Table S1. Chemical Groups, Physicochemical Properties and Mode of Action of all Detected Fungicides.

Chemical Group	Active substance/ (Chemical Subgroup) [1]	CAS Nº	Molecular mass [2]	Mode of action [2]
Amide	Benalaxyl (acylalanine)	71626-11-4	325.40	Ribosomal RNA synthesis inhibitor
	Metalaxyl (acylalanine)	57837-19-1	279.33	Ribosomal RNA synthesis inhibitor
	Pyracarbolid (anilide)	24691-76-7	217.27	NA
	Methfuroxam (anilide - furancarboxamide)	28730-17-8	229.27	Glucose and acetate oxidative metabolism inhibitor
	Mepronil (anilide – phenylbenzamide)	55814-41-0	269.33	Mitochondrial succinate dehydrogenase inhibitor (SGHI)
	Dimethomorph (cinnamamide)	110488-70-5	387.86	Cell wall biosynthesis inhibitor
	Furmecyclox (furamide)	60568-05-0	251.32	Mitochondrial function inhibitor
	Oxycarboxin ** (oxathiincarboxamide)	5259-88-1	267.31	Mitochondrial succinate dehydrogenase inhibitor (SDHI)
	Cyflufenamid ** (phenylacetamide)	180409-60-3	412.36	NA
Antibiotic	Cycloheximide **	66-81-9	281.16	Protein biosynthesis inhibitor

Table S1. *Cont.*

Chemical Group	Active substance/ (Chemical Subgroup) [1]	CAS Nº	Molecular mass [2]	Mode of action [2]
Azole	Imazalil * (Imidazole)	35554-44-0	297.18	Sterol biosynthesis inhibitor[3]
	Flusilazole ** (triazole)	85509-19-9	315.39	Sterol biosynthesis inhibitor
	Propiconazole (triazole)	60207-90-1	342.22	Sterol biosynthesis inhibitor
	Tebuconazole ** (triazole)	107534-96-3	307.82	Sterol biosynthesis inhibitor
	Tetraconazole * (triazole)	112281-77-3	372.15	Sterol biosynthesis inhibitor
	Tricyclazole *	41814-78-2	189.24	Melanin biosynthesis inhibitor in cell wall
Benzimidazole	Benomyl *	17804-35-2	290.32	Inhibition of mitosis and cell division (Beta-tubulin assembly)
	Carbendazim **	10605-21-7	191.21	Inhibition of mitosis and cell division (Beta-tubulin assembly)
	Rabenzazole	40341-04-6	212.25	Inhibition of mitosis and cell division (Beta-tubulin assembly)
	Thiabendazole *	148-79-8	201.25	Inhibition of mitosis and cell division (Beta-tubulin assembly)
Benzoisothiazole	Probenazole	27605-76-1	223.25	Host plant defence induction

Table S1. *Cont.*

Chemical Group	Active substance/ (Chemical Subgroup) [1]	CAS Nº	Molecular mass [2]	Mode of action [2]
Carbamate	Propamocarb	24579-73-5	188.3	Lipid synthesis inhibitor
	Diethofencarb (phenylcarbamate)	87130-20-9	267.32	Inhibition of mitosis and cell division (Beta-tubulin assembly)
Dithiolane	Isoprothiolane	50512-35-1	290.40	Phospholipid biosynthesis inhibitor
Imidazolinone	Fenamidone	161326-34-7	311.40	Quinone outside inhibitor (QoI) [4]
Morpholine	Dodemorph	1593-77-7	281.48	Sterol biosynthesis inhibitor
	Fenpropimorph *	67564-91-4	303.48	Sterol biosynthesis inhibitor
Organophosphorus	Iprobenfos **	26087-47-8	288.34	Phospholipid biosynthesis inhibitor
Oxazolidinedione	Famoxadone	131807-57-3	374.39	Quinone outside inhibitor (QoI) [4]
Oxazolidinone	Oxadixyl	77732-09-3	278.30	Ribosomal RNA synthesis inhibition
Phenylpyrrole	Fludioxonil *	131341-86-1	248.19	Effect on signal transduction
Pyrimidine	Ferimzone (pyrimidinonehydrazone)	89269-64-7	254.33	Uncoupler of oxidative phosphorylation [4]
Pyrroloquinolinone	Pyroquilon *	57369-32-1	173.21	Melanin biosynthesis inhibitor in cell wall
Quinoline	Ethoxyquin	91-53-2	271.34	Antioxidant (food preservative) [5]

