Supplementary Material

Research on the Distribution of Neonicotinoid and Fipronil Pollution in the Yangtze River by High-performance Liquid Chromatography

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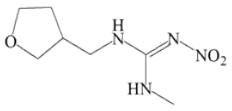
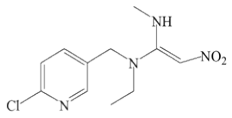
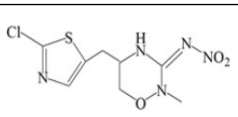
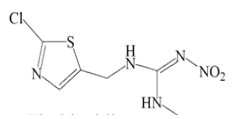
Table. S1 The chemical structures and physicochemical properties of the eight neonicotinoids, fipronil and its metabolites measured in this study

(Source: Footprint Database http://sitem.herts.ac.uk/aeru/iupac/)

Compounds	Chemical structure	Molecular Mass (g/mol)	Solubility (g/L)	Partition coeffificient (log K_{ow})
Dinotefuran		202.2	39	-0.549
Nitenpyram		270.7	840	-0.66
Thiamethoxam		291.7	4.1	-0.13
Clothianidin		249.7	12.7	0.905

Imidacloprid		255.7	0.61	0.57
Imidaclothiz		261.7	0.31	n.a
Acetamiprid		222.7	42	0.8
Thiacloprid		252.7	0.19	1.26
Fipronil desulfinyl		389.1	n.a[a]	n.a
Fipronil		437.2	1.9	3.75
Fipronil sulfoxide		435.1	n.a	n.a
Fipronil sulfone		421.2	n.a	n.a

[a].n.a. = not available.

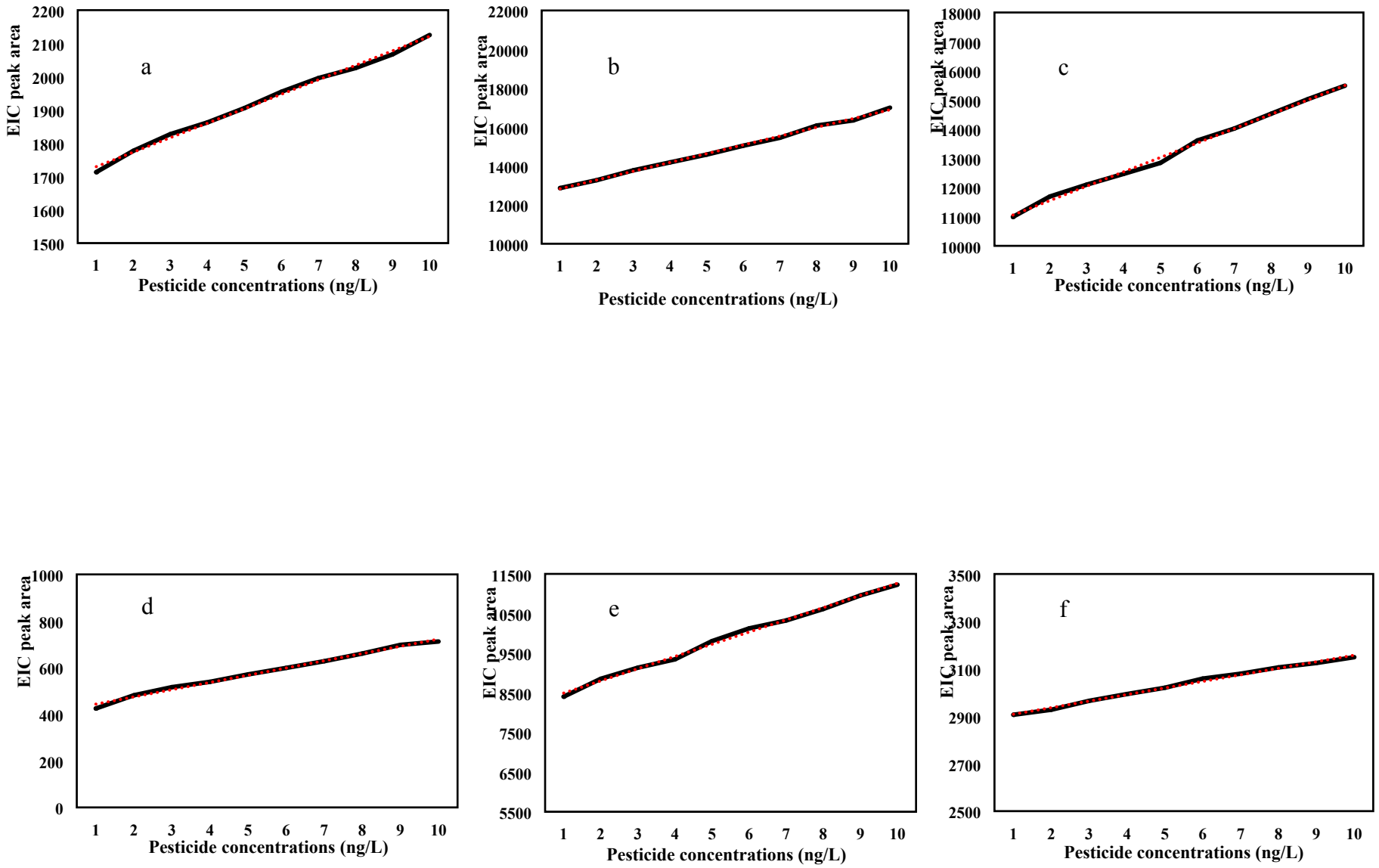
Table. S2 The locations of the 20 sampling sites along the Yangtze River Basin

