Environmental Pollution 363 (2024) 125056

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Assessing pesticide residue occurrence and risks in the environment across Europe and Argentina☆

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ARTICLE INFO

Keywords:
Soil
Crop
Water
Sediment
Maximum residue level
Risk assessment

ABSTRACT

The widespread and extensive use of pesticides in European crop production to reduce losses from weeds, diseases, and insects may have serious consequences on the ecosystem and human health. This study aimed to identify 20 active substances of high health risk, based on their detection frequency within and across the environmental matrices (soil, crop, water, and sediment) and to identify their associated hazardous effects. A sampling campaign was conducted across 10 case study sites in Europe and 1 in Argentina and included conventional and organic farming systems. In 31% of cases, the detected substances were found at a higher concentration in the soil than in the corresponding crops, 93% of the compounds were fungicides, and the remainder were insecticides. 43% of the substances, 57% of which were insecticides, were detected only in soil. There was a clear relationship between soils and crops in terms of contamination, but not between water and sediment. Portuguese soil (wine grapes) had the highest number of substances (12) with average concentrations (AC) varying between 1 and 162 μg/kg, followed by French (11 substances in wine grapes) (1≤AC≤64 μg/kg) and Spanish soils (9 substances in vegetables) (3≤AC≤59 μg/kg). The crops corresponding to these soils contained a relatively high number of detected substances and several in high average concentrations (AC). The risk quotient was consistently higher for conventional farms than for organic farms. For the soils from conventional farms, 5 active substances (chlorpyrifos, glyphosate, boscalid, difenoconazole, lambda-cyhalothrin, and one metabolite: AMPA) were considered high risk. For water samples, 2 substances (dieldrin and terbuthylazine) found were high risk, and for sediment, there were 3 substances (metalaxyl-M, spiroxamine, and lambda-cyhalothrin). There were 6 substances detected in crops that are suspected to cause human health effects. Uncontaminated soil is a prerequisite for the adoption of sustainable alternatives to pesticides. Efforts are needed to elucidate the unknown effects of mixtures, including biocides and banned compounds in addition to the substances used in agriculture.

☆ This paper has been recommended for acceptance by Dr. Klaus Kümmerer.

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https://doi.org/10.1016/j.envpol.2024.125056
Received 6 July 2024; Received in revised form 19 September 2024; Accepted 29 September 2024

1. Introduction

Pesticides are used to protect crops and increase yields. Nearly one-third of global agricultural yields are produced using pesticides. In the European Union (EU), that amounts to between 8.79 and 13.76 kg/ha/year (FAOSTAT, 2020). In 2017, 362,626 tons of pesticides were sold on the EU market alone, with Spain accounting for the highest percentage of sales (72,118 t), followed by France, Italy, and Germany (MAPAMA, 2017). Pesticides are used on nearly all crops (e.g., cereals, vegetables, vineyards, olive groves, and orchards), and they can accumulate in different matrices in the environment (Close et al., 2021; Tauchnitz et al., 2020). The widespread occurrence of pesticide residues in the environment is a result of their movement from target to off-target areas as evidenced by their frequent detection in soil, water, and air (Kruse-Plaß et al., 2021; Dulsat-Masvidal et al., 2023; Silva et al., 2023) as well as non-target plants (Zioga et al., 2023; Qi et al., 2020; Duffner et al., 2020).

Pesticides are of special environmental interest because of their potential toxicity to non-target species as well as their high mobility and/or persistence. Pesticide leaching due to rain or irrigation (Chaplain et al., 2011) can contaminate drinking water (Barbieri et al., 2020). Concentrations of pesticides in agricultural wastewater can reach as high as 500 mg L^{-1} and are predominately introduced into aquatic systems through runoff, leaching, and spray drift (Tudi et al., 2021). Some pesticides are more toxic than others and have been found to exceed regulatory threshold values for several aquatic species (Islam et al., 2018).

The persistence of pesticides in soil depends on several factors including chemical, photochemical, and microbial transformations as well as sorption, volatilization, plant uptake, and leaching to surface and groundwater, with sorption and biodegradation being the most relevant processes (Chaudhari et al., 2023; Collard et al., 2023; Yadav et al., 2016). Pesticides have been shown to contribute to the decline of bee and bird populations, and reduce aquatic biodiversity (Rundlöf et al., 2015; Hallmann et al., 2014; Zhang et al., 2022). Although some pesticides have been banned, residues can persist in the environment for decades, posing an additional threat to biodiversity and water quality as well as ecosystem services and functioning (Beketov et al., 2013; Stehle et al., 2015).

The fact that pesticide residues can remain in the environment long after their application has been widely reported and studied around the world (de Souza et al., 2020). However, the simultaneous presence of pesticides in both soil and water has rarely been studied, even though persistent pesticides contaminating soils could also contaminate surface water (Tauchnitz et al., 2020). Shallow topsoil in certain areas could also facilitate the leaching of compounds into groundwater (Sánchez-González et al., 2013). Aggregate exposure assessment of pesticides requires intensive field measurements of pesticide levels in environmental media, which requires a large amount of resources (Geissen et al., 2015; Li, 2023). As quantifying exposure doses from different exposure pathways to assess the overall exposure risk of pesticides based on measurements is challenging, modelling studies are emerging as a key element in population health risk assessment. However, modelling does not take into account factors such as weather and geographical conditions, which are necessary for regional risk assessment. To this end, field measurements could help calibrate models to better manage pesticide emissions and derive environmental standards (Nordborg et al., 2014; Li, 2022).

The objectives of this work were to (i) identify the 20 most frequently detected substances in each environmental matrix, soil, water, sediment, and crop in one Argentinian and 10 European case study sites, (ii) provide a cross-sectional overview of the most frequently detected substances across the environmental matrices, and (iii) determine the related risk of the selected substances to species living in water and sediment as well as earthworms.