Table S1. *Cont.*

Chemical Group	Active substance/ (Chemical Subgroup) [1]	CAS Nº	Molecular mass [2]	Mode of action [2]
Spiroketalamine	Spiroxamine	118134-30-8	217.34	Sterol biosynthesis inhibitor
Strobilurin	Azoxystrobin ** (methoxyacrylate)	131860-33-8	403.40	Quinone outside inhibitor (QoI) [4]
	Picoxystrobin ** (methoxyacrylate)	117428-22-5	367.32	Quinone outside inhibitor (QoI) [4]
	Kresoxim-Methyl ** (oximinoacetate)	143390-89-0	313.35	Quinone outside inhibitor (QoI) [4]
	Trifloxystrobin ** (oximinoacetate)	141517-21-7	408.37	Quinone outside inhibitor (QoI)[4]

[1]Data retrieved from BCPC- British Crop Production Council's [91]. [2]Data retrieved from PPDB: Pesticide Properties Database [22]. [3]Data retrieved from [22]. [4]Data retrieved from [92]. [5]Data retrieved from [54]. *Fungicide detected once in surface water; **Fungicide detected once in groundwater. NA= Not available.

Table S2. Surface Water: Characterisation of the Sampling Stations

Regions	River Basin District (HR)	Water bodies	Sampling Station number	Station code /geographic coordinates	Localisation	UWWTP[1] equivalent inhabitants	Potential Pressures
North	HR2	Ave river	1	PT05G/06 Lat. (ºN): 41,49565 Long (ºW): -8,3212	Taipas, Downstream of Prazins	-----	Agriculture / Animal production
			2	PT05G/53 Lat. (ºN): 41,40951 Long (ºW): -8,38342	Guimarães, Downstream of UWWTP Serzedelo I and II.	Serzedelo I:126.000 Serzedelo II: 270 822	Urban Agriculture / Animal production
	HR3	Tâmega river (international body water)	3	Chaves Lat. (ºN): 41,713199 Long (ºW): -7,507799	Chaves, Downstream of UWWTP, A tributary (sub-basin) of the Douro river	Chaves: 57 748	Urban Agriculture / Animal production
		Tinto river	4	PT07F/05 Lat. (ºN): 41,1539428 Long (ºW): -8,5702716	Porto, Freixo, Rio Tinto Campanhã, Downstream of UWWTP. A tributary (sub-basin) of Douro river	Freixo: 170 000	Urban
Center	HR4A	Vouga river	5	PT09F/29 Lat. (ºN): 40,672777 Long (ºW): -8,560407	Angeja, Downstream of Angeja	-----	Agriculture / Animal production
West and Tejo Region	HR5A	S. Domingos (west - (reservoir)	6	PT18B/01 Lat. (ºN): 39,33406 Long (ºW): -9,31713	S. Domingos	-----	Agriculture / Animal production
		Tejo river (international body water)	7	PT16L/05 Lat. (ºN): 39,660322 Long (ºW): -7,569093	Perais, near the border Portugal /Spain	-----	Rural
			8	PT16K/11 Lat. (ºN): 39,5474596	Fratel reservoir	-----	Rural

				Long (ºW): -7,7934542			
			9	PT21B/22 Lat. (ºN): 38,69522 Long (ºW): -9,234269	Marina Algés, transitional water downstream of 3 UWWTP:	Beirolas: 213 500 Chelas: 255 000 Alcântara: 756 000	Urban, Agriculture
Alentejo	HR6 /HR7	Caia river	10	PT20O/04 Lat. (ºN): 38,8831 Long (ºW): -7,0356	Caia, Posto Fiscal, near the border Portugal /Spain	-----	Agriculture / Animal production
Algarve	HR8	Ria Formosa (Coastal water)	11	PT31J/20 Lat. (ºN): 37,01814 Long (ºW): -7,84396	Olhão, Downstream of UWWTP	Faro / Olhão: 113 200	Urban Fish stocking Fishing activity
			12	PT31J/02 Lat. (ºN): 37,00194 Long (ºW): -7,92199	Faro, Downstream of UWWTP	Faro / Northwest 44 530	Urban
		Arade river (Transitional water)	13	PT31F/01S Lat. (ºN): 37,14425 Long (ºW): -8,51528	Portimão UWWTP	Portimão: 140 000	Urban