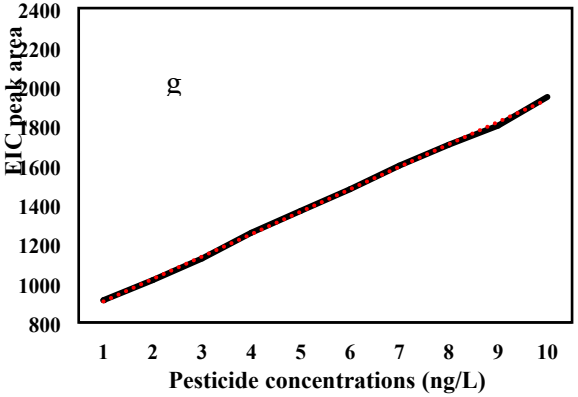
Sites	Longitude, °	Latitude, °

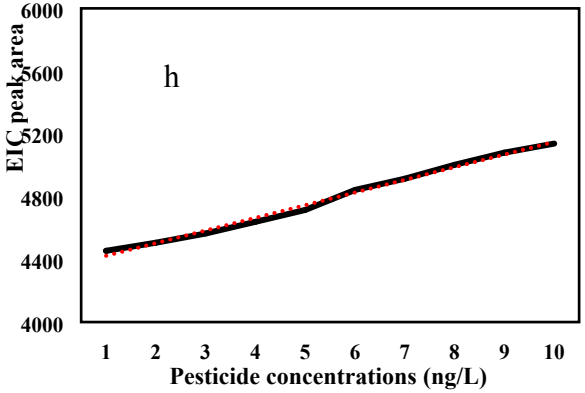
A1	121°5.954′	31°44.682′
A2	121°12.757′	31°39.758′
A3	121°19.303′	31°34.181′
A4	121°26.529′	31°9.178′
A5	121°33.374′	31°24.224′
A6	121°41.162′	31°20.437′
A7	121°47.256′	31°14.564′
A8	121°53.343′	31°9.084′
A9	122°0.243′	31°4.598′
A10	122°7.597′	31°0.391′
A11	122°14.928′	30°55.222′
A12	122°30.130′	30°50.067′
A13	122°45.036′	30°44.798′
A14	123°0.089′	30°39.898′
A15	123°15.054′	30°34.922′
B1	123°0.102′	31°0.020′
B2	123°0.046′	31°20.059′
B3	122°59.957′	31°40.040′
C1	122°15.471′	31°13.218′
C2	122°30.012′	31°30.240′

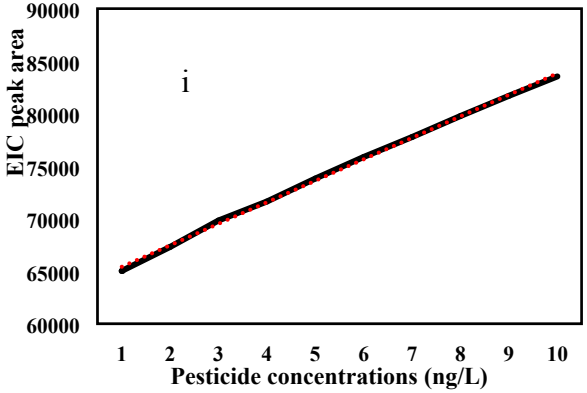
Table S3. The Linear ranges, LOD, and LOQ of 12 target pesticides