2. Material and methods

2.1. Sampling design

A total of 529 samples were considered in this study. The samples originated from 11 case study sites (CSS), 10 in Europe and 1 in Argentina, and were distributed as follows: 215 soil, 212 crop, 64 water, and 38 sediment samples. Water bodies, with distinct typology (creeks, streams, channels, ditches, rivers, lakes, ponds and reservoirs), were located in regions with high agricultural activity across the 11 CSS. The sampling sites were distributed as follows: Spain (case study site 1, CSS1, n = 7), Portugal (CSS2, n = 8), France (CSS3, n = 6), Switzerland (CSS4, n = 5), Italy (CSS5, n = 6), Croatia (CSS6, n = 3), Slovenia (CSS7, n = 6), the Czech Republic (CSS8, n = 8), the Netherlands (CSS9, n = 6), Denmark (CSS10, n = 3) and Argentina (CSS11, n = 6). Each case study site included an average of 10 fields under conventional/integrated pest management and 10 organic fields. One composite soil sample and one composite crop sample was taken for each field following a standardized method for sampling, storage, and shipment (Alaoui et al., 2021, **SM1**). Soil and crop sampling was carried out in both conventional and organic fields. However, it was not possible to assign a farming system to the water and sediment samples since the sampled water bodies drained multiple fields at once.

A list of analytes was compiled at the project level which were then tested in all field samples. The list included pesticides that were known or expected to have been applied in the 11 SPRINT case study sites as well as the pesticides known or expected to be found in the sampled matrices (based on pre-screening results and a literature review; Silva et al., 2021). The final list contained 209 substances (Vested et al., 2022). We were able to analyze 192 substances in soil, 192 in crops, 193 in water, and 195 in sediment (**SM2**). The analyses of sediment, soil, water, and crops are described in detail in Alaoui et al. (2021) and briefly reported in **SM3**. Crop types and livestock production are shown in **SM4**. Organic fields/farms were only considered for this study when the transition had occurred at least 10 years before the sampling campaign.

For each of the analyzed compounds (active substances and metabolites) we considered all measurements equal to or above its limit of detection (LOD) in calculating the Merdian concentration (MC), the 5th percentile (p5) and the 95th percentile (p95). The detection frequency (DF) of a pesticide residue was calculated as the total number of measurements ≥ LOD divided by the number of samples that where tested.

2.2. Quality control

Chemical determinations and quality control of analytical data were performed according to EU guidance documents SANTE/2020/12830 and SANTE/11312/2021. Several sets of multi-pesticide calibration standards were prepared for LC-MS/MS-based multi-method, GC-MS/MS-based multi-method, GC-HRMS-based multi-method and glyphosate/AMPA analysis. Each set of calibration standards was prepared from a mixed solution combining the reference standards of all compounds to be analyzed by the respective analytical method. Calibration standards for LC-MS/MS analysis were prepared in solvent (multi-method: ACN 1% HAc + Millipore water; glyphosate/AMPA: Millipore water), while the calibration standards for GC-HRMS analysis were matrix-matched. For initial validation, the linearity of the response was determined using solvent calibration standards.

Selectivity was assessed by analysing two blank samples. Recovery and repeatability were determined by analysis of spiked samples (Alaoui et al., 2024; Silva et al., 2023) at different levels. The LOQ was defined as the lowest level that met the criteria for recovery (default 70–120%) and precision (RSD ≤20%). The LOD was defined as the concentration corresponding to S/N = 3 for both quantifier and qualifier and was estimated from the data obtained for the lowest spike level. For quality control during sample analysis, linearity was re-assessed by analysis of a set of solvent-based standards. The response of the GC-HRMS analytes was normalised to the response of PCB-198 and the response of glyphosate and AMPA was normalised to the response of the isotopically labelled analogs.

For LC-MS/MS analysis, a calibration curve was constructed using calibration standards (multi-method: 0.1 to 2000 μg/ml, 2 to 43 points depending on matrix) injected at the start, middle and end of each sample sequence (Alaoui et al., 2024). For GC-MS/MS analysis, the calibration curve was established using calibration standards from 0.125 to 50 μg/kg, 2 to 9 points injected at the start and end of each sequence depending on the matrix considered. For GC-HRMS, a calibration curve was established using calibration standards (multi-method: 1, 10 and 50 μg/mL for indoor dust samples; 5, 10 and 100 ng/kg to 2000 μg/mL for water samples) was injected at the beginning and end of each sequence. For GC-MS analysis, a calibration curve (2, 20 μg/mL for crop; 5, 10 and 100 ng for water and 1 and 5 μg/kg for wristbands) was injected at the start and end of each sequence. Additional information on quality control and sensitivity analysis is briefly described in **SM5**, see also Silva et al. (2023).

2.3. *Ecotoxicological data collection for pesticides analyzed in the SPRINT project*

To get ecotoxicological information on the top 20 compounds and related metabolites detected in our samples, we used the Pesticide Properties DataBase (PPDB) (Lewis et al., 2016). This database is a collection of data published by regulatory bodies, including the plant protection products (PPP) Renewal Assessment Reports (RAR), Draft Assessment Reports (DAR), and Conclusion dossiers by EFSA, as well as data found in literature.

The data are mostly verified data used for regulatory purposes, and the thresholds considered are consistent with EU regulatory thresholds (PPDB, 2023). According to the PPDB, classification was assigned to the qualitative class of hazard (low/moderate/high/no data). In the first stage of preparing this review, all information available concerning median Lethal or Effect Concentrations (LC_{50} or EC_{50}, respectively) and No Observed Effect Concentrations (NOEC) for aquatic and terrestrial species were collected. The different test procedures were also documented to allow for the identification of non-standard procedures and support decisions concerning the inclusion of data in subsequent steps. There were cases where there was limited ecotoxicological information on pesticides or metabolites that could be potentially enriched with records from other databases or current literature. However, considering the low number of such cases and assuming the inherent pitfalls to the inclusion of such external information (e.g., use of non-standard test protocols or conditions or use of inadequate models to estimate benchmarks), we opted out of including this information in the current review. For sediments, the lack of available data was limiting. Among the pesticide residues found in the CSS sediments and considered for the classification protocol, toxicity records for benthic species (*Chironomus* sp.) were found in the PPDB database and EFSA dossiers for only 23 PPPs, and no information about other benthic species was available.

