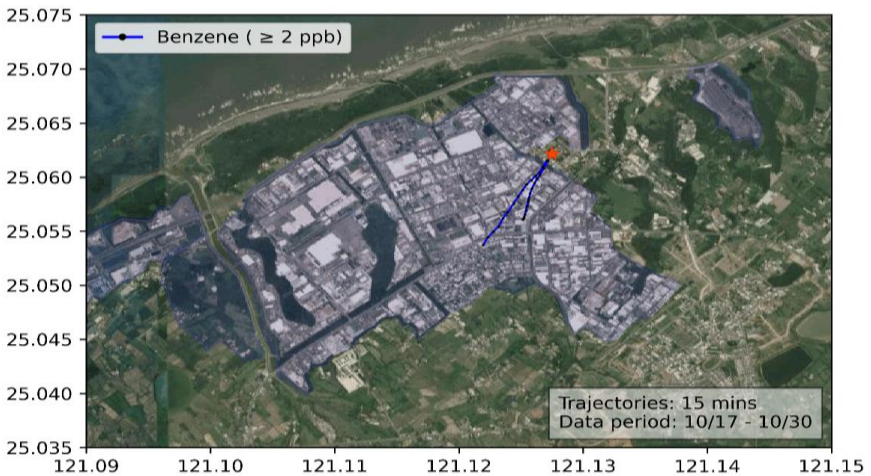


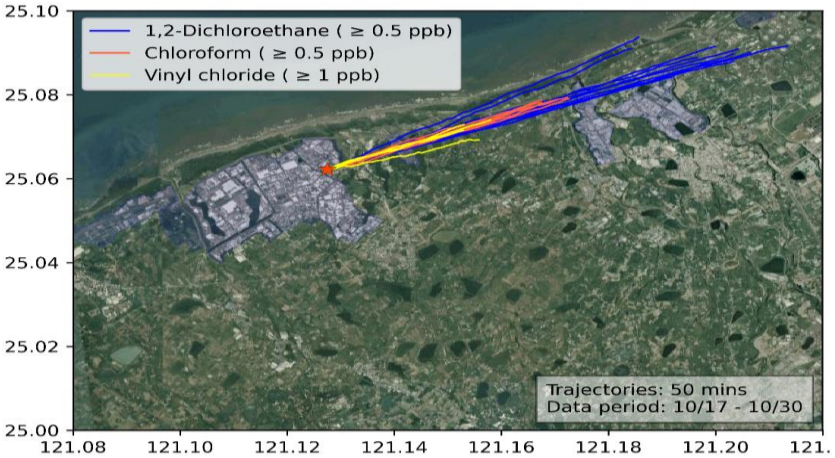


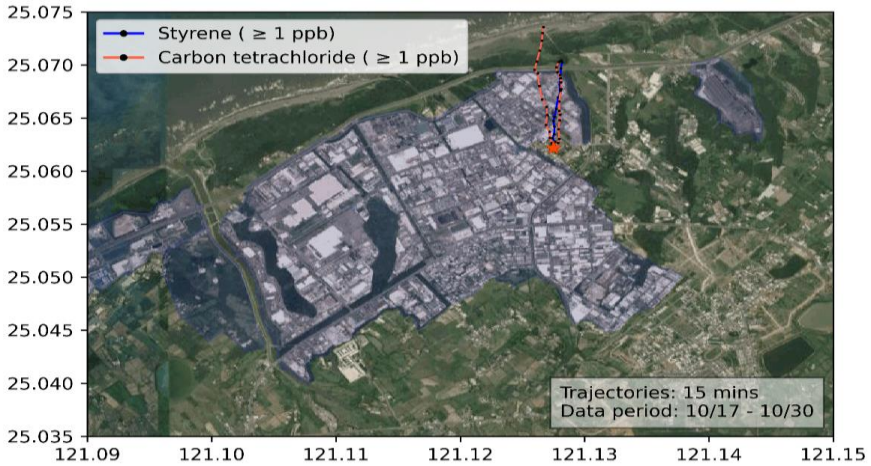
Both PTR-QMS and TD-GC/MS effectively detected pollution plumes as data spikes for the non-chlorinated species.

Selected non-chlorinated and chlorinated air toxics by online TD-GC/MS validated by canister samples.









Back trajectories toxic volatile organic compounds.

The backward trajectories of the spikes in the time series data can be deduced from the monitoring site acting as a receptor to track possible emission origins, followed by administrative means for mitigation.

Conclusion

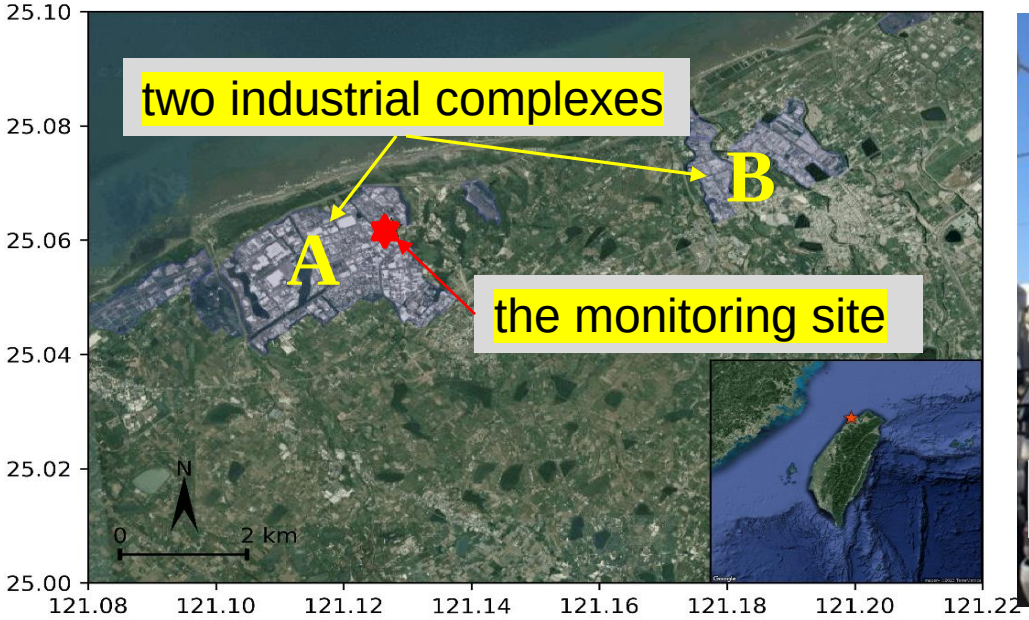
The online TD-GC/MS was validated by the offline flask sampling method and direct inlet mass spectrometry (i.e., PTR-QMS). It has demonstrated its effectiveness in detecting trace-level toxic VOCs with high accuracy and revealing emission plumes as data spikes.

EGU General Assembly 2023

國立中央大學 National Central University

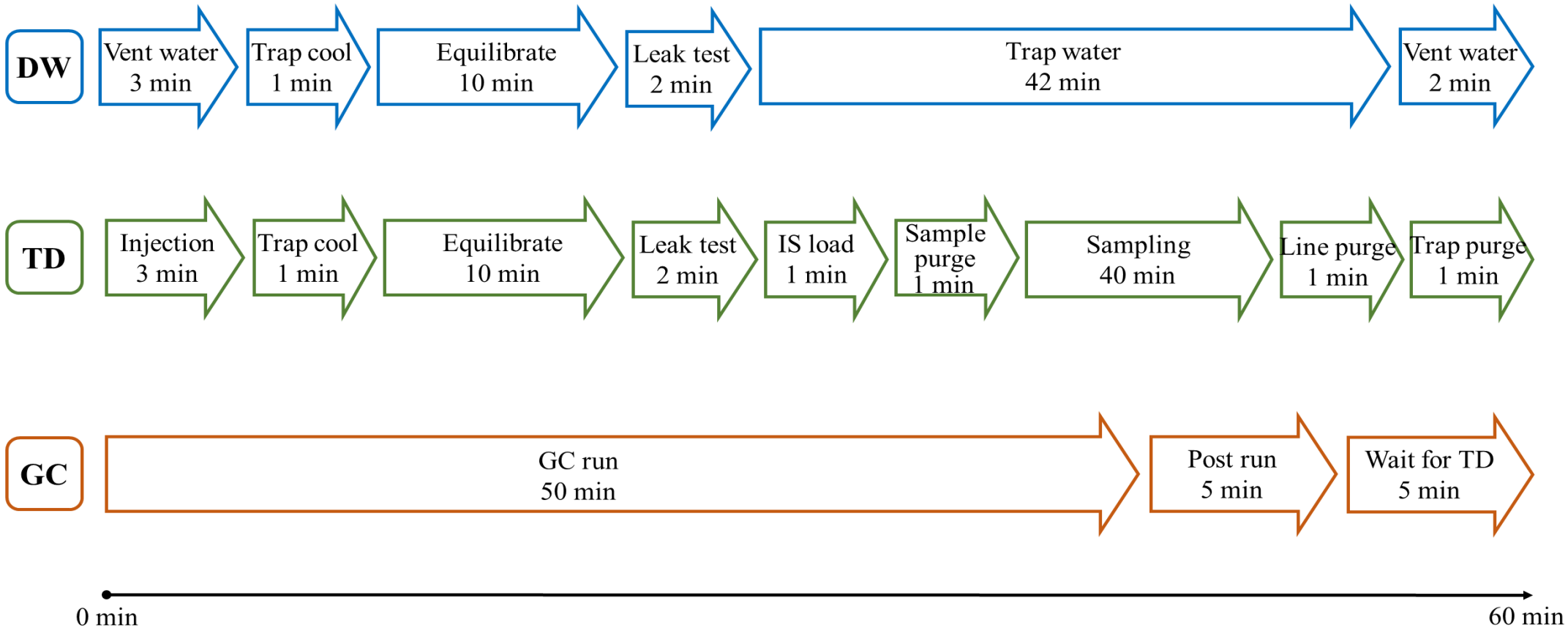
EGU23-1940 (supplementary materials)