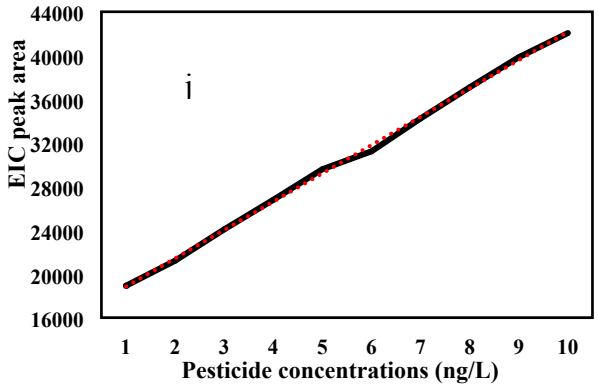
Compounds	Linear range (pg)	LOD （ng/L）	LOQ （ng/L）
Dinotefuran	5~100	0.10	0.25
Nitenpyram	5~100	0.10	0.25
Thiamethoxam	5~100	0.10	0.25
Clothianidin	10~200	0.10	0.50
Imidacloprid	10~200	0.10	0.25
Imidaclothiz	5~200	0.10	0.25
Acetamiprid	5~100	0.10	0.25
Thiacloprid	5~100	0.10	0.25
Fipronil Desulfinyl	1~100	0.02	0.05
Fipronil	1~100	0.02	0.05
Fipronil Sulfide	1~200	0.02	0.05
Fipronil Sulfone	1~100	0.02	0.05

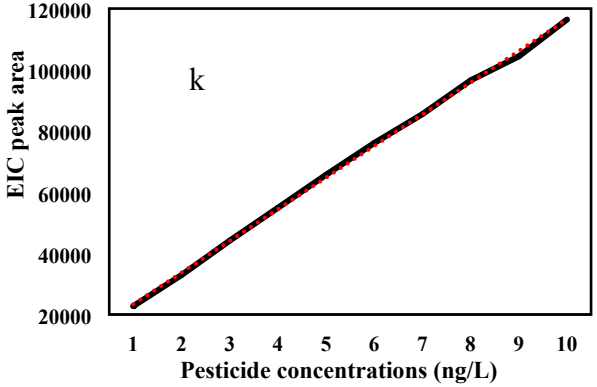

a
EIC peak area
2200
2100
2000
1900
1800
1700
1600
1500
1 2 3 4 5 6 7 8 9 10
Pesticide concentrations (ng/L)
b
EIC peak area
22000
20000
18000
16000
14000
12000
10000
1 2 3 4 5 6 7 8 9 10
Pesticide concentrations (ng/L)
c
EIC peak area
18000
17000
16000
15000
14000
13000
12000
11000
10000
1 2 3 4 5 6 7 8 9 10
Pesticide concentrations (ng/L)
d
EIC peak area
1000
800
600
400
200
0
1 2 3 4 5 6 7 8 9 10
Pesticide concentrations (ng/L)
e
EIC peak area
11500
10500
9500
8500
7500
6500
5500
1 2 3 4 5 6 7 8 9 10
Pesticide concentrations (ng/L)
f
EIC peak area
3500
3300
3100
2900
2700
2500
1 2 3 4 5 6 7 8 9 10
Pesticide concentrations (ng/L)


g
EIC peak area
2400
2200
2000
1800
1600
1400
1200
1000
800
1 2 3 4 5 6 7 8 9 10
Pesticide concentrations (ng/L)


h
EIC peak area
6000
5600
5200
4800
4400
4000
1 2 3 4 5 6 7 8 9 10
Pesticide concentrations (ng/L)


i
EIC peak area
90000
85000
80000
75000
70000
65000
60000
1 2 3 4 5 6 7 8 9 10
Pesticide concentrations (ng/L)


i
EIC peak area
44000
40000
36000
32000
28000
24000
20000
16000
1 2 3 4 5 6 7 8 9 10
Pesticide concentrations (ng/L)


k
EIC peak area
120000
100000
80000
60000
40000
20000
1 2 3 4 5 6 7 8 9 10
Pesticide concentrations (ng/L)