Ecotoxicological data was used to determine predicted no-effect concentrations (PNEC). Assessment factors (AF) were used to address uncertainties, but also to calibrate low tier effects. Based on the EFSA guidelines (EFSA, 2013), distinct endpoints and Assessment Factors (AF) were used according to the group of organisms considered. For earthworms and springtails, an AF of 5 or 10 was used for NOEC or LC/EC50 values, respectively. For bees, an AF of 50 was used for LC50. For beneficial insects, an AF of 2 was applied to tissue residue LR50. For crops, an AF of 5 or 1 was used for the effective rate ER50 or hazardous concentration HC50, respectively. For microbes, no AF was used since only one endpoint was considered. Ecotoxicological risk for each matrix is given in **SM6**.

Measured PPP concentrations in terrestrial and aquatic environments were compared with the calculated PNECs. The percentage of samples exceeding the PNEC were determined and listed according to the CSS and the farming system. PNEC values were calculated for the 20 most frequently detected substances per matrix and across all samples collected in the CSS.

2.4. *Risk assessment*

Once the compounds were selected according to their DF (concentration > LOD), the risk quotients (RQi) for the individual pesticides were calculated as the ratio between the measured concentration of a compound in the given matrix (MECmatrix) and the PNEC. The RQi is a measure used to determine the risk of a pesticide across different environmental matrices (soil, water, and sediment). The risk ratios were classified into four risk levels: negligible risk ($RQ < 0.01$), low risk ($0.01 < RQ < 0.1$), medium risk ($0.1 < RQ < 1$), and high risk ($RQ > 1$) (Sanchéz-Bayo et al., 2002). For crops, we used the MRL instead of the PNEC values. The MRL is a limit value above which consumer health is no longer safeguarded. For this purpose, we calculated the ratio of the pesticide residue level to its corresponding MRL, which we refer to as the relative pesticide residue level (RPRL). To assess acute and chronic risk to consumer health, dietary exposure to pesticide residues should be estimated and compared with health-based guidance values (EFSA et al., 2022b).

2.5. *Association between exposure and ecological health impacts*

Once the substances were ranked according to their risk, we selected only those substances with a moderate or high risk for the current assessment. This evaluation was based on data from the PPDB. The toxicological descriptors and the endpoints covered in the database are in line with those required by EFSA. The data is mostly verified data used for regulatory purposes, and the thresholds considered are consistent with EU regulatory thresholds (PPDB, 2023; Silva et al., 2023). Based on the PPDB (2023), two distinct types of classifications were assigned depending on the matrix considered: (i) qualitative class of hazard, based on thresholds applied to LC/EC_{50} and (ii) quantitative RQ values for the selected species, defined as low, moderate, or high. We compiled qualitative data concerning the health issues for the specific compartments as presented in the PPDB. For the environment, for example, we considered the effects on earthworms (acute and chronic), honeybees (acute and chronic), and other beneficial insects. Thus, the substances designated as high hazards pose potential health hazards.

3. Results

3.1. *Detection frequency analysis*

In the 529 samples, 104 substances (out of 192 analyzed) were detected in soil, 85 (out of 192 analyzed) were detected in crops, 115 (out of 193 analyzed) were detected in water, and 99 (out of 195 analyzed) were detected in sediment.

3.1.1. *The twenty most frequently detected substances in soil*

The number of pesticide residues exceeding the LOD was higher for soil samples from conventional fields than soil samples from organic fields (*SM6*). The number of fields where concentrations exceeded the LOD was consistently higher for conventional systems than for organic systems, except in the case of DDT p,p' with 23 and 28 fields, respectively. Table 1A lists the 20 most frequently detected pesticide residues in soil: 10 fungicides, 6 insecticides (of which 2 are metabolites), and 4 herbicides (of which 1 is a metabolite). Seven active substances that were detected have not been approved for use (DDE p,p', hexachlorobenzene, chlorpyrifos, DDT p,p', DDT o,p', DDD p,p', and epoxiconazole).

Taking into account the different substances detected in soils per country and crop (Fig. 1), conventional farms had higher residue

Table 1
The most frequently detected pesticide residues in A) soil, B) crop, C) water, and D) sediment, selected for the risk assessment; the table gives the number of fields where pesticide residues were detected.