Online measurement of ambient toxic volatile organic compounds using thermal desorption gas chromatography-mass spectrometry (TD-GC/MS)



Study area & Instruments

Synergic actions between DW, TD, and GC

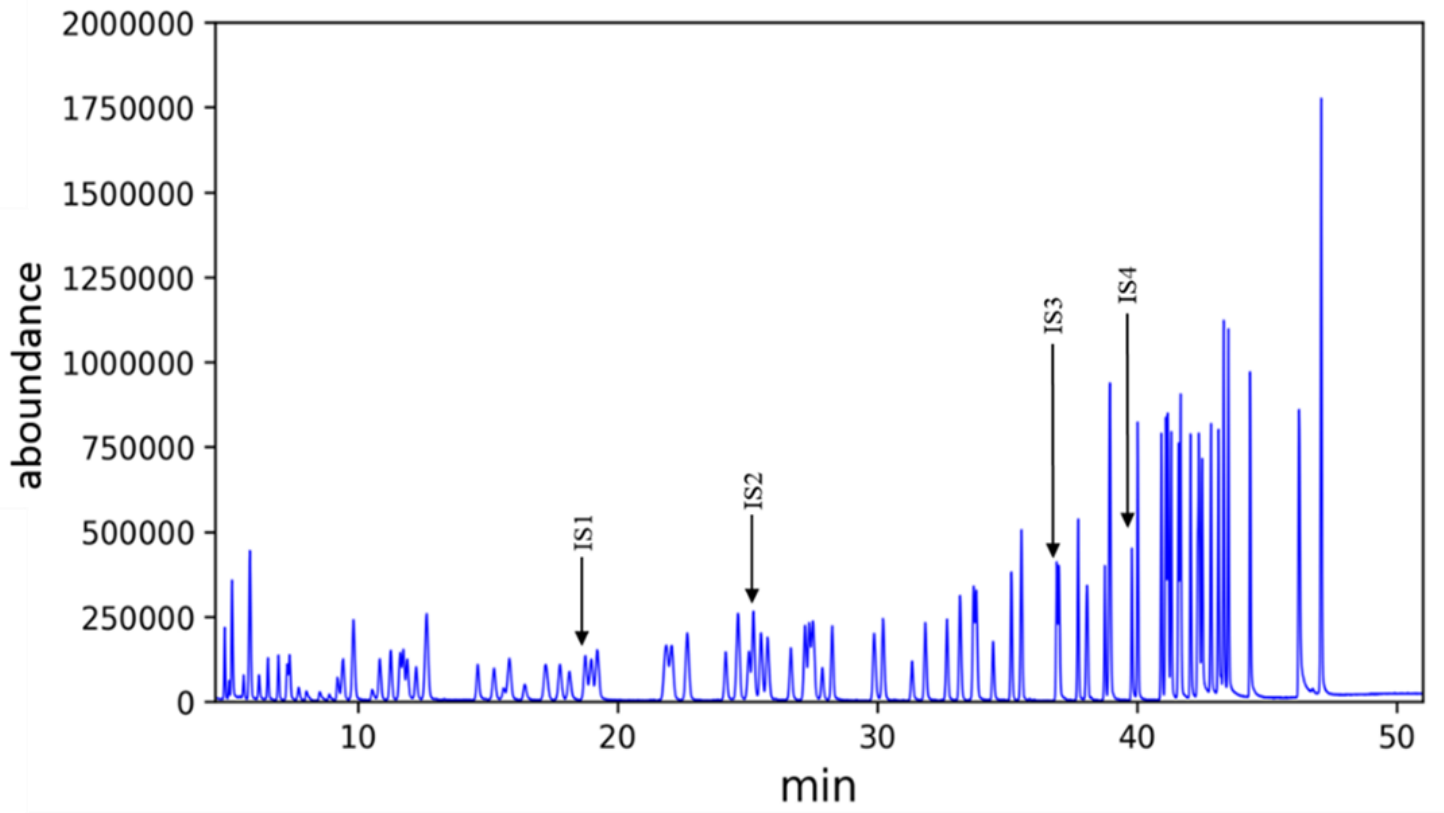


Synergic actions between DW, TD, and GC for a typical analysis of TD-GC/MS within an hour of analysis time.

