Supplementary Information for

Methodologies for the analysis of pesticides and pharmaceuticals in sediments and plant tissue

Pedro N. Carvalho[1*†], Yang Zhang[1,2‡], Tao Lyu[1§], Carlos A. Arias[1], Kai Bester[3], Hans Brix[1]

[1]*Department of Bioscience, Aarhus University, Ole Worms Allé 1, Building 1135, 8000 Aarhus C., Denmark*
[2] *College of Life Science, South China Normal University, Guangzhou 510631, PR China*
[3]*Department of Environmental Science, Aarhus University, Frederiksborgvej 399, 4000 Roskilde, Denmark*

** Corresponding author:*
Tel.: Tel.: +45 87158462
E-mail address: pedro.carvalho@envs.au.dk
ORCID: 0000-0002-7131-9102

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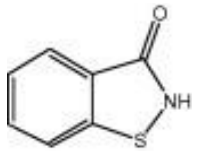
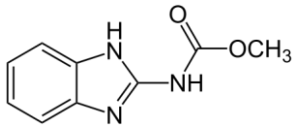
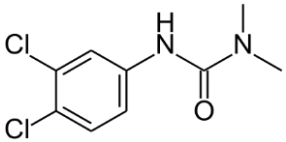
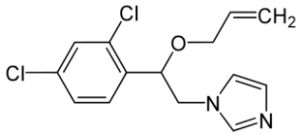
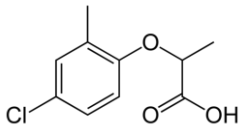
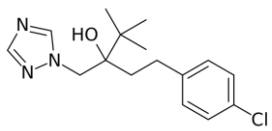
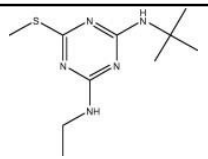
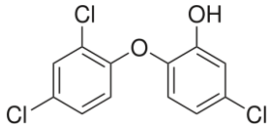
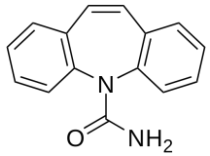
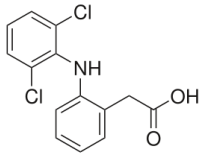
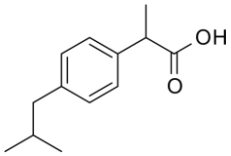
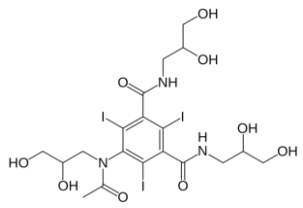
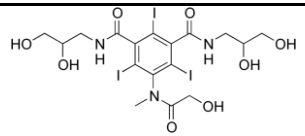
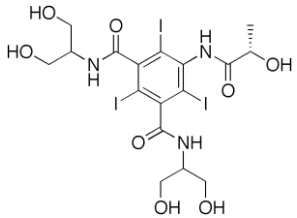
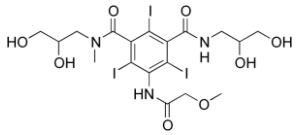
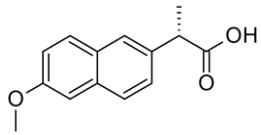
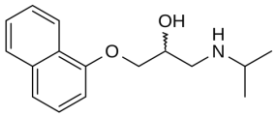
† Current address: Department of Environmental Science, Aarhus University, Frederiksborgvej 399, 4000 Roskilde, Denmark
‡ Current address: School of environmental Science and Engineering, Southern University of Science and Technology, Shenzhen 518055, PR China
§ Current address: School of Animal, Rural and Environmental Sciences, Nottingham Trent University, Nottinghamshire NG25 0QF, UK