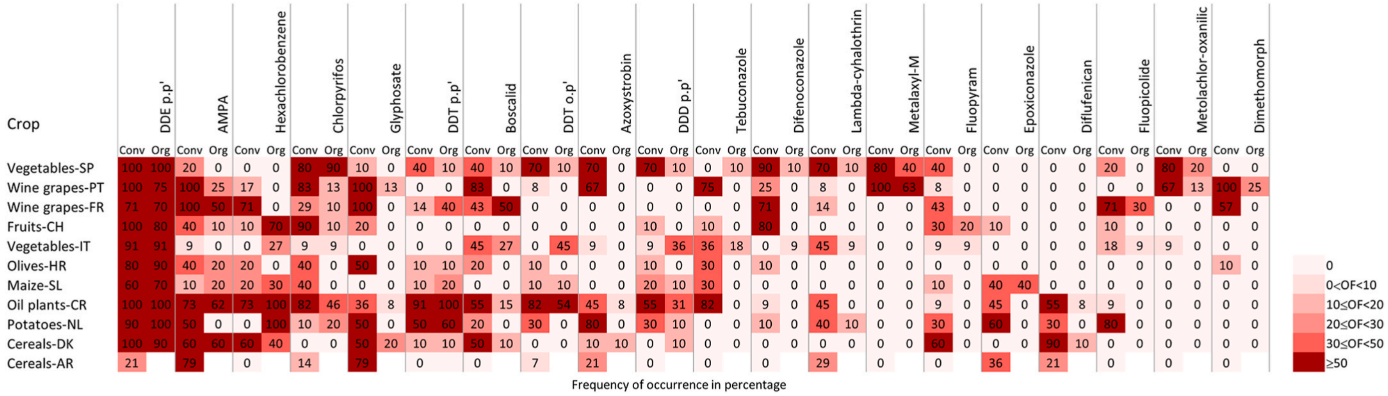
A)		Total (N)		Detected (%)		Type & status	
Substance		analyzed	detected	Conv.	Organic	Type	Status
A) Soil	DDE p,p’	215	183	44	41	Insecticide (M)	NA
	AMPA	215	87	28	12	Herbicide	App
	Hexachlorobenzene*	215	83	20	19	Fungicide	NA
	Chlorpyrifos*	215	71	23	10	Insecticide	NA
	Glyphosate	215	56	24	2	Herbicide	App
	DDT p,p’	215	51	11	13	insecticide	NA
	Boscalid	215	49	17	6	Fungicide	App
	DDT o,p’	215	37	11	7	Insecticide	NA
	Azoxystrobin	215	35	15	1	Fungicide	App
	DDD p,p’	215	33	10	6	Insecticide (M)	NA
	Tebuconazole	215	32	13	1	Fungicide	App
	Difenoconazole	215	30	13	1	Fungicide	App
	Lambda-cyhalothrin	215	30	13	1	Insecticide	App
	Metalaxyl-M	215	29	9	4	Fungicide	App
	Fluopyram	215	26	11	1	Fungicide	App
	Epoxiconazole	215	25	10	2	Fungicide	NA
	Diflufenican	215	23	10	1	Herbicide	App
	Fluopicolide	215	23	9	2	Fungicide	App
	Metolachlor oxanilic acid	215	20	8	1	Herbicide (M)	App
	Dimethomorph	215	19	8	1	Fungicide	App
B) Crop	Dimethomorph	212	18	7	2	Fungicide	App
	Metalaxyl-M	212	19	7	2	Fungicide	App
	Azoxystrobin	212	18	8	1	Fungicide	App
	Tebuconazole	212	16	7	0	Fungicide	App
	Deltamethrin	212	17	7	1	insecticide	App
	Dieldrin	212	29	6	8	insecticide	**NA**
	Difenoconazole	212	17	7	1	Fungicide	App
	Fluopyram	212	16	7	0	Fungicide	App
	Lambda-cyhalothrin	212	17	8	0	Insecticide	App
	Acetamiprid	212	15	7	0	Insecticide	App
	Fluopicolide	212	13	6	0	Fungicide	App
	Mandipropamid	212	12	6	0	Fungicide	App
	Boscalid	212	17	7	1	Fungicide	App
	Cypermethrin	212	13	4	2	Insecticide	App
	Chlorpyrifos	212	10	3	1	Insecticide	**NA**
	Permethrin	212	9	4	0	Insecticide	**NA**
	Zoxamid	212	9	4	0	Fungicide	App
	Bifenthrin	212	8	2	2	Insecticide	**NA**
	Cyprodinil	212	7	2	1	Fungicide	App
	Chlorpropham	212	7	1	2	Herbicide	**NA**
C) Water	Glyphosate	63		100	0	Herbicide	App
	Hexachlorobenzene	63		100	0	Fungicide	**NA**
	Lindane gamma HCH	63		100	0	Insecticide	**NA**
	Dieldrin	63		98	2	insecticide	**NA**
	DDE p,p’	63		95	5	Insecticide (M)	**NA**
	AMPA	63		81	19	Herbicide	App
	DDD p,p’	63		78	22	Insecticide (M)	**NA**
	DDT p,p’	63		78	22	insecticide	**NA**
	DDD o,p’	63		73	27	insecticide (M)	**NA**
	Terbuthylazine	64		72	28	Herbicide	App
	DDT o,p’	63		68	32	insecticide	**NA**
	DDE o,p’	63		63	37	insecticide (M)	**NA**
	Trifloxystrobin acid (M)	64		45	55	Fungicide (M)	App
	Tebuconazole	64		44	56	Fungicide	App
	Terbuthylazine desethyl	64		44	56	Herbicide (M)	App
	Atrazine	64		39	61	Herbicide	**NA**
	Piperonyl butoxide	64		39	61	Other	**NA**
	Terbutryn	64		38	63	Herbicide	**NA**
	Fluopyram	64		36	64	Fungicide	App
	Azoxystrobin	64		30	70	Fungicide	App
D) Sediment	AMPA	38		76	24	Herbicide	App
	Glyphosate	38		61	39	Herbicide	App
	Fludioxonil	38		34	66	Fungicide	App
	Azoxystrobin	38		32	68	Fungicide	App
	Fluopicolide	38		32	68	Fungicide	App
	Boscalid	38		29	71	Fungicide	App
	Fluopyram	38		24	76	Fungicide	App
	Metalaxyl.M.	38		16	84	Fungicide	App
	Spiroxamine	38		16	84	Fungicide	App
	Bixafen	38		13	87	Fungicide	App

(*continued on next page*)

Table 1 (*continued*)

Fenpropidin	38	13	87	Fungicide	App
Lambda Cyhalothrin	38	13	87	Insecticide	App
Pendimethalin	38	13	87	Herbicide	App
Chlorantraniliprole	38	11	89	Insecticide	App
Cypermethrin	38	11	89	Insecticide	App
Diflufenican	38	11	89	Herbicide	App
Fluxapyroxad	38	11	89	Fungicide	App
Imazalil	38	11	89	Fungicide	App
Metrafenone	38	11	89	Fungicide	App
Pencycuron	38	11	89	Fungicides	App

For water: Trifloxystrobin acid (M): Trifloxystrobin CGA 321113, metabolite; for crops, relative pesticide residue level (RPRL) was assessed for the substances listed; App, Approved; NA, not approved.