Cpds

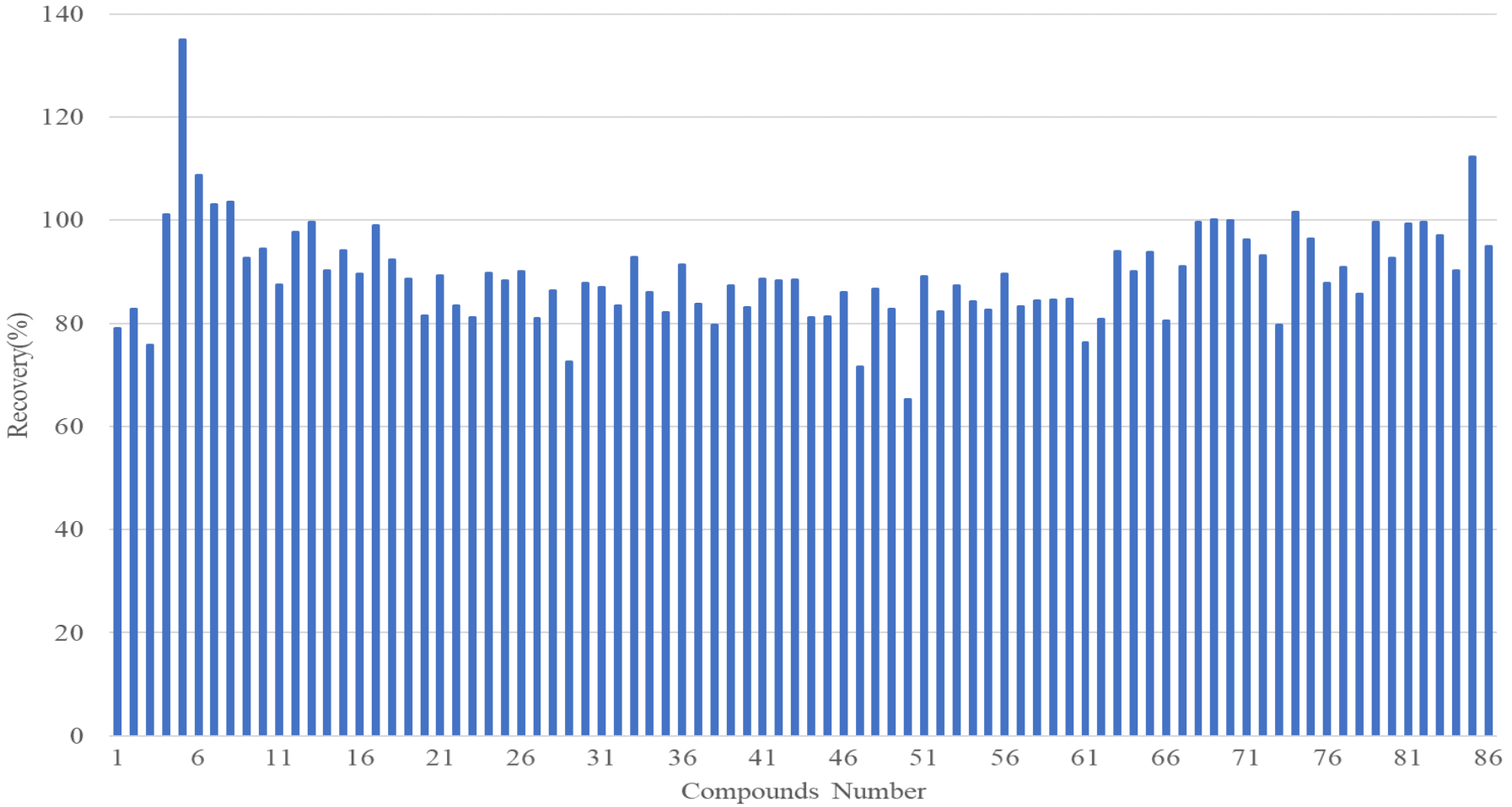
NO.	Name	NO.	Name	NO.	Name
1	Difluorochloromethane	31	1-Hexene	61	Tetrachloroethylene
2	Propane	32	trans-1,2-Dichloroethylene	62	Chlorobenzene
3	Dichlorodifluoromethane	33	Hexane	63	Ethylbenzene
4	Chloromethane	34	Chloroform	64	m,p-Xylene
5	Dichlorotetrafluoroethane	35	1,2-dichloroethane	65	Styrene
6	Vinyl chloride	36	methylcyclopentane	66	1,1,2,2-Tetrachloroethane
7	1,3-Butadiene	37	2,4-Dimethylpentane	67	o-Xylene
8	trans-2-Butene	38	1,1,1-trichloroethane	68	Isopropylbenzene
9	Bromomethane	39	Benzene	69	n-Propylbenzene
10	cis-2-Butene	40	Carbon Tetrachloride	70	m-Ethyltoluene
11	Chloroethane	41	Cyclohexane	71	p-Ethyltoluene
12	Acetonitrile	42	2-Methylhexane	72	1,3,5-Trimethylbenzene
13	Acrolein	43	2,3-Dimethylpentane	73	alpha.-Methylstyrene
14	Acetone	44	1,2-dichloropropane	74	1,2,4-Trimethylbenzene
15	Isopentane	45	Bromodichloromethane	75	o-Ethyltoluene
16	Trichloromonofluoromethane	46	Trichloroethylene	76	Benzyl chloride
17	Acrylonitrile	47	2,2,4-Trimethylpentane	77	1,4-Dichlorobenzene
18	Pentane	48	Methyl methacrylate	78	1,3-Dichlorobenzene
19	trans-2-Pentene	49	Heptane	79	1,2,3-Trimethylbenzene
20	1,1-dichloroethene	50	cis-1,3-Dichloro-1-Propene	80	1,2-Dichlorobenzene
21	cis-2-Pentene	51	Methyl Isobutyl Ketone	81	m-diethylbenzene
22	Methylene chloride	52	Methylcyclohexane	82	p-Diethylbenzene
23	3-Chloro-1-propene	53	trans-1,3-Dichloro-1-Propene	83	n-Undecane
24	1,1,2-Trichloro-1,2,2-trifluoroethane	54	1,1,2-Trichlorethane	84	n-Dodecane
25	cis-1,2-Dichloroethylene	55	Toluene	85	1,2,4-Trichlorobenzene
26	1,1-dichloroethane	56	2-Methylheptane	86	Hexachlorobutadiene
27	Vinyl acetate	57	3-Methylheptane		
28	2-Methylpentane	58	Dibromochloromethane		
29	2-Butanone	59	1,2-Dibromaethane		
30	3-methypentane	60	Octane		

A typical TIC chromatogram from analysis of 86 target compounds.



Selected peaks are numbered and can be referred to Table 1 for compounds. Four internal standards (IS) are shown: bromochloromethane (IS1), 1,4-difluorobenzene (IS2), chlorobenzene-d5 (IS3), and p-bromofluorobenzene (IS4).

Recoveries of 86 target compounds for the standard mixture at 90% R.H. standard mixture.



calibration curve

NO.	Name	R^2	RSD(%)	NO.	Name	R^2	RSD(%)	NO.	Name	R^2	RSD(%)
1	Difluorochloromethane	1.000	13.78	31	1-Hexene	0.994	7.26	61	Tetrachloroethylene	0.997	6.60
2	Propane	0.997	14.76	32	trans-1,2-Dichloroethylene	0.993	7.78	62	Chlorobenzene	0.997	3.20
3	Dichlorodifluoromethane	0.999	7.09	33	Hexane	0.994	7.58	63	Ethylbenzene	0.999	2.56
4	Chloromethane	0.990	23.69	34	Chloroform	0.995	6.89	64	m,p-Xylene	0.999	3.89
5	Dichlorotetrafluoroethane	0.999	11.11	35	1,2-dichloroethane	0.998	3.93	65	Styrene	0.998	5.65
6	Vinyl chloride	1.000	13.40	36	methylcyclopentane	0.999	4.70	66	1,1,2,2-Tetrachloroethane	0.997	3.97
7	1,3-Butadiene	0.997	13.35	37	2,4-Dimethylpentane	0.999	6.76	67	o-Xylene	0.998	4.57
8	trans-2-Butene	0.998	16.77	38	1,1,1-trichloroethane	0.998	5.82	68	Isopropylbenzene	0.997	4.48
9	Bromomethane	1.000	11.81	39	Benzene	0.999	3.73	69	n-Propylbenzene	0.996	4.27
10	cis-2-Butene	0.996	19.03	40	Carbon Tetrachloride	0.998	4.31	70	m-Ethyltoluene	0.997	3.15
11	Chloroethane	1.000	14.18	41	Cyclohexane	0.999	4.42	71	p-Ethyltoluene	0.999	5.22
12	Acetonitrile	0.999	19.01	42	2-Methylhexane	0.999	8.53	72	1,3,5-Trimethylbenzene	0.998	2.89
13	Acrolein	0.998	13.21	43	2,3-Dimethylpentane	0.999	4.67	73	alpha.-Methylstyrene	0.995	5.04
14	Acetone	0.993	26.98	44	1,2-dichloropropane	0.999	3.90	74	1,2,4-Trimethylbenzene	0.998	2.59
15	Isopentane	0.998	24.41	45	Bromodichloromethane	0.999	2.64	75	o-Ethyltoluene	0.998	2.61
16	Trichloromonofluoromethane	1.000	12.76	46	Trichloroethylene	0.999	3.70	76	Benzyl chloride	0.995	4.44
17	Acrylonitrile	0.999	3.50	47	2,2,4-Trimethylpentane	0.999	2.14	77	1,4-Dichlorobenzene	0.997	4.58
18	Pentane	0.999	17.08	48	Methyl methacrylate	0.996	8.17	78	1,3-Dichlorobenzene	0.997	4.54
19	trans-2-Pentene	0.999	14.78	49	Heptane	0.998	5.67	79	1,2,3-Trimethylbenzene	0.996	4.00
20	1,1-dichloroethene	0.999	15.55	50	cis-1,3-Dichloro-1-Propene	0.996	5.05	80	1,2-Dichlorobenzene	0.997	3.63
21	cis-2-Pentene	0.998	16.18	51	Methyl Isobutyl Ketone	0.995	7.64	81	m-diethylbenzene	0.996	3.85
22	Methylene chloride	0.999	15.95	52	Methylcyclohexane	0.997	4.88	82	p-Diethylbenzene	0.998	3.54
23	3-Chloro-1-propene	0.999						83	n-Undecane	0.998	5.21
24	1,1,2-Trichloro-1,2,2-trifluoroethane	**0.904**						84	n-Dodecane	**0.979**	17.74
25	cis-1,2-Dichloroethylene	1.000						85	1,2,4-Trichlorobenzene	0.996	9.75
26	1,1-dichloroethane	0.999						86	Hexachlorobutadiene	0.996	12.62
27	Vinyl acetate	0.996	4.96	57	3-Methylheptane	0.995	7.45				
28	2-Methylpentane	1.000	2.93	58	Dibromochloromethane	0.994	6.47				
29	2-Butanone	**0.986**	8.71	59	1,2-Dibromaethane	0.994	6.35				
30	3-methypentane	0.995	7.59	60	Octane	0.998	4.71				