Table S1. Compounds studied description and chemical properties

Systematic (common) name Family / Application	**Common abbreviation**	**CAS no.**	**Structural formula**	**MW** **(g mol⁻¹)**	**Log K_{ow}**
Pesticides					
1,2-Benzisothiazol-3(2H)-one (Benzisothiazolinone) Isothiazolinones / Microbiocide and fungicide	BIT	2634-33-5		151	0.64[a]
Methyl-benzimidazol-2-yl carbamate (Carbendazim) Carbamates / Fungicide	CD	10605-21-7		191	1.55[a]
3-(3,4-dichloro-phenyl)-1,1-dimethylurea (Diuron) Phenylureas / herbicide	DR	330-54-1		233	2.67[a]
(*RS*)-1-[2-(Allyloxy)-2-(2,4-dichlorophenyl)ethyl]-1*H*-imidazole (Imazalil) Imidazoles / Fungicide and veterinary medicine	IMZ	35554-44-0		297	4.10[a]
2-(4-Chloro-2-methylphenoxy)propionic acid (Mecoprop) Isothiazolinones / Herbicide	MCPP	7085-19-0		214	2.94[a]
1-(4-Chlorophenyl)-4,4-dimethyl-3-(1*H*-1,2,4-triazol-1-ylmethyl)-3-pentanol (Tebuconazole) Triazoles / Fungicide	TBU	107534-96-3		307	3.89[a]

N^2-tert-butyl-N^4-ethyl-6-(methylthio)-1,3,5-triazine-2,4-diamine (Terbutryn) Triazines / Algaecide and herbicide	TB	886-50-0		241	3.77[a]
Antibacterial (analysed together with the pesticides)					
5-Chloro-2-(2,4-dichlorophenoxy)phenol (Triclosan) Phenoxyphenols / Antimicrobial and fungicide	TCS	3380-34-5		289	4.66[a]
Pharmaceuticals					
5*H*-Dibenz[*b*,*f*]azepine-5-carboxamide (Carbamazepine) - / Anticonvulsant	CBZ	298-46-4		236	2.25[a]
2-[(2,6-Dichlorophenyl)amino]benzeneacetic acid sodium salt (Diclofenac) - / Nonsteroidal anti-inflammatory drug (NSAID)	DCF	15307-79-6		296	4.02[a]
(*RS*)-2-(4-(2-methylpropyl)phenyl)propanoic acid (Ibuprofen) - / Nonsteroidal anti-inflammatory drug (NSAID)	IBP	15687-27-1		206	3.79[a]
1-*N*,3-*N*-bis(2,3-dihydroxypropyl)-5-[*N*-(2,3-dihydroxypropyl)acetamido]-2,4,6-triiodobenzene-1,3-dicarboxamide (Iohexol) - / Radiocontrast agents	IHE	66108-95-0		821	-4.16[b]

1-*N*,3-*N*-*bis*(2,3-dihydroxypropyl)-5-(2-hydroxy-*N*-methylacetamido)-2,4,6-triiodobenzene-1,3-dicarboxamide (Iomeprol) - / Radiocontrast agents	IME	78649-41-9		777	-3.08[b]
1-*N*,3-*N*-*bis*(1,3-dihydroxypropan-2-yl)-5-[(2*S*)-2-hydroxypropanamido]-2,4,6-triiodobenzene-1,3-dicarboxamide (Iopamidol) - / Radiocontrast agents	IPA	60166-93-0		777	-2.54[b]
1-*N*,3-*N*-*bis*(2,3-dihydroxypropyl)-2,4,6-triiodo-5-(2-methoxyacetamido)-1-*N*-methylbenzene-1,3-dicarboxamide (Iopromide) - / Radiocontrast agents	IPR	73334-07-3		791	-2.95[b]
(2S)-2-(6-methoxynaphthalen-2-yl)propanoic acid (Naproxen) - / Nonsteroidal anti-inflammatory drug (NSAID)	NPX	22204-53-1		230	3.10[a]
(±)-1-Isopropylamino-3-(1-naphthyloxy)-2-propanol hydrochloride (Propanolol) - / Beta blocker	PPL	318-98-9		259	2.60[a]

[a] Values from EPISuites
[b] Values from ACD/Labs

M&M1. Solid-phase extraction (SPE) procedures

Strata-X cartridges were conditioned with 5 mL of MeOH followed by 5 mL of MilliQ water and a 100 mL sample (water:methanol 95:5, v/v) was loaded. After washing with 5 mL of water:methanol (95:5, v/v), the cartridges were dried for 30 min prior to being eluted with 5 mL of methanol:formic acid (90:10). Florisil cartridges were conditioned with 5 mL of *n*-hexane followed by loading of 5 mL methanolic samples. After washing with 5 mL of *n*-hexane:acetone (99:1, v/v), cartridges were dried for 5 min prior to being eluted with 5 mL of *n*-hexane:acetone (90:10, v/v).