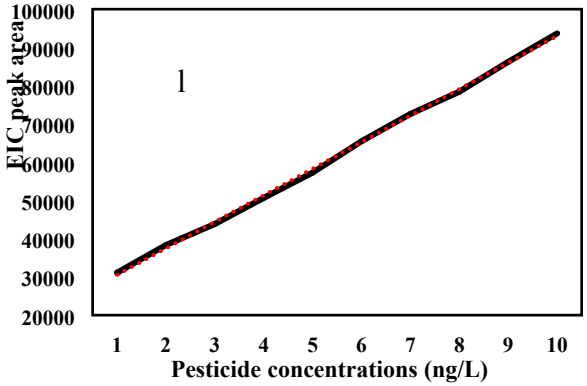

l
EIC peak area
100000
90000
80000
70000
60000
50000
40000
30000
20000
1 2 3 4 5 6 7 8 9 10
Pesticide concentrations (ng/L)

Fig. S1. The standard calibration curves of 12 target pesticides: (a) dinotefuran, (b) nitenpyram, (c) thiamethoxam, (d) clothianidin, (e) imidacloprid, (f) imidaclothiz, (g) acetamiprid, (h) thiacloprid, (i) fipronil, (j)fipronil desulfinyl, (k) fipronil sulfide, (l) fipronil sulfone.

Table. S4 The concentration (ng L−1) and detection rate (%) of neonicotinoids and fipronil in surface waters of the Yangtze River Estuary

Site	pH	Salinity	Dinotefuran	Nitenpyram	Thiamethoxam	Clothianidin	Imidacloprid	Imidaclothiz	Acetamiprid	Thiacloprid	Fipronil	Fluoronitrile	Fipronil sulfoxide	Fipronil sulfone	ΣNEOs[a]	ΣFIPs[b]
A1	8.31	0.13	2.03	1.76	1.08	ND[c]	3.46	ND	0.65	0.39	0.49	0.36	0.35	0.36	9.37	1.57
A1	8.11	0.14	1.47	2.33	1.50	ND	5.39	ND	1.35	0.40	0.57	0.43	0.38	0.48	12.45	1.85

A3	7.96	0.14	0.70	2.40	1.84	ND	6.89	ND	ND	ND	0.62	0.52	0.52	0.80	11.83	2.45
A4	8.32	0.13	<LOQ[d]	2.05	1.18	ND	7.20	ND	0.96	ND	0.42	0.46	0.45	0.84	11.50	2.17
A5	8.39	0.13	2.68	2.18	1.76	ND	4.80	ND	ND	ND	0.59	0.46	0.44	0.75	11.41	2.23
A6	8.37	0.13	2.27	1.26	0.68	ND	0.63	ND	ND	ND	0.20	0.24	0.13	0.20	4.84	0.77
A7	8.35	0.17	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
A8	8.37	2.73	0.11	ND	0.64	ND	ND	ND	ND	ND	0.14	0.21	0.09	0.17	0.77	0.60
A9	7.95	14.1	0.37	ND	0.58	ND	3.20	ND	ND	ND	0.08	0.32	0.21	0.38	4.14	0.99
A10	7.56	13.2	0.11	ND	0.28	ND	ND	ND	ND	ND	ND	0.20	ND	0.11	0.38	0.31
A11	7.68	15.4	0.31	ND	0.36	ND	ND	ND	ND	ND	0.13	0.50	0.18	0.32	0.56	1.12
A12	7.98	17.7	ND	ND	0.37	ND	ND	ND	ND	ND	ND	0.16	<LOQ	0.13	0.25	0.32
A13	8.15	27.8	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.13	ND	0.06	ND	0.19

A14	7.86	32.6	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.08	<LOQ	0.10	ND	0.21
A15	8.18	31.9	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.12
B1	7.94	28.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	<LOQ	ND	0.12	ND	0.15
B2	8.09	30.3	ND	ND	ND	ND	ND	ND	ND	ND	ND	<LOQ	ND	ND	ND	0.03
B3	8.07	31.2	ND	ND	<LOQ	ND	ND	ND	<LOQ	ND	ND	0.08	ND	0.11	0.38	0.19
C1	7.84	17.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	<LOQ	ND	ND	ND	0.03
C2	7.79	27.2	0.70	ND	0.44	ND	ND	ND	ND	0.16	0.05	0.17	0.11	0.26	1.31	0.59
Detection rate（%）	/	/	55.0	30.0	65.0	ND	35.0	ND	20.0	15.0	50.0	90.0	60.0	80.0	65.0	95.0

[a] Sum of neonicotinoids detected in water samples.

[b] Sum of fipronil detected in water samples.

[c] Not detected. Data not calculated due to its low signal.

[d] Below the limit of quantitation. Data <LOQ is calculated as half of the limit of quantitation