R^2:0.993~1.00
RSD(%):2.59~27.0

MDL

N=7

NO.	化合物名稱	MDL(ppb)	NO.	化合物名稱	MDL(ppb)	NO.	化合物名稱	MDL(ppb)
1	Difluorochloromethane	0.78	31	1-Hexene	0.13	61	Tetrachloroethylene	0.15
2	Propane	0.67	32	trans-1,2-Dichloroethene	0.79	62	Chlorobenzene	0.85
3	Dichlorodifluoromethane	0.65	33	Hexane	0.14	63	Ethylbenzene	0.65
4	Chloromethane	0.50	34	Chloroform	0.18	64	m/p-Xylene	0.24
5	Dichlorotetrafluoroethane	0.22	35	1,2-Dichloroethane	0.70	65	Styrene	0.28
6	Vinyl chloride	0.29	36	Methylcyclopentane	0.93	66	1,1,2,2-Tetrachloroethane	0.30
7	1,3-Butadiene	0.28	37	2,4-Dimethylpentane	0.23	67	o-Xylene	0.69
8	trans-2-Butene	0.25	38	1,1,1-Trichloroethane	0.30	68	Isopropylbenzene	0.19
9	Bromomethane	0.62	39	Benzene	0.44	69	n-Propylbenzene	0.98
10	cis-2-Butene	0.16	40	Carbon tetrachloride	0.32	70	m-Ethyltoluene	0.17
11	Chloroethane	0.72	41	Cyclohexane	1.18	71	p-Ethyltoluene	0.21
12	Acetonitrile	0.60	42	2-Methylhexane	0.20	72	1,3,5-Trimethylbenzene	1.10
13	Acrolein	**2.46**	43	2,3-Dimethylpentane	0.17	73	alpha-Methylstyrene	0.75
14	Acetone	1.76	44	1,2-Dichloropropane	0.20	74	o-Ethyltoluene	0.17
15	Isopentane	0.50	45	Trichloroethene	0.13	75	1,2,4-Trimethylbenzene	0.18
16	Trichlorofluoromethane	0.14	46	2,2,4-Trimethylpentane	1.09	76	Benzyl chloride	0.34
17	Acrylonitrile	0.32	47	Methyl methacrylate	0.62	77	1,3-Dichlorobenzene	0.19
18	Pentane	0.14	48	Heptane	0.31	78	1,4-Dichlorobenzene	0.20
19	trans-2-Pentene	0.09	49	cis-1,3-Dichloro-1-pro...	0.97	79	1,2,3-Trimethylbenzene	0.90
20	1,1-Dichloroethene	0.11	50	Methyl Isobutyl Ketone	0.21	80	1,2-Dichlorobenzene	0.20
21	cis-2-Pentene	0.12	51	Methylcyclohexane	1.03	81	m-Diethylbenzene	0.21
22	Methylene chloride	0.39	52	Bromodichloromethane	0.26	82	p-Diethylbenzene	0.16
23	3-Chloro-1-propene	0.13	53	trans-1,3-Dichloro-1-p...	0.24	83	n-Undecane	0.91
24	1,1,2-Trichloro-1,2,2-…	0.					n-Dodecane	0.82
25	cis-1,2-Dichloroethene	0.					1,2,4-Trichlorobenzene	0.24
26	1,1-Dichloroethane	0.					Hexachlorobutadiene	0.24
27	Vinyl acetate	1.87	57	3-Methylheptane	1.09			
28	2-Methylpentane	0.12	58	Dibromochloromethane	1.16			
29	2-Butanone	0.32	59	1,2-Dibromoethane	0.15			
30	3-Methylpentane	0.11	60	Octane	0.99			

MDL：0.11~1.76ppb

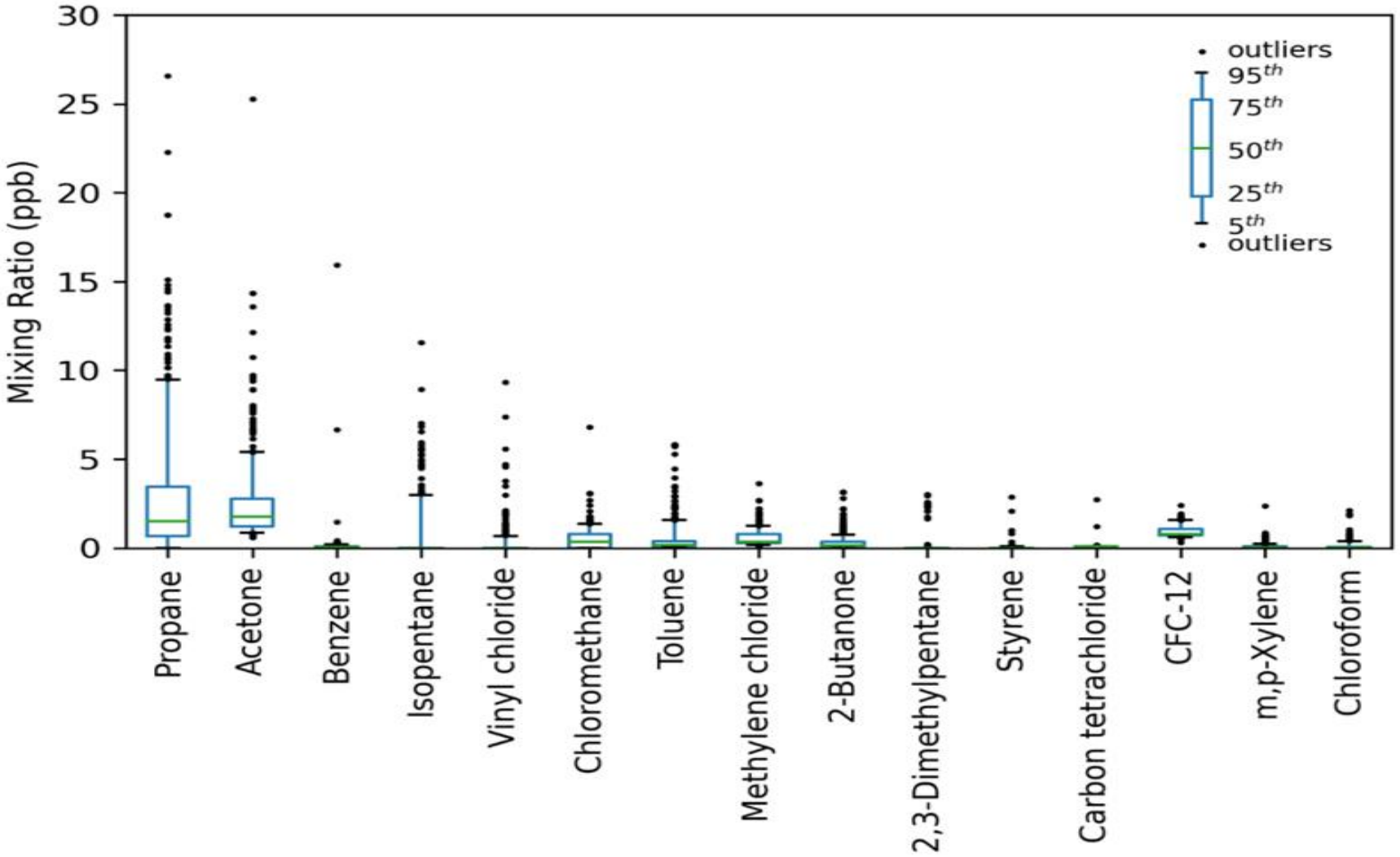
RSD & Recovery Rate (%)