Table S2. Instrument (HPLC-DAD) analytical figures of merit (LOD, LOQ, linearity range and R^2)*

Pesticides	λ (nm)	Retention time (min)	Linear range (mg L^{-1})	R^2 (n=8)	ILOD (mg L^{-1})	ILOQ (mg L^{-1})
Carbendazim	240	9.6	0.2 -10	0.9968	0.05	0.2
Benzoisothiazolinone	240	10.7	0.1 -10	0.9964	0.01	0.05
Imazalil	220	11.5	0.5 -10	0.9974	0.2	0.5
Terbutryn	240	12.2	0.1 -10	0.9957	0.01	0.05
Diuron	240	12.5	0.1 -10	0.9951	0.01	0.05
Mecoprop	220	13.0	0.3 -10	0.9965	0.1	0.3
Tebuconazole	220	14.3	0.4 -10	0.9959	0.1	0.4
Triclosan	240	15.3	0.2 -10	0.9967	0.08	0.2
Pharmaceuticals	λ (nm)	Retention time (min)	Linear range (mg L^{-1})	R^2 (n=8)	LOD (mg L^{-1})	LOQ (mg L^{-1})
Iopamidol	240	8.4	0.2 -10	0.9951	0.05	0.2
Iohexol	240	8.9	0.3 -10	0.9952	0.1	0.3
Iomeprol	240	9.0	0.3 -10	0.9947	0.1	0.3
Iopromide	240	9.4	0.2 -10	0.9943	0.05	0.2
Propanolol	240	11.2	0.2 -10	0.9947	0.03	0.2
Carbamazepine	240	12.4	0.1 -10	0.9945	0.05	0.1
Naproxen	240	13.5	0.1 -10	0.9942	0.05	0.1
Ibuprofen	220	13.8	0.3 -10	0.9951	0.1	0.3
Diclofenac	240	14.7	0.2 -10	0.9964	0.05	0.2

* determined before any sample extraction and clean-up step using analytical standards and methanolic solutions