Crop	DDE p.p'		AMPA		Hexachlorobenzene		Chlorpyrifos		Glyphosate		DDT p.p'		Boscalid		DDT o.p'		Azoxystrobin		DDD p.p'		Tebuconazole		Difenoconazole		Lambda-cyhalothrin		Metalaxyl-M		Fluopyram		Epoxiconazole		Diflufenican		Fluopicolide		Metolachlor-oxanilic		Dimethomorph	
	Conv	Org	Conv	Org	Conv	Org	Conv	Org	Conv	Org	Conv	Org	Conv	Org	Conv	Org	Conv	Org	Conv	Org	Conv	Org	Conv	Org	Conv	Org	Conv	Org	Conv	Org	Conv	Org	Conv	Org	Conv	Org	Conv	Org	Conv	Org
Vegetables-SP	100	100	20	0	0	0	80	90	10	0	40	10	40	10	70	10	70	0	70	10	0	10	90	10	70	10	80	40	40	0	0	0	0	0	20	0	80	20	0	0
Wine grapes-PT	100	75	100	25	17	0	83	13	100	13	0	0	83	0	8	0	67	0	0	0	75	0	25	0	8	0	100	63	8	0	0	0	0	0	0	0	67	13	100	25
Wine grapes-FR	71	70	100	50	71	0	29	10	100	0	14	40	43	50	0	0	0	0	0	0	0	0	71	0	14	0	0	0	43	0	0	0	0	0	71	30	0	0	57	0
Fruits-CH	100	80	40	10	10	70	90	10	20	0	0	0	0	0	0	0	0	0	10	0	10	0	80	0	0	0	0	0	30	20	10	0	0	0	10	0	0	0	0	0
Vegetables-IT	91	91	9	0	0	27	9	9	0	0	0	0	45	27	0	45	9	0	9	36	36	18	0	9	45	9	0	0	9	9	0	0	0	0	18	9	9	0	0	0
Olives-HR	80	90	40	20	20	0	40	0	50	0	10	10	20	0	10	0	0	0	10	0	30	0	10	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	10	0
Maize-SL	60	70	10	20	20	30	40	0	0	0	10	20	0	0	10	10	0	0	20	10	30	0	0	0	0	0	0	0	10	0	40	40	0	0	0	0	0	0	0	0
Oil plants-CR	100	100	73	62	73	100	82	46	36	8	91	100	55	15	82	54	45	8	55	31	82	0	9	0	45	0	0	0	9	0	45	0	55	8	9	0	0	0	0	0
Potatoes-NL	90	100	50	0	0	100	10	20	50	0	50	60	20	0	30	0	80	0	30	10	0	0	10	0	40	10	0	0	30	0	60	0	30	0	80	0	0	0	0	0
Cereals-DK	100	90	60	60	60	40	0	0	50	20	10	10	50	10	0	0	10	10	0	10	0	0	0	0	0	0	0	0	60	0	0	0	90	10	0	0	0	0	0	0
Cereals-AR	21		79		0		14		79		0		0		7		21		0		0		0		29		0		0		36		21		0		0		0	

Fig. 1. Occurrence frequency of the 20 substances in soil per crop and farming system.

frequencies than organic farms for most substances, except for tebuconazole (0% for conventional vs. 10% for organic) and difenoconazole (9% vs. 0%) in the soil samples from Spain and Italy (vegetables); DDT p, p' (40% vs. 14%) and boscalid (50% vs. 43%) in soil from France (wine grapes); hexachlorobenzene (70% vs 10%), DDT o,p (40% vs. 14%), DDD p,p (36% vs. 9%), and difenoconazole (9% vs. 0%) in soil from Italy (vegetables); DDE p,p' (90% vs. 80%) in soil from Croatia (olives); DDE p,p' (70 % vs. 60%), AMPA (20 % vs. 10%), hexachlorobenzene (30 % vs. 20%), and DDT p,p' (20 % vs. 10%) in soil from Slovenia (olives); hexachlorobenzene (100% vs. 73%), and DDT p,p' (100% vs. 91%) in soil from the Czech Republic (oil plants); DDE p,p' (100% vs. 90%), chlorpyrifos (20% vs. 10%), DDT p,p (60% vs 50%) in soil from the Netherlands (potatoes); DDD p,p' (10% vs. 0%) in soil from Denmark (cereals), respectively. For the soil from Argentina, no data was available for organic farms. Fig. 1 shows the DF of substances in soil per crop and per case study site in conventional and organic farms (refer to **SM7**). It is worth mentioning that DDE p,p' (a banned insecticide) had the highest DF in European soils from both conventional (60%–100%) and organic farms (70%–100%) across all crops. The DF for this substance was similar in both farming systems (FS) for the vegetables from Spain and Italy and in oil plants from the Czech Republic. Similarly, AMPA was detected at a high frequency in conventional soil from all crops (9%–100%), followed by chlorpyrifos (banned insecticide) for 10 crops (9% – 83%), and glyphosate for 9 crops (10% – 100%).

Of the 11 fungicides detected, 8 were detected in soil from Portugal (wine grapes, 8% – 100%) and the Czech Republic (oil plants, 9% – 82%); 6 were detected in soil from Spain (vegetables, 20% – 90%), Switzerland (fruits, 10% – 80%), and the Netherlands (potatoes, 10% – 80%); 5 in soil from Italy (vegetables, 9% – 45%) and Croatia (olives, 10% – 30%); 4 in soil from Slovenia (maize, 10% – 40%) and Denmark (cereals, 10% – 60%); and finally, 2 in soil from Argentina (cereals, 21 and 36%). As for insecticides, 6 were detected in soil from Spain (vegetables, 40% – 100%), the Czech Republic (oil plants, 45% – 100%), and the Netherlands (potatoes, 10% – 90%); 5 in soil from Croatia (olives, 10% – 80%), and Slovenia (maize, 10% – 60%); and 4 in soil from Portugal (wine grapes, 8% – 100%), France (wine grapes, 14% – 71%), Italy (vegetables, 9% – 91%), and Argentina (cereals, 7% – 21%) (Fig. 1).