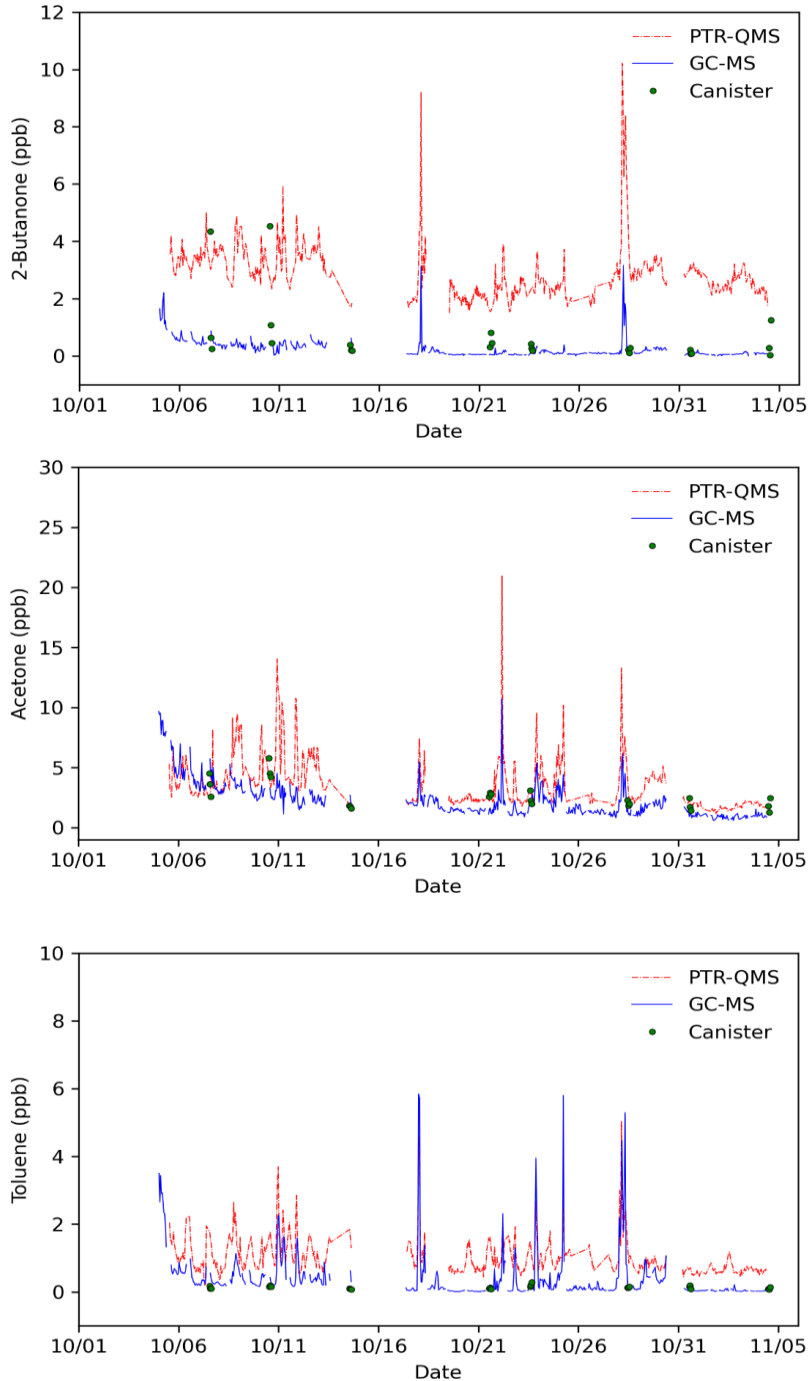
N=7

NO.	Name	回收率	RSD%	NO.	Name	回收率	RSD%	NO.	Name	回收率	RSD%
1	Difluorochloromethane	81.90	16.94	31	1-Hexene	109.24	9.54	61	Tetrachloroethylene	115.12	5.02
2	Propane	83.88	5.31	32	trans-1,2-Dichloroethene	117.94	7.52	62	Chlorobenzene	112.94	3.46
3	Dichlorodifluoromethane	98.86	9.55	33	Hexane	108.08	7.55	63	Ethylbenzene	108.54	3.33
4	Chloromethane	86.06	**28.05**	34	Chloroform	122.74	6.70	64	m/p-Xylene	100.02	5.37
5	Dichlorotetrafluoroethane	126.38	10.99	35	1,2-Dichloroethane	118.70	9.39	65	Styrene	97.08	6.77
6	Vinyl chloride	**79.40**	10.20	36	Methylcyclopentane	118.38	6.61	66	1,1,2,2-Tetrachloroethane	**145.86**	4.18
7	1,3-Butadiene	114.12	10.69	37	2,4-Dimethylpentane	114.70	5.74	67	o-Xylene	99.56	6.26
8	trans-2-Butene	124.18	9.33	38	1,1,1-Trichloroethane	130.06	5.68	68	Isopropylbenzene	101.86	4.77
9	Bromomethane	80.06	10.36	39	Benzene	101.40	7.96	69	n-Propylbenzene	117.30	1.42
10	cis-2-Butene	113.98	8.65	40	Carbon tetrachloride	130.50	8.08	70	m-Ethyltoluene	113.00	6.46
11	Chloroethane	83.16	11.73	41	Cyclohexane	116.08	12.94	71	p-Ethyltoluene	112.72	3.61
12	Acetonitrile	**74.12**	13.68	42	2-Methylhexane	106.42	8.73	72	1,3,5-Trimethylbenzene	110.00	4.51
13	Acrolein	129.60	5.88	43	2,3-Dimethylpentane	114.00	12.00	73	alpha-Methylstyrene	101.56	4.97
14	Acetone	115.24	8.95	44	1,2-Dichloropropane	111.74	6.16	74	o-Ethyltoluene	109.60	3.27
15	Isopentane	108.84	5.79	45	Trichloroethene	127.82	5.58	75	1,2,4-Trimethylbenzene	103.54	4.10
16	Trichlorofluoromethane	**133.06**	7.81	46	2,2,4-Trimethylpentane	104.24	3.89	76	Benzyl chloride	110.44	6.58
17	Acrylonitrile	119.98	13.90	47	Methyl methacrylate	116.98	2.15	77	1,3-Dichlorobenzene	108.34	3.73
18	Pentane	118.36	6.79	48	Heptane	106.34	6.52	78	1,4-Dichlorobenzene	102.64	5.24
19	trans-2-Pentene	116.48	7.38	49	cis-1,3-Dichloro-1-pro...	113.00	4.58	79	1,2,3-Trimethylbenzene	100.52	3.84
20	1,1-Dichloroethene	126.26	7.62	50	Methyl Isobutyl Ketone	109.36	4.74	80	1,2-Dichlorobenzene	100.72	4.27
21	cis-2-Pentene	118.14	7.27	51	Methylcyclohexane	117.42	4.20	81	m-Diethylbenzene	101.68	3.00
22	Methylene chloride	101.30	6.77	52	Bromodichloromethane	126.74	8.04	82	p-Diethylbenzene	101.06	3.06
23	3-Chloro-1-propene	122.28	8.88	53	trans-1,3-Dichloro-1-p...	112.64	2.83	83	n-Undecane	84.64	11.92
24	1,1,2-Trichloro-1,2,2-...	128.16							ane	**72.40**	12.74
25	cis-1,2-Dichloroethene	114.56							obenzene	92.30	9.34
26	1,1-Dichloroethane	120.50							tadiene	104.32	7.08
27	Vinyl acetate	120.40									
28	2-Methylpentane	107.36	7.74	58	Dibromochloromethane	128.26	6.07				
29	2-Butanone	119.48	6.71	59	1,2-Dibromoethane	114.70	4.01				
30	3-Methylpentane	115.06	4.59	60	Octane	90.28	7.34				