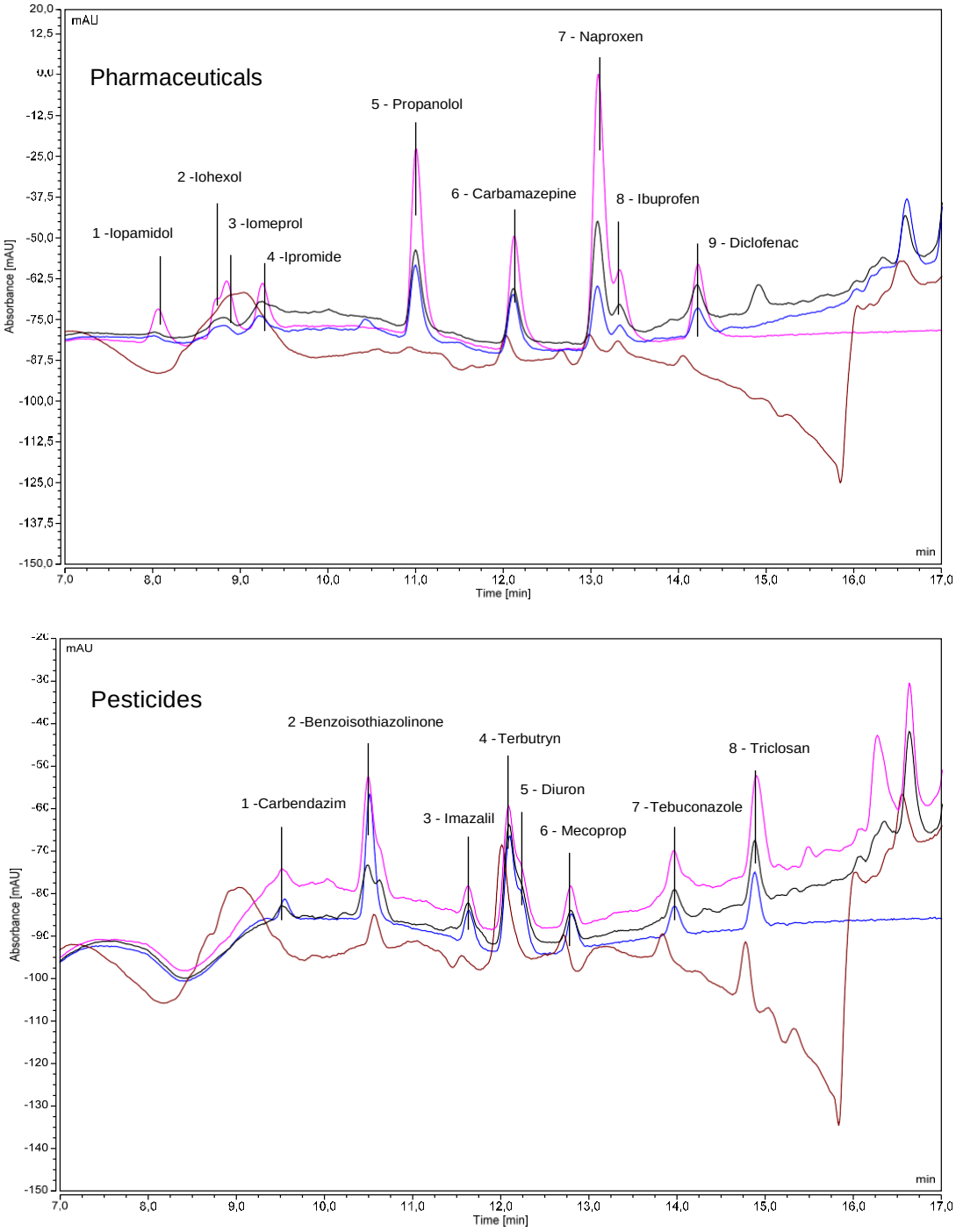


Figure S1. Typical chromatogram (DAD λ = 220 nm; background blank corrected) obtained for standard solution (■) and hexane (■); methanol:formic acid 96:4 v:v (■); methanol:acetone 95:5 v:v (■) extracts of spiked sediment (0.5 µg micropollutant $g_{dry\ sediment}^{-1}$ spiking level, theoretically 10 ng of micropollutant injected) after 30 min of ultrasonication