[1]Urban Waste Water Treatment Plants

Table S3. Groundwater: **Characterization** of the Sampling Stations

Regions	River basin district (RH)	Sampling station	Station code /geographic coordinates	Localisation Well (W) Piezometer (P)	Potential Pressures
North	RH2	1	68/12 41.490; -8.744	Esposende (W)	Mainly Animal production
		2	68/11 41.5324; -8.75967	Esposende (W)	Mainly Animal production
Center	RH4A	3	163/125 40.767; -8.599	Murtosa (W)	Urban Mainly Agriculture
		4	240/26 40.18863; -8.58919	Formoselha (P)	Urban Mainly Agriculture (Region of rice-fields)
		5	- 39.808; -8.751	Martos Leiria (W)	Mainly Agriculture
West and Tejo	RH5A	6	377/94 39.073; -8.728	Salvaterra de Magos (W)	Mainly Agriculture (Region of rice-fields)
		7	405/17 38.939; -8.863	Samora Correia (W)	Mainly Agriculture (Region of rice-fields)
		8	- 38.567035; -8.727683	Marateca (W)	Mainly Agriculture (Region of rice-fields)
Alentejo	RH6/RH7	9	401/36 38.97793; -7.00075	Campo Maior (P)	Mainly Animal production (Region of rice-fields)
		10	- 38.377273; -7.750984	Monte Trigo (W)	Agriculture Animal production
		11	- 38.052; -8.399	Vale da Eira (Ermidas Sado) (W)	Agriculture (Region of rice-fields)
		12	- 37.996; -8.607	São Bartolomeu da Serra (Santiago do Cacém) (W)	Agriculture

Algarve	RH8	13	595/309 37.16934 -8.45791	Querença-Silves (P)	Agriculture (Orchard zone)

Table S4. Detection of Frequency and Geographic Distribution of Fungicides in Surface Water (2017-2019)

Fungicides	2017- 2019													Frequency (d/n)x100% d- Nr. of detections n- Nr. of stations
	Sampling stations (n=13)													
	Ave river Taipas	Ave river Serzedelo I - II	Tâmega river- Chaves	Tinto river Freixo	Vouga river Angeja	S. Domingos	Tejo river Perais	Tejo river Fratel	Tejo river Marina de Algés	Caia river	Ria Formosa Olhão	Ria Formosa Faro	Arade river Portimão	
	1	2	3	4	5	6	7	8	9	10	11	12	13	
Azocystrobin					X	X			X	X				31
Benalaxil	X					X					X			23
Carbendazim				X		X								15
Dimethomorph		X				X								15
Dodemorph		X	X			X			X		X		X	46
Ethoxyquin	X	X			X				X		X	X	X	54
Fenamidone	X	X	X	X					X	X				46
Ferimzone	X				X	X	X		X		X	X		54
Furmecyclox		X		X		X			X				X	38
Iprobenfos			X						X		X			23
Isoprothiolane									X		X	X	X	31

Kresoxim methyl		X	X	X	X				X		X	X	X	61
Metalaxyl		X		X		X			X					31
Oxadixyl (acetamide)	X	X		X	X				X		X	X	X	61
Propamocarb						X			X					15
Propiconazole		X	X					X			X			31
Rabenzazole	X	X			X		X	X	X		X		X	61
Spiroxamine	X		X											15
Tebuconasole		X			X	X				X				31
Geographic distribution	7	11	6	6	7	9	2	2	13	3	10	7	7	∑ 89 detected fungicides
Regions	North	North	North	North	Center	West and Tejo	West and Tejo	West and Tejo	West and Tejo	Alentejo	Algarve	Algarve	Algarve	North-34 Center-8 West and Tejo-29 Alentejo-3 Algarve-26

Table S5. Detection of Frequency and Geographic Distribution of Fungicides in Groundwater (2016-2019)

Antifungals	2016 - 2019													Frequency (d/n)x100 % d-Nr. of detections n-Nr. of stations
	Sampling stations (n=13)													
	Esposende	Esposende	Murtosa	Formoselha	Martos	Leiria Salvaterra de Magos	Samora Correia	Marateca	Campo Maior	Monte Trigo	Vale da Eira Ermidas Sado	S. Bartolomeu da Serra	Querença Silves	
	1	2	3	4	5	6	7	8	9	10	11	12	13	
Benalaxyl					X		X	X						23
Diethofencarb						X	X							15
Dodemorph	X				X	X			X		X		X	46
Ethoxyquin	X	X	X		X	X	X	X		X	X	X		77
Famoxadone						X		X						15
Fenamidone						X				X				15
Ferimzone		X			X			X	X	X	X	X		54
Furmecyclox	X	X	X						X				X	38
Mepronil					X					X	X			23
Metalaxyl			X		X	X		X					X	31
Methfuroxam					X			X		X				23

Oxadixyl					X						X			15
Pyracarbolid					X						X			15
Probenazole								X		X				15
Rabenzazole	X	X	X	X	X	X	X	X	X	X	X	X		92
Spiroxamine											X	X		15
Geographic distribution	4	4	4	1	10	7	4	8	4	7	8	4	3	∑ 68 detected fungicides
Regions	North	North	Center	Center	Center	West and Tejo	West and Tejo	West and Tejo	Alentejo	Alentejo	Alentejo	Alentejo	Algarve	North-12 Center-22 West and Tejo-28 Alentejo-34 Algarve-4

Document S6. Analytical Method Description

Qualitative Analysis Method Used for the Characterisation of Fungicides in Surface-Groundwater

This methodology involved two steps corresponding to the extraction of the adsorbent of POCIS extraction disks and subsequent qualitative determination by Ultra Performance Liquid Chromatography-High Resolution Mass Spectrometry (UHPLC-QqTOF-MS).

Sample Extraction

After drying the POCIS disks, the membrane on one side of the support was cut. The adsorbent was transferred to an empty cartridge extracted five times with 2 mL of methanol, making a total volume of 10 mL collected in a glass vial. This extract was concentrated under nitrogen current to a final volume of about 1 ml. To the extract was added the 13C3 internal caffeine standard. The extract in methanol is taken to dryness in rotavapor under vacuum at 35ºC and reconstituted in a mixture of water/methanol (v:v 4:1) for subsequent injection into the UHPLC-QqTOF-MS system. For surface water samples, two discs for sampling collection were analysed. The adsorbents of the duplicated discs were extracted simultaneously. In the case of groundwater samples, only one POCIS sampler was used per collection point.

Ultra-Performance Liquid Chromatography-High Resolution Mass Spectrometry (UHPLC-QqTOF-MS) Analysis

Extracts were analysed on a UHPLC-QqTOF-MS system composed of an UltiMate® 3000 RSLCnano system (Thermo Scientific Inc., Waltham, MA, USA), interfaced with a QqTOF Impact II mass spectrometer with an ESI source (Bruker Daltonics, Bremen, Germany). Three aliquots were analysed in both ESI positive and negative mode for each water extract, and as a control, a "blank" sample of the mixture of water/methanol (4:1).

Chromatographic separation was achieved with a Kinetex C18 column (150 X 2.1 mm; 2.6 μm particle size; Phenomenex: pore size A^{o}= 100; surface area = 200 m^{2}/g; carbon load = 9%) using an elution gradient of 0.1% v/v formic acid in water (mobile phase A) and 0.1% v/v formic acid in acetonitrile (mobile phase B), at a flow rate of 200 mL/min. The elution conditions were as follows: 0–1.4 min, isocratic 7% B; 1.4–10.0 min, linear gradient to 50% B; 10–15 min, linear gradient to 100% B; 15–18 min isocratic 100% B; 18–19 min, linear gradient to 7% B; 19–25 min, isocratic to 7% B. The injection volume was 20 mL. The column and the autosampler were

maintained at 35ºC, respectively. The mass spectrometer parameters were set as follows: endplate offset: 500 V; capillary voltage: 4.5 and 2.5 kV (positive and negative mode, respectively); nebuliser: 2.8 bars; dry gas: 8 L/min; dry temperature: 200ºC. Internal calibration was performed for sodium formate clusters, with a sodium formate solution of 10 mM introduced to the ion source via a 20 L loop at the beginning of each analysis using a six-port valve. Calibration was then performed using high-precision calibration mode (HPC). The mass spectra were acquired in the broadband collision-induced dissociation (bbCID) mode in a range between 50–1000 m/z, with a scan speed of 1 Hz. MS/MS experiments were performed in a data-dependent-acquisition (DDA) mode with an acquisition rate of 3 Hz using a dynamic method with a fixed cycle time of 3s. Dynamic exclusion duration was 0.4 min. The 49 standards were analysed in the MRM acquisition mode, with collision energy defined according to the mass, load of each ion and an isolation window of 5 Da. Under the instrumental conditions used, the TOF (FWHM) resolution power is between 36,000–40,000 to m/z 226.1593, 430.9137 and 702.8636.

Data Analysis and Validation

Mass spectrometry data were processed using the Data Analysis 4.4 and Target Analysis 1.3 software (Bruker Daltonics). An in-house mass library was built for 49 standards plus 620 suspected substances (insecticides, fungicides, herbicides, drugs, metabolites). For the 49 standards (Sigma-Aldrich) previously analysed by MRM, the database includes the expected retention time, accurately measured mass, molecular formula, and qualifier ions for each standard compound. The (possible) elemental composition of peaks of interest was calculated using the algorithm Smart Formula 3D within Bruker software for the remaining compounds. This library was used for accurate mass screening for (non)target compounds and unknowns using the Find-Compounds-Chromatogram via SigmaFiTTM tools of the Target Analysis software, which creates a "peak chromatogram base" for m/z values above a threshold intensity value. Values for retention time deviation lower than 0.3 min; mass deviation less than 5 ppm and mSigma less than 100 were considered acceptable for positive confirmation (mSigma <100, acceptable, <50 good, and <25 excellent). After screening in Target Analysis, the Data Analysis potentialities were used to check the data manually.

Analysing the samples with a QqTOF mass spectrometer, the fungicides in complex matrices were detected at concentrations as low as 50 ng/L.