Recovery rate：81.9~130.5%
RSD：1.42~16.94%

Box plot for the most variable species observed in the month-long measurement





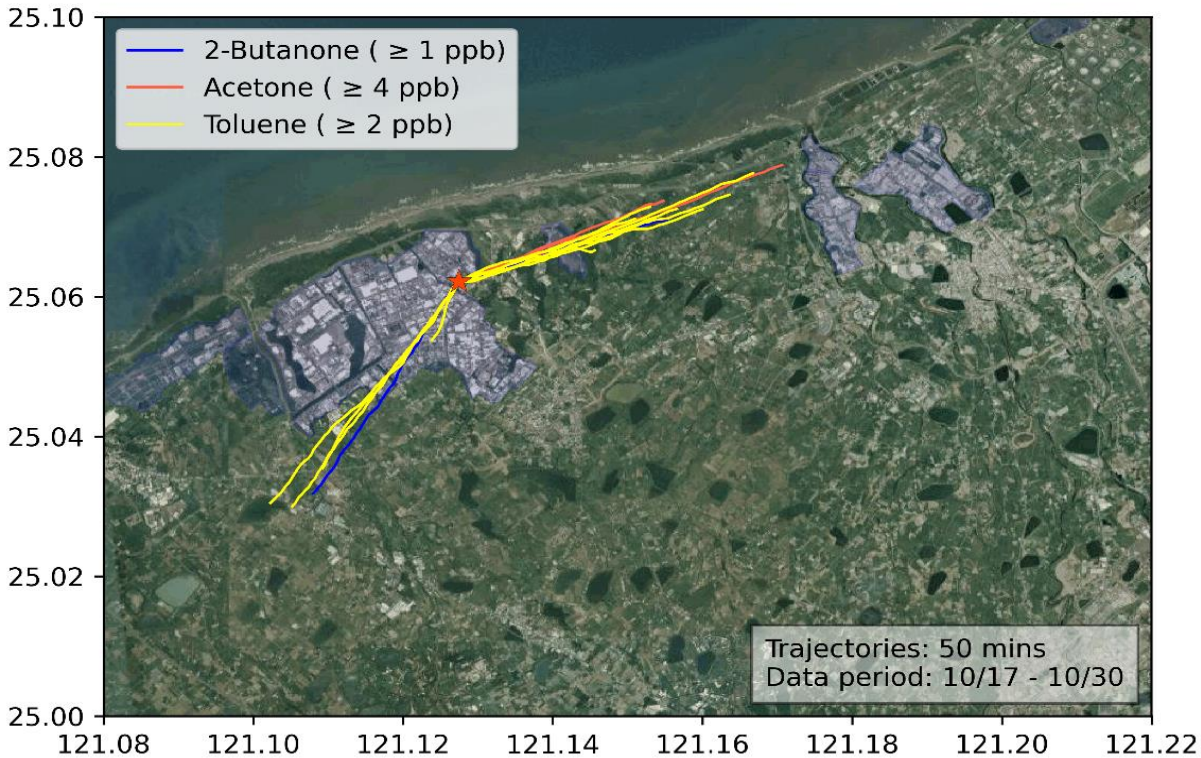
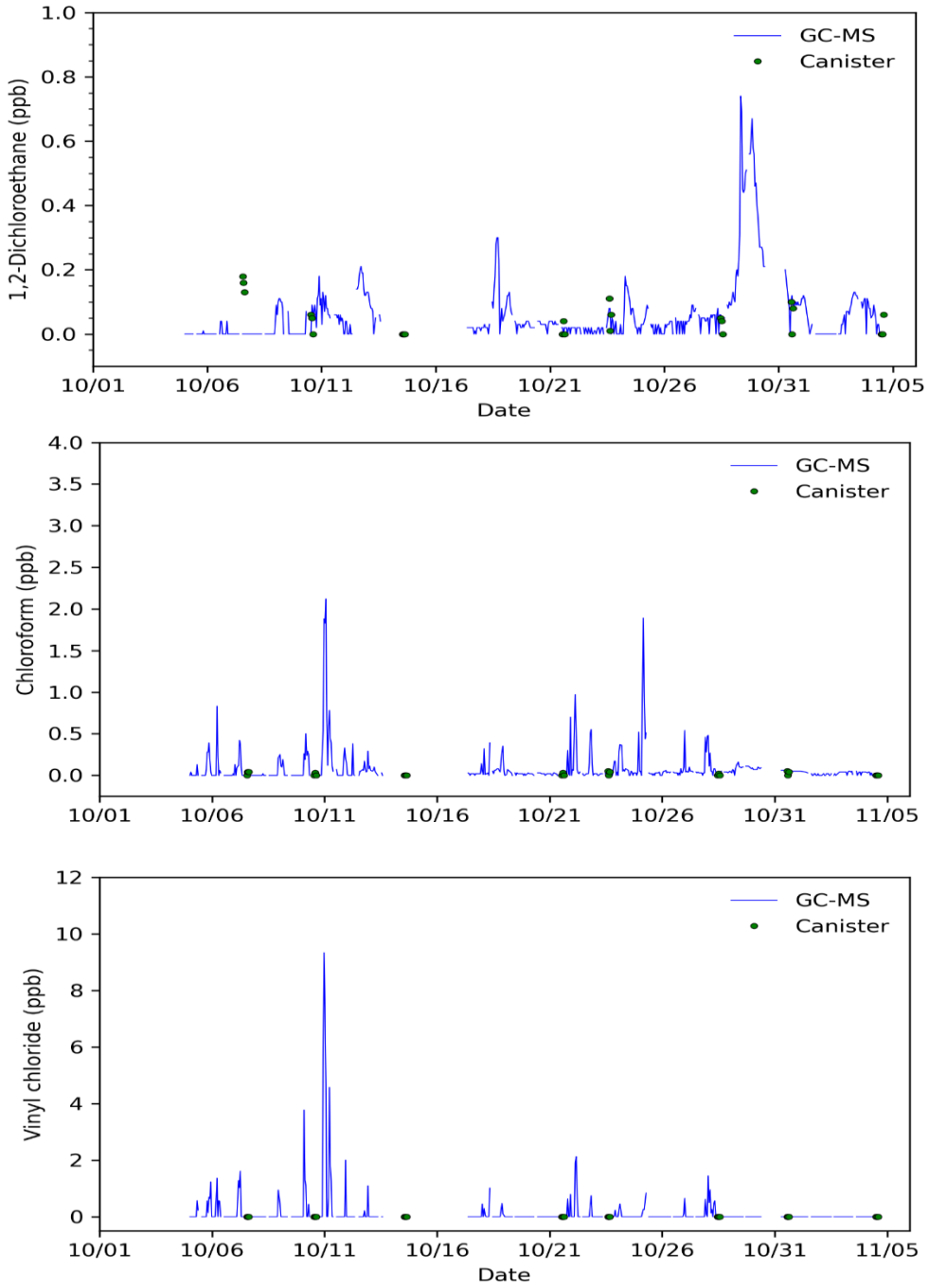


Fig. 6. Back trajectories for 2-butanone, acetone, and toluene. The concentration threshold for identifying spikes and calculating trajectories for each compound is indicated in the legend.