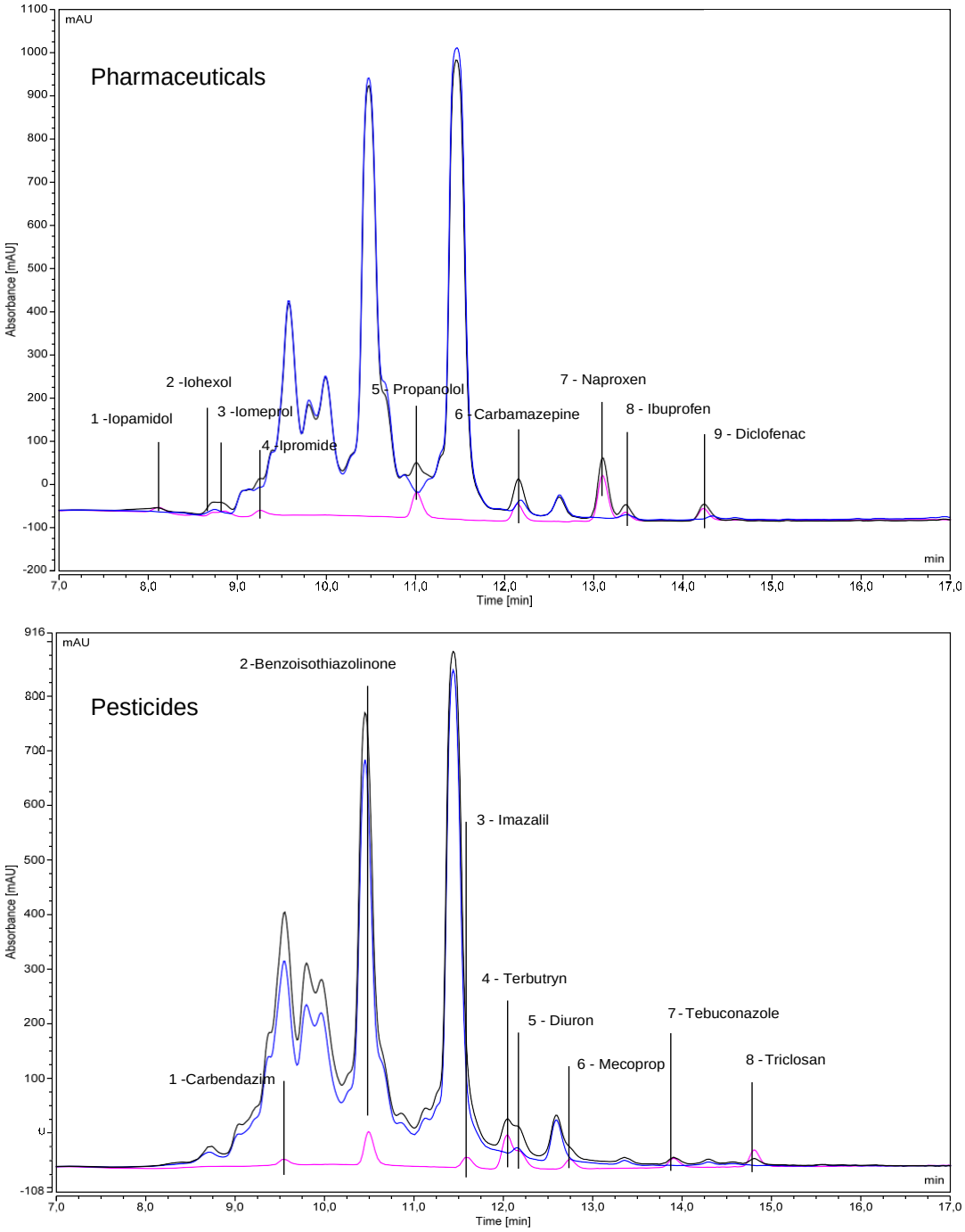


Figure S2. Typical chromatogram (DAD λ = 220 nm; background blank corrected) obtained for standard solution (■) and methanol: acetone 95:5 v:v extracts of spiked plant material (5 µg micropollutant $g_{dry\ sediment}^{-1}$ spiking level; theoretically 10 ng of micropollutant injected) (■) and non-spiked plant material (■) after 30 min of ultrasonication, no clean-up

Table S3. Comparison of the present method characteristics for sediment analysis with relevant multi-residue methods published

Pesticides					
Reference	Methodology	LOD (ng g^{-1})	LOQ (ng g^{-1})	RSD (%)	Recovery (%)
This work	USE-HPLC-DAD	5 - 100	25 - 250	4 - 30	53 – 101
[13]	PLE-LL-LC-HRMS/MS	0.01 - 4	0.03 - 14	1 - 30	57 - 139
[15]	USE-SPE-LC-MS/MS	0.7 – 1.2	-	9 - 12	68 - 102
[29]	*LC-MS/MS	3	10	26 - 45	40 - 60
[34]	QuEChERS-LC-MS/MS	0.1 - 2	1 - 6	8	46 - 102
[37]	MAE-SPME-GC-MS	0.01 – 0.1	0.02 – 0.45	7 - 17	86 - 112
[39]	SLE-LC-MS/MS	-	0.1 - 49	3 - 28	40 - 125
[40]	PLE-SPE-LC-MS/MS	0.02 - 17		2 - 17	67 - 118
Pharmaceuticals					
Reference	Methodology	LOD (ng g^{-1})	LOQ (ng g^{-1})	RSD (%)	Recovery (%)
This work	USE-HPLC-DAD	15 -50	50 - 150	6 - 12	50 - 98
[11]	MAE-GC-MS	30 - 80	-	< 11	25 - 81
[11]	MAE-HPLC-DAD	< 167	-	< 11	> 70
[13]	PLE-LL-LC-HRMS/MS	0.01 - 4	0.03 - 14	1 - 30	57 - 139
[15]	USE-SPE-LC-MS/MS	0.9 – 9.4	-	6 - 14	41 - 92
[21]	USE-SPE-LC-MS/MS	0.08 – 4.2	-	-	41 - 151
[30]	MAE–SPE–GC–MS	0.3 – 5.7	0.9 – 17.1	0.7 – 14.7	> 50
[35]	MAE- LC-MS/MS	0.3	1.0	1 - 8	98 - 103
[36]	USE-SPE-LC-MS/MS	-	0.6 – 5.6	-	< 10 - 343
[38]	USE-SPE-HPLC-DAD/FL	-	1 - 187	-	< 15 - 103