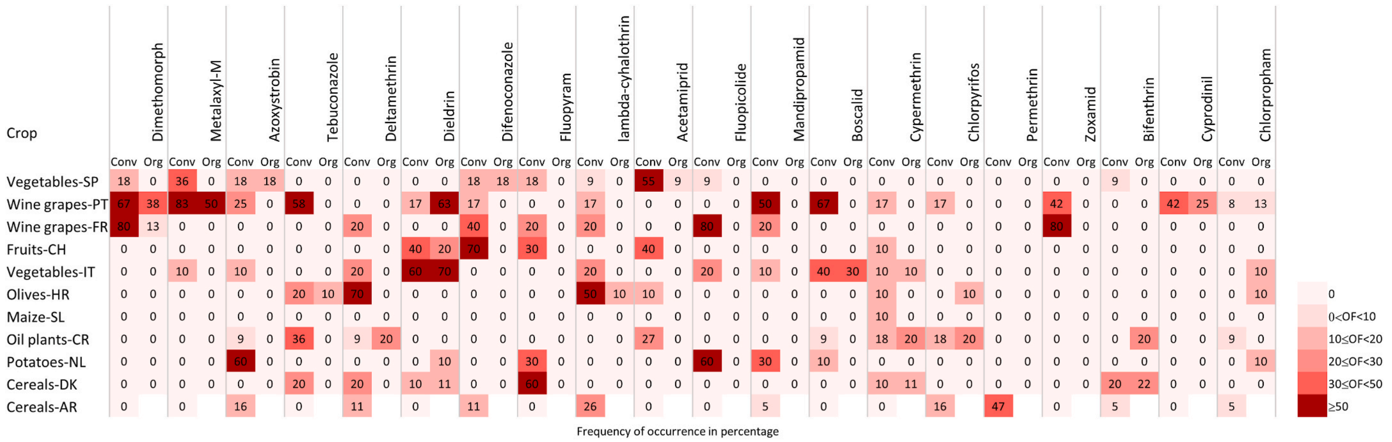
In comparison, the number of substances and their frequencies were lower for organic farms for the same crops and the same substances except in two cases: 6 substances exceeded a DF of 10% (5 in conventional and 6 in organic farms) for vegetables from Italy, and 9 substances exceeded a DF of 10% for cereals from both farming systems in Denmark. Similarly, the concentrations of the substances detected were higher in conventional fields than in organic fields (**SM8**).

3.1.2. *The twenty most frequently detected substances in crops*

The 20 substances most frequently detected in crops are listed in Table 1B. There were more detected substances found in conventional fields than in organic ones except for dieldrin, bifenthrin, and chlorpropham (refer to **SM9**). Similarly, the concentrations of the detected substances were higher in conventional fields than in organic fields (**SM10**). The ranked substances include 11 fungicides, 8 insecticides, and 1 herbicide. Five substances have not been approved for use in agriculture (Dieldrin, Chlorpyrifos, Permethrin, Bifenthrin, and Chlorpropham).

Ten out of 20 substances were found in both soil and crop matrices, eight were fungicides (dimethomorph, metalaxyl-M, azoxystrobin, tebuconazole, difenoconazole, fluopyram, fluopicolide, and boscalid), and 2 were insecticides (lambda-cyhalothrin and chlorpyrifos).

Fig. 2 shows the DF of substances per crop and per case study site in conventional and organic fields. With few exceptions, the frequency of detection of substances is higher in conventional crops than in organic crops. The frequency of detection of 6 substances in organic crops exceeds that of the conventional crops in four crop types for chlorpropham (wine grapes from Portugal, vegetables from Italy, olives from Croatia, and Potatoes from the Netherlands), and for dieldrin (wine grapes from Portugal, vegetables from Italy, Potatoes from the Netherlands, and cereals from Denmark), in 2 crops for cypermethrin (oil plants from Czech Republic, and cereals from Denmark), chlorpyrifos (oil plants



Crop	Dimethomorph Conv	Dimethomorph Org	Metalaxyl-M Conv	Metalaxyl-M Org	Azoxystrobin Conv	Azoxystrobin Org	Tebuconazole Conv	Tebuconazole Org	Deltamethrin Conv	Deltamethrin Org	Dieldrin Conv	Dieldrin Org	Difenoconazole Conv	Difenoconazole Org	Fluopyram Conv	Fluopyram Org	lambda-cyhalothrin Conv	lambda-cyhalothrin Org	Acetamiprid Conv	Acetamiprid Org	Fluopicolide Conv	Fluopicolide Org	Mandipropamid Conv	Mandipropamid Org	Boscalid Conv	Boscalid Org	Cypermethrin Conv	Cypermethrin Org	Chlorpyrifos Conv	Chlorpyrifos Org	Permethrin Conv	Permethrin Org	Zoxamid Conv	Zoxamid Org	Bifenthrin Conv	Bifenthrin Org	Cyprodinil Conv	Cyprodinil Org	Chlorpropham Conv	Chlorpropham Org
Vegetables-SP	18	0	36	0	18	18	0	0	0	0	0	0	18	18	18	0	9	0	55	9	9	0	0	0	0	0	0	0	0	0	0	0	0	0	9	0	0	0	0	0
Wine grapes-PT	67	38	83	50	25	0	58	0	0	0	17	63	17	0	0	0	17	0	0	0	0	0	50	0	67	0	17	0	17	0	0	0	42	0	0	0	42	25	8	13
Wine grapes-FR	80	13	0	0	0	0	0	0	20	0	0	0	40	0	20	0	20	0	0	0	80	0	20	0	0	0	0	0	0	0	0	0	80	0	0	0	0	0	0	0
Fruits-CH	0	0	0	0	0	0	0	0	0	0	40	20	70	0	30	0	0	0	40	0	0	0	0	0	0	0	10	0	0	0	0	0	0	0	0	0	0	0	0	0
Vegetables-IT	0	0	10	0	10	0	0	0	20	0	60	70	0	0	0	0	20	0	0	0	20	0	10	0	40	30	10	10	0	0	0	0	0	0	0	0	0	0	0	10
Olives-HR	0	0	0	0	0	0	20	10	70	0	0	0	0	0	0	0	50	10	10	0	0	0	0	0	0	0	10	0	0	10	0	0	0	0	0	0	0	0	0	10
Maize-SL	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	10	0	0	0	0	0	0	0	0	0	0	0	0	0
Oil plants-CR	0	0	0	0	9	0	36	0	9	20	0	0	0	0	0	0	0	0	27	0	0	0	0	0	9	0	18	20	18	20	0	0	0	0	0	20	0	0	9	0
Potatoes-NL	0	0	0	0	60	0	0	0	0	0	0	10	0	0	30	0	0	0	0	0	60	0	30	0	10	0	0	0	0	0	0	0	0	0	0	0	0	0	0	10
Cereals-DK	0	0	0	0	0	0	20	0	20	0	10	11	0	0	60	0	0	0	0	0	0	0	0	0	0	0	10	11	0	0	0	0	0	0	20	22	0	0	0	0
Cereals-AR	0		0		16		0		11		0		11		0		26		0		0		5		0		0		16		47		0		5		0		5	

0
0<OF<10
10≤OF<20
20≤OF<30
30≤OF<50
≥50

Frequency of occurrence in percentage

Fig. 2. Occurrence frequency of the 20 substances in crops from the case study sites per farming system; For cereals from Argentina, only conventional farms were investigated.

from Croatia and Czech Republic), and bifenthrin (oil plants from Czech, and cereals from Denmark); and in 1 crop for deltamethrin (oil plants from Czech) (**SM9**).

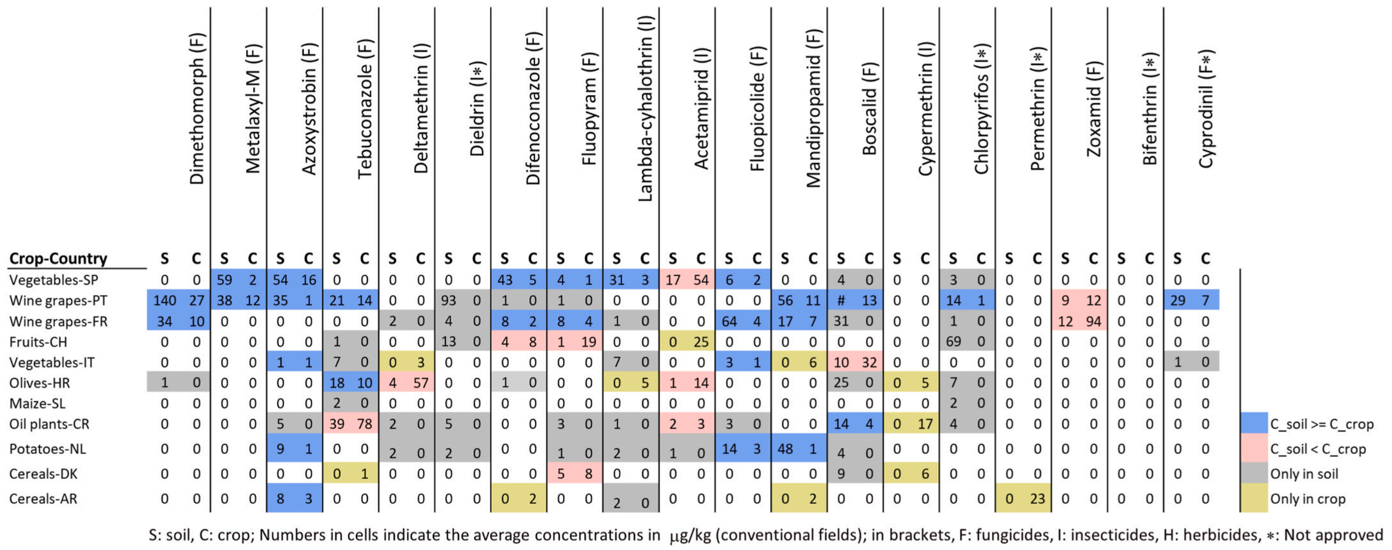
Of the 11 fungicides most frequently found in conventional crops, 11 were detected in wine grapes (Portugal and France) with a DF between 17 and 83%; 6 were detected in vegetables, with a DF between 9 and 40%; and 5 were detected in potatoes from the Netherlands with a DF between 10 and 60%. Of the 8 insecticides detected in crops, 5 were detected in wine grapes from Portugal and France with a frequency varying between 17 and 20%; 4 were detected in vegetables (9%≤ OF≤60%), olives from Croatia (10%≤OF≤70%), oil plants from the Czech Republic (9%≤OF≤27%), and cereals from Denmark and Argentina (10%≤OF≤47%). Herbicides were only detected in vineyards in Portugal (8%) and cereals from Argentina (5%).

To shed light on the link between the substances detected in crops and those detected in the soil from which the crops originate, we compared the DF and the average concentration (AC) of each substance in a crop with its occurrence frequency in the soil (Fig. 3).

For the substances detected in the crops, 31% were detected in the corresponding soil samples at a higher AC than what was detected in the crops. Fungicides made up 93% of these detected compounds and the remainder were insecticides. Only chlorpyrifos (a banned insecticide) was detected in wine grapes in Portugal. 13% of the substances detected in crops had a higher AC than those found in the corresponding soil, 56% of which were fungicides. 43% of the substances were detected only in the soil, 57% of which were insecticides. 13% of the substances were detected only in the crops, 64% of which were insecticides.

Portuguese soil (wine grapes) had the highest number of substances (12) with an AC varying between 1 and 162 μg/kg, most likely affecting the crop grown there (9 substances, 1 − 27 μg/kg). French soil (wine grapes) had 11 substances detected in soil (1 − 64 μg/kg) and 6 substances detected in crops (1 − 94 μg/kg, the highest AC was recorded for zoxamide). Spanish soil (vegetables) contained 9 substances (AC ranging from 3 to 59 μg/kg), 6 of which were detected in the crops (AC ranging from 1 to 57 μg/kg). The highest AC was recorded for boscalid in Portuguese soil (wine grapes) (162 μg/kg), followed by dimethomorph in the soil under the same crop (140 μg/kg). The total number of fields where the substances were detected in the crops per FS, is higher in conventional FS than in organic FS, except for dieldrin (**SM11**).

Regarding substances detected in the soil and not in the crop, the soil from the annual crops had a higher DF (22 times, or 59%) than that of the permanent crops (15 times, or 41%). For substances detected in the crop but not in the corresponding soil, the DF in the annual crops was higher (7 times or 70%) than in the permanent crops. In permanent crops, in 54% of cases, the concentration of the substances detected in the soil exceeded that detected in the crop, and conversely, in 55% of the



Crop-Country	Dimethomorph (F) S	Dimethomorph (F) C	Metalaxyl-M (F) S	Metalaxyl-M (F) C	Azoxystrobin (F) S	Azoxystrobin (F) C	Tebuconazole (F) S	Tebuconazole (F) C	Deltamethrin (I) S	Deltamethrin (I) C	Dieldrin (I*) S	Dieldrin (I*) C	Difenoconazole (F) S	Difenoconazole (F) C	Fluopyram (F) S	Fluopyram (F) C	Lambda-cyhalothrin (I) S	Lambda-cyhalothrin (I) C	Acetamiprid (I) S	Acetamiprid (I) C	Fluopicolide (F) S	Fluopicolide (F) C	Mandipropamid (F) S	Mandipropamid (F) C	Boscalid (F) S	Boscalid (F) C	Cypermethrin (I) S	Cypermethrin (I) C	Chlorpyrifos (I*) S	Chlorpyrifos (I*) C	Permethrin (I*) S	Permethrin (I*) C	Zoxamid (F) S	Zoxamid (F) C	Bifenthrin (I*) S	Bifenthrin (I*) C	Cyprodinil (F*) S	Cyprodinil (F*) C
Vegetables-SP	0	0	59	2	54	16	0	0	0	0	0	0	43	5	4	1	31	3	17	54	6	2	0	0	4	0	0	0	3	0	0	0	0	0	0	0	0	0
Wine grapes-PT	140	27	38	12	35	1	21	14	0	0	93	0	1	0	1	0	0	0	0	0	0	0	56	11	#	13	0	0	14	1	0	0	9	12	0	0	29	7
Wine grapes-FR	34	10	0	0	0	0	0	0	2	0	4	0	8	2	8	4	1	0	0	0	64	4	17	7	31	0	0	0	1	0	0	0	12	94	0	0	0	0
Fruits-CH	0	0	0	0	0	0	1	0	0	0	13	0	4	8	1	19	0	0	0	25	0	0	0	0	0	0	0	0	69	0	0	0	0	0	0	0	0	0
Vegetables-IT	0	0	0	0	1	1	7	0	0	3	0	0	0	0	0	0	7	0	0	0	3	1	0	6	10	32	0	0	0	0	0	0	0	0	0	0	1	0
Olives-HR	1	0	0	0	0	0	18	10	4	57	0	0	1	0	0	0	0	5	1	14	0	0	0	0	25	0	0	5	7	0	0	0	0	0	0	0	0	0
Maize-SL	0	0	0	0	0	0	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2	0	0	0	0	0	0	0	0	0
Oil plants-CR	0	0	0	0	5	0	39	78	2	0	5	0	0	0	3	0	1	0	2	3	3	0	0	0	14	4	0	17	4	0	0	0	0	0	0	0	0	0
Potatoes-NL	0	0	0	0	9	1	0	0	2	0	2	0	0	0	1	0	2	0	1	0	14	3	48	1	4	0	0	0	0	0	0	0	0	0	0	0	0	0
Cereals-DK	0	0	0	0	0	0	0	1	0	0	0	0	0	0	5	8	0	0	0	0	0	0	0	0	9	0	0	6	0	0	0	0	0	0	0	0	0	0
Cereals-AR	0	0	0	0	8	3	0	0	0	0	0	0	0	2	0	0	2	0	0	0	0	0	0	2	0	0	0	0	0	0	0	23	0	0	0	0	0	0

🟦 C_soil >= C_crop
🟥 C_soil < C_crop
⬜ Only in soil
🟨 Only in crop

S: soil, C: crop; Numbers in cells indicate the average concentrations in μg/kg (conventional fields); in brackets, F: fungicides, I: insecticides, H: herbicides, ∗: Not approved

Fig. 3. Comparison of the concentrations of the substances in soil and those in crops; list based on the top 20 most frequent substances detected in crops (refer to Table 1B).

cases, the concentration of the substances detected in crops exceeded that detected in the soil (data not shown).

3.1.3. The twenty most frequently detected substances in water

The 20 most frequent substances detected in water, including 8 insecticides (of which 4 are metabolites), 6 herbicides (1 metabolite), and 5 fungicides (1 metabolite) are listed in Table 1C. Twelve of the compounds have not been approved for use. Glyphosate, hexachlorobenzene, and lindane gamma had the highest DF (100%).

3.1.4. The twenty most frequently detected substances in sediment

In sediment, AMPA was detected with the highest frequency (76%), followed by glyphosate (61%). Interestingly, all substances detected in sediment were approved for use. Among the substances, there were 13 fungicides, 4 herbicides, and 3 insecticides (Table 1D). Only four approved substances were found in both water and sediment, two herbicides (AMPA and glyphosate) and two fungicides (azoxystrobin and fluopyram).

3.2. Risk assessment

3.2.1. Risk assessment in soil using the PNEC approach

To assess the relevance of the risk, we calculated the DF for each level of risk, i.e. how many times each level of risk was attained. For the conventional farms, the high-risk level was recorded for 5 out of the 20 most frequently detected substances: chlorpyrifos (41%), glyphosate (4%), boscalid (4%), difenoconazole (3%), lambda Cyhalothrin (17%) and one metabolite, AMPA (2%). For organic farm soils, chlorpyrifos (6%) was the only compound which was found to be a high risk (Fig. 4). Moderate risk was observed in conventional farms in 9 cases: AMPA (28%), chlorpyrifos (30%), glyphosate (27%), DDT pp (4%), boscalid (35%), azoxystrobin (14%), difenoconazole (63), lambda-cyhalothrin (53%), and epoxiconazole (48%). In organic farm soils, the frequency was lower or zero for these substances. However, for tebuconazole, the frequency was 3% for organic farms (0% for conventional farms).