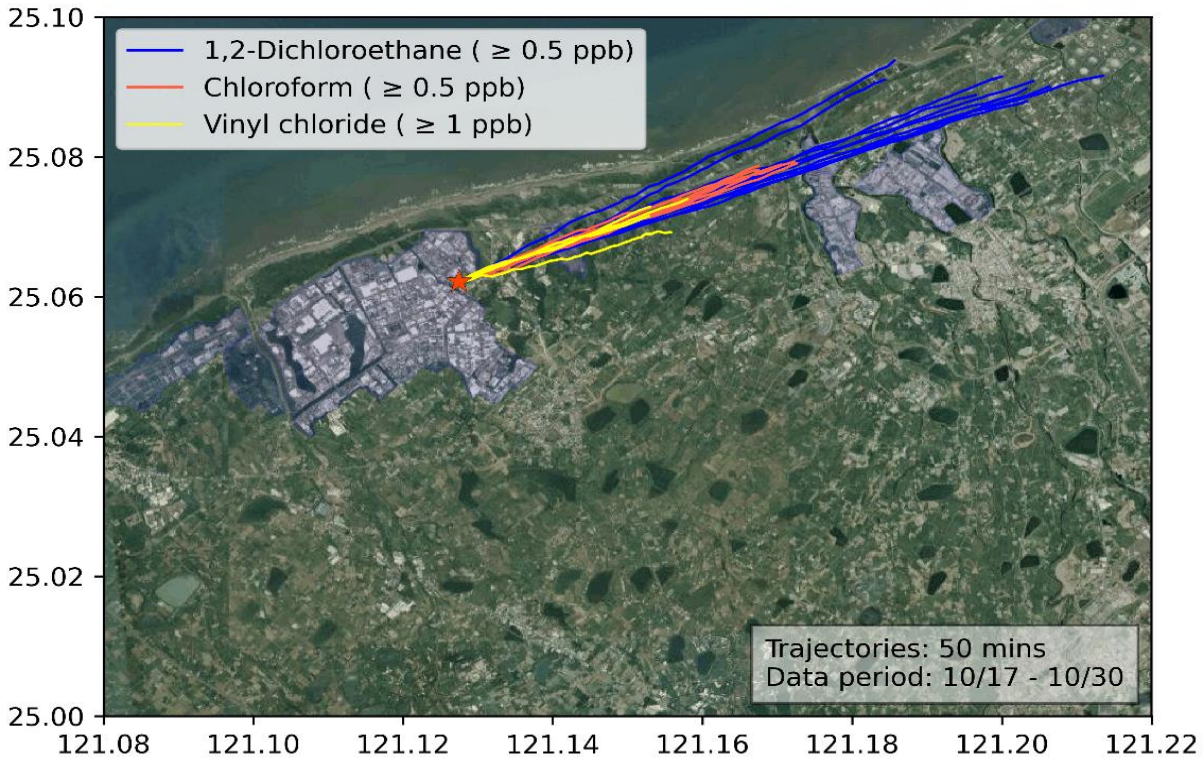
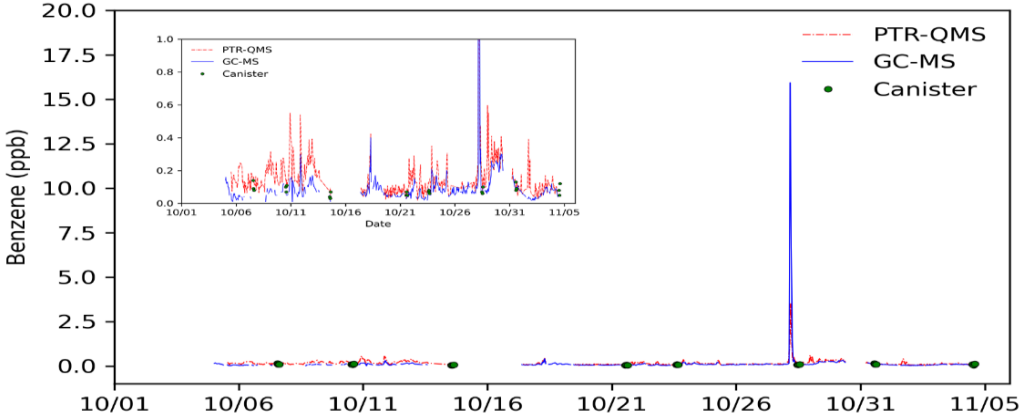
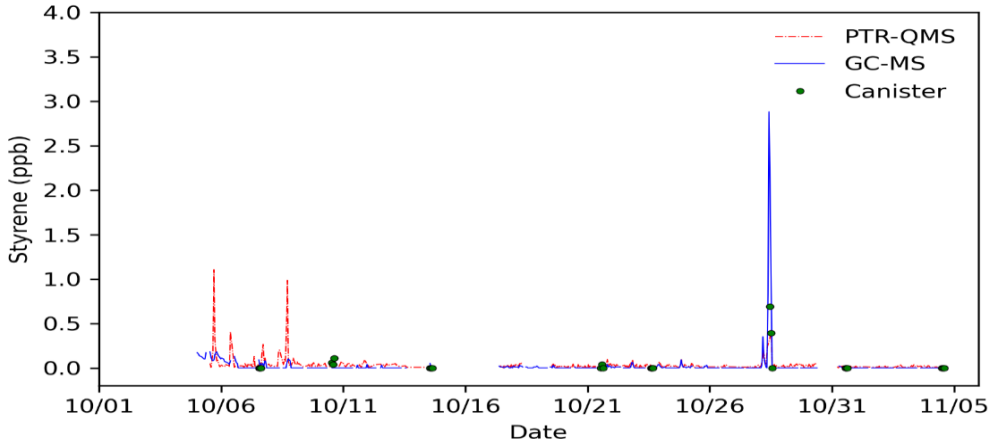
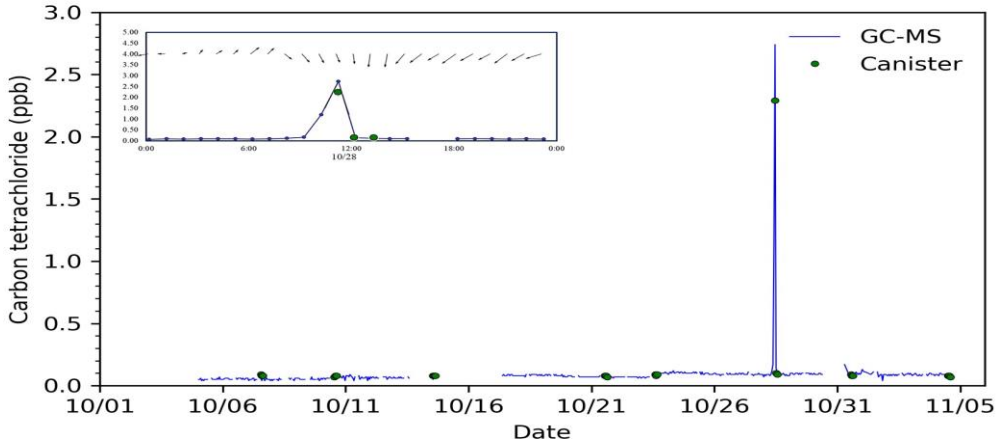
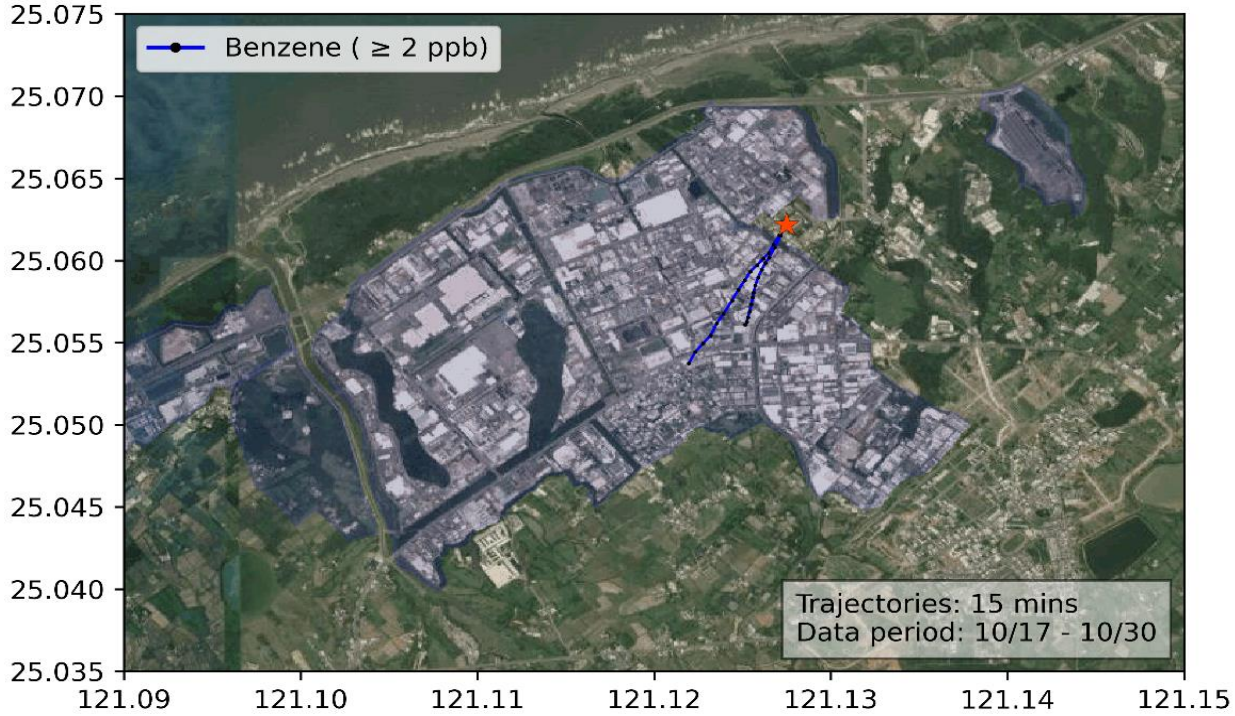


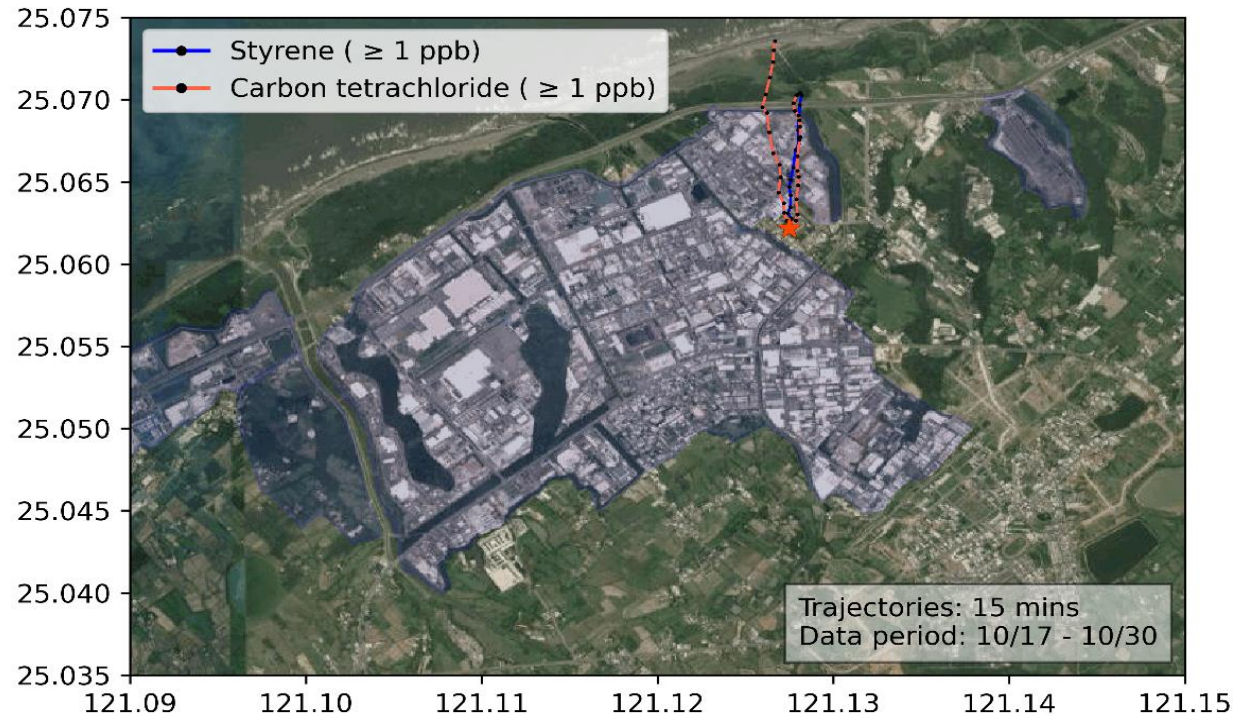
Fig. 6. Back trajectories for 1,2-dichloroethane, chloroform, and vinyl chloride. The concentration threshold for identifying spikes and calculating trajectories for each compound is indicated in the legend.

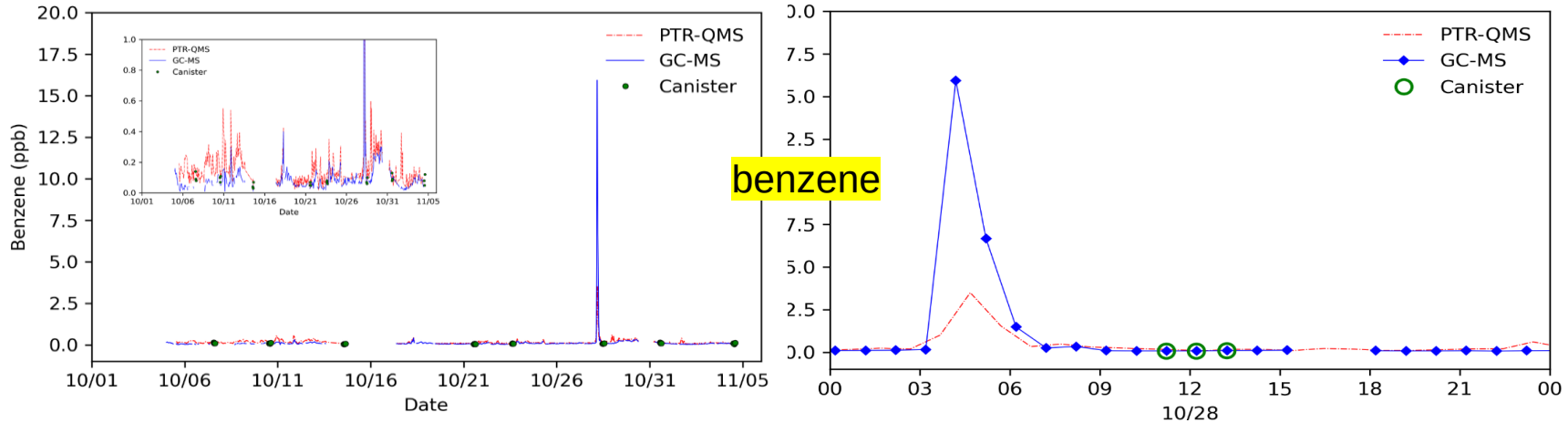

Benzene (ppb)
PTR-QMS
GC-MS
Canister
10/01
10/06
10/11
10/16
10/21
10/26
10/31
11/05


Styrene (ppb)
PTR-QMS
GC-MS
Canister
Date

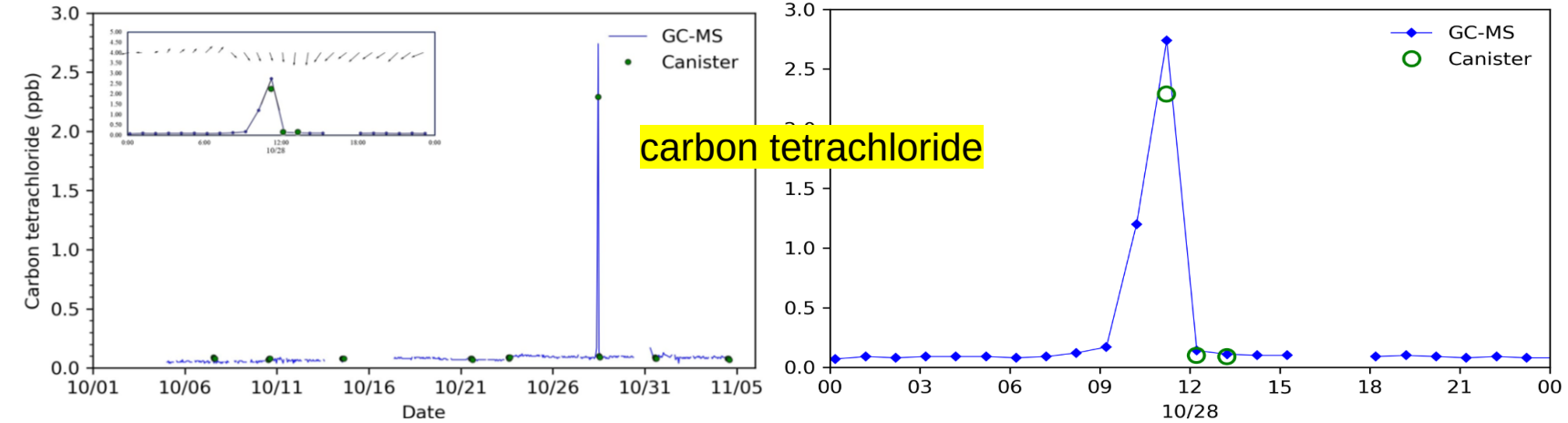

Carbon tetrachloride (ppb)
GC-MS
Canister
Date


Benzene (≥ 2 ppb)
Trajectories: 15 mins
Data period: 10/17 - 10/30

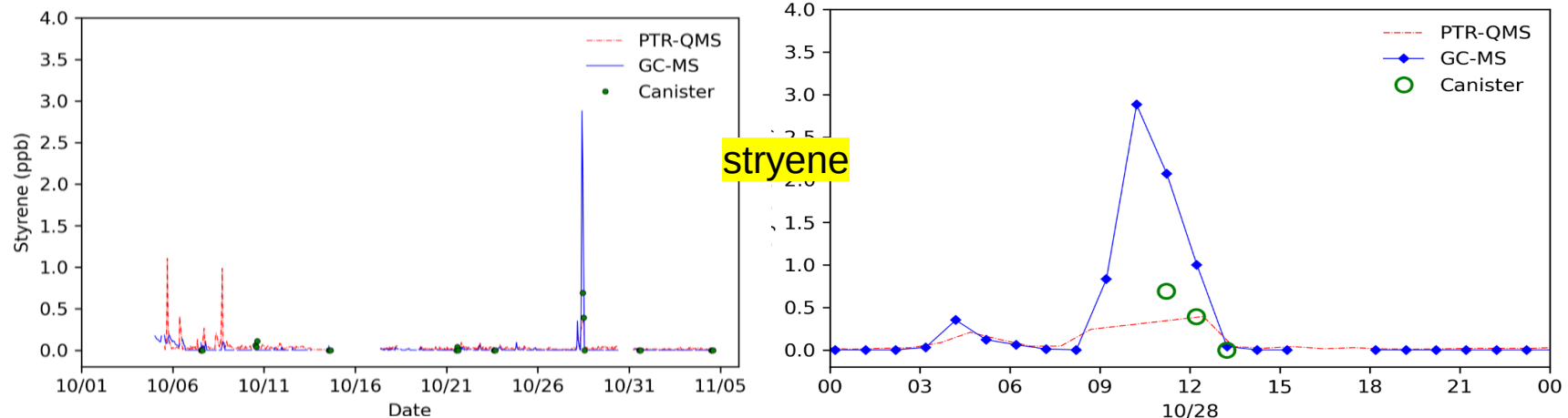

Styrene (≥ 1 ppb)
Carbon tetrachloride (≥ 1 ppb)
Trajectories: 15 mins
Data period: 10/17 - 10/30



benzene



carbon tetrachloride



stryene

Blowups of (a) benzene, (b) carbon tetrachloride, and (c) styrene spikes from Fig. 3(a), Fig. 4(c), and Fig. S4, respectively. Hourly data points of the online TD-GC/MS are also shown.

Conclusion

- In this study, the online TD-GCMS technique was used in the field close to industrial zones to detect toxic VOCs of high health risks.
- Achieving such a goal would rely heavily on high data quality and sufficient instantaneity.
- The online TD-GCMS was validated by the offline flask sampling method and direct inlet mass spectrometry (i.e., PTR-QMS). It has demonstrated its effectiveness in detecting trace-level toxic VOCs with high accuracy and revealing emission plumes as data spikes.
- The accuracy of the online TD-GCMS approached that of canisters or better since the wall effect was largely avoided.
- The data instantaneity although is slower than the direct inlet MS, the hourly time resolution of TD-GCMS can still meet most online requirements but with much higher accuracy in reporting compound identities and absolute mixing ratios.
- The backward trajectories of the spikes in the time series data can be deduced from the monitoring site acting as a receptor to track possible emission origins, followed by administrative means for mitigation.
- The online TD-GCMS has demonstrated its ability as an effective environmental forensic tool by providing sufficient accuracy, sensitivity, and speed in measuring ambient toxic VOCs.