USE – Ultrasonic solvent extraction, HPLC – High performance liquid chromatography, DAD diode array detector, PLE - pressurized liquid extraction, LL – liquid-liquid partitioning clean-up, LC- liquid chromatography, HRMS/MS high resolution Orbitrap mass spectrometry, SPE – solid-phase extraction, MS/MS – tandem mass spectrometry, *extraction not stated, QuEChERS - Quick Easy Cheap Effective Rugged Safe method, DMAE - dynamic microwave-assisted extraction, CFME - continuous-flow microextraction, GC – gas chromatography, MS – mass spectrometry, MAE – microwave assisted extraction, SPME – solid-phase microextraction, SLE – solid-liquid extraction, FL - fluorescence detectors,

Table S4. Comparison of the present method characteristics for plant analysis with other multi-residue methods published

Pesticides					
Reference	Methodology	LOD (ng g^{-1})	LOQ (ng g^{-1})	RSD (%)	Recovery (%)
This work	USE-HPLC-DAD	50 - 1000	250 - 2500	4 - 30	53 – 101
[29]	*LC-MS/MS	3	10	21 - 43	45 - 50
[41]	DMAE-CFME-GC-MS	0.6 – 1.6	2 - 5	9	81 - 107
[42]	dispersive-SPE– LC-MS/MS		10	3 - 16	72 - 104
[43]	QuEChERS-LC-MS/MS		10 - 50	< 20	80 - 136
[44]	SLE-SO-SPE-GC-MS/MS		10	< 20	70 - 120
Pharmaceuticals					
Reference	Methodology	LOD (ng g^{-1})	LOQ (ng g^{-1})	RSD (%)	Recovery (%)
This work	USE-HPLC-DAD	150 - 500	500 - 1500	6 - 12	50 - 98
[14]	USE-SPE-LC-MS/MS	0.5 – 1.5	2 - 4	-	73 - 92
[14]	BE-SPE-GC-MS	10 - 20	20 - 75	-	15 - 98
[14]	PLE- SPE-LC-MS	2 - 23	-	-	46 - 176
[14]	BE-SPE-LC-MS/MS	25	-	-	40 - 120
[14]	PLE- SPE-GC-MS	7 - 58	-	-	46 - 94
[45]	PLE-LC-MS/MS	2 - 12	-	< 20	70 - 134
[45]	QuEChERS-LC-MS/MS	0.7 - 8	-	< 20	70 - 119

USE – Ultrasonic solvent extraction, HPLC – High performance liquid chromatography, DAD diode array detector, dispersive-SPE - dispersive solid phase extraction, LC- liquid chromatography, MS/MS – tandem mass spectrometry, *extraction not stated, SLE – solid-liquid extraction, SO – salting out, SPE – solid-phase extraction, GC – gas chromatography, QuEChERS - Quick Easy Cheap Effective Rugged Safe method, BE – buffer extraction, MS – mass spectrometry, PLE - pressurized liquid extraction

