

Supplementary information.

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Title: Evaluation of river pollution of neonicotinoids in Osaka City (Japan) by LC/MS with
dopant-assisted photoionisation

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Fig. S1 Extracted ion chromatogram of the sample in which dinotefuran was detected at the highest concentration. Extracted mass range was 158.1287 ± 0.001 Da. Desnitrodinotefuran ($C_7H_{15}N_3O$) is known as one of degradation products of dinotefuran. Its protonated molecule has an exact mass of 158.1287.

Table S1 Signal-to-noise (S/N) values of each neonicotinoid in a standard and an extract.

Table S2a Concentration of neonicotinoids in rivers of Osaka City and their estuaries in summer sampling campaign.

Table S2b Concentration of neonicotinoids in rivers of Osaka City and their estuaries in spring sampling campaign.

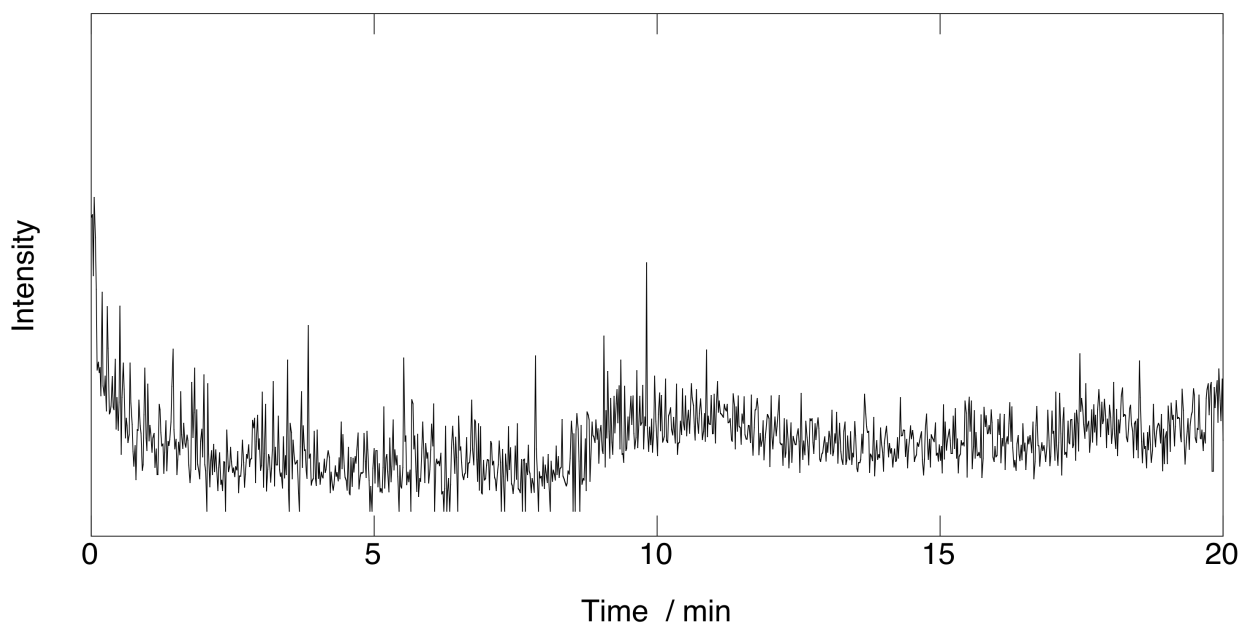


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Table S1 Signal-to-noise (S/N) values of each neonicotinoid in a standard solution and an extract.

	Standard solution ^a			Real sample extract ^b		
	ESI	APCI	APPI	ESI	APCI	APPI
Acetamiprid	7.4	8.4	99	3.0	11	31
Clothianidin	2.2	27	11		18	15
Dinotefuran	4.8	5.3	41	3.1	7.1	24
Imidacloprid	1.5	30	59		21	38
Nitenpyram	11	6.5	11	6.7	5.0	5.5
Thiamethoxam ^c	2.8	9.8	56		13	31

^a The concentration was adjusted to 5 ng mL⁻¹. ^b The extract was fortified with neonicotinoids at 5 ng mL⁻¹. ^c Except for thiamethoxam, same SRMs as APPI were monitored in positive ion mode. SRM of thiamethoxam for ESI and APCI was 292.0 → 210.9.

Table S2a Concentration of neonicotinoids in rivers of Osaka City and their estuaries in summer sampling campaign.

	Concentration / ng L ⁻¹					
	Acetamiprid	Clothianidin	Dinotefuran	Imidacloprid	Nitenpyram	Thiamethoxam
St. 1	nd ^a	5.7	35	1.3	nd	1.0
St. 2	na ^b	na	na	na	na	na
St. 3	nd	3.3	36	2.3	nd	0.8
St. 4	nd	3.3	38	2.7	nd	2.7
St. 5	nd	12	31	1.3	nd	1.7
St. 6	nd	2.4	45	3.5	nd	1.8
St. 7	nd	2.0	34	1.8	nd	2.7
St. 8	na	na	na	na	na	na
St. 9	nd	nd	63	4.5	nd	nd
St. 10	nd	nd	63	7.0	nd	2.3
St. 11	nd	nd	54	5.6	nd	3.1
St. 12	nd	nd	100	4.1	nd	3.2
St. 13	nd	5.6	18	nd	nd	0.7
St. 14	nd	6.1	21	nd	nd	nd
St. 15	nd	5.5	21	nd	nd	0.7
St. 16	nd	5.1	21	nd	nd	nd
St. 17	nd	2.8	38	3.5	nd	2.2
St. 18	nd	6.8	53	1.3	nd	2.3
St. 19	nd	3.5	20	nd	nd	1.0
St. 20	nd	3.5	21	nd	nd	nd
St. 21	nd	2.2	30	2.9	nd	nd
St. 22	nd	3.1	28	1.8	nd	nd
St. 23	nd	2.7	19	0.9	nd	0.7
St. 24	nd	4.7	27	2.1	nd	1.8
St. 25	nd	0.8	16	2.6	nd	0.8
St. 26	nd	1.6	9.4	nd	nd	0.8

^a nd, not detected. ^b na, not analyzed.

Table S2b Concentration of neonicotinoids in rivers of Osaka City and their estuaries in spring sampling campaign.

	Concentration / ng L ⁻¹					
	Acetamiprid	Clothianidin	Dinotefuran	Imidacloprid	Nitenpyram	Thiamethoxam
St. 1	nd ^a	3.7	6.7	6.3	nd	2.6
St. 2	na ^b	na	na	na	na	na
St. 3	nd	3.4	4.9	10	nd	3.0
St. 4	na	na	na	na	na	na
St. 5	na	na	na	na	na	na
St. 6	nd	2.9	8.9	nd	nd	3.9
St. 7	1.4	5.7	21	25	nd	11
St. 8	1.4	1.0	30	19	nd	8.1
St. 9	nd	2.5	21	16	nd	3.5
St. 10	nd	1.5	31	15	nd	3.3
St. 11	nd	1.4	18	8.9	nd	2.6
St. 12	nd	1.7	16	12	nd	4.5
St. 13	nd	7.8	6.8	6.5	nd	4.4
St. 14	nd	2.3	20	16	nd	6.8
St. 15	nd	6.2	11	9.1	nd	5.1
St. 16	nd	4.9	12	13	nd	7.6
St. 17	nd	4.9	10	11	nd	4.0
St. 18	nd	1.2	6.7	4.4	nd	1.5
St. 19	nd	3.5	6.5	5.7	nd	3.4
St. 20	nd	3.0	3.7	3.7	nd	2.9
St. 21	nd	3.4	5.4	4.3	nd	2.2
St. 22	nd	3.4	3.7	4.9	nd	2.6
St. 23	nd	3.7	6.3	5.4	nd	3.1
St. 24	na	na	na	na	na	na
St. 25	nd	1.5	5.8	4.9	nd	3.2
St. 26	na	na	na	na	na	na

^a nd, not detected. ^b na, not analyzed.