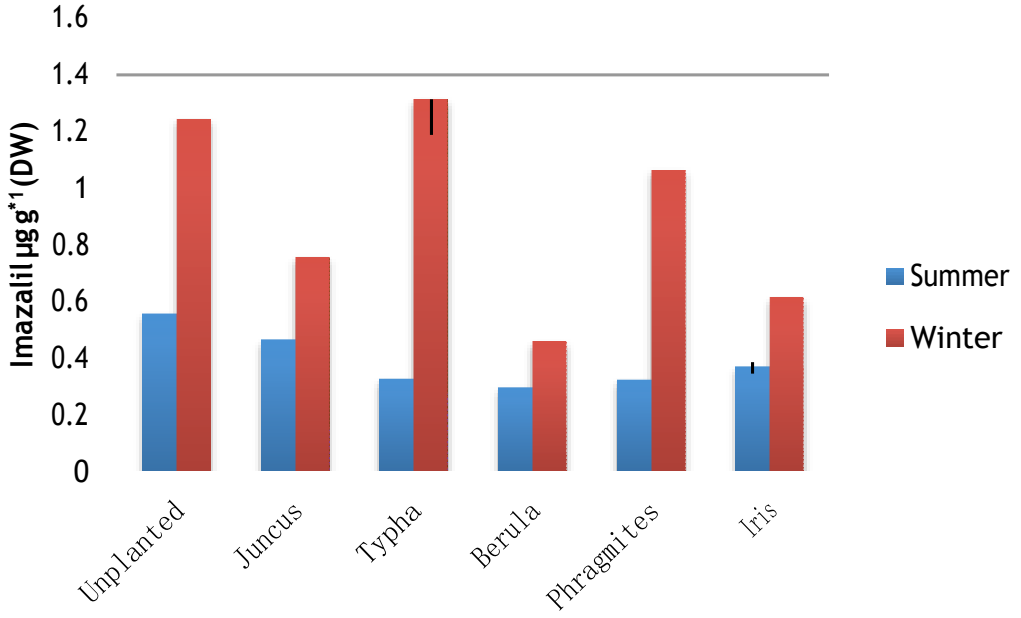


Figure S3. Imazalil concentration in substrate samples (sediment) from 6 different constructed wetland bed mesocosms (unplanted and planted with different plants) continuously run over 9 months under various hydraulic loading rates and imazalil concentration of both 10 and 100 µg L^{-1} in the influent

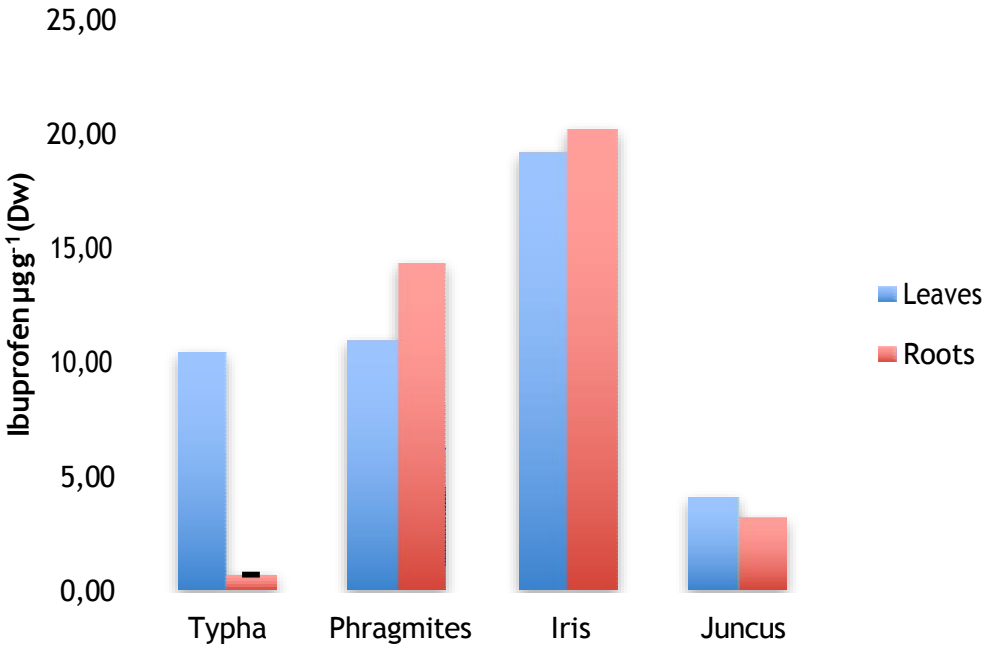


Figure S4. Ibuprofen concentration in plant tissue (leaves and roots) in different plant species after exposure for 24 days in spiked hydroponic media (water concentration of 10 mg L^{-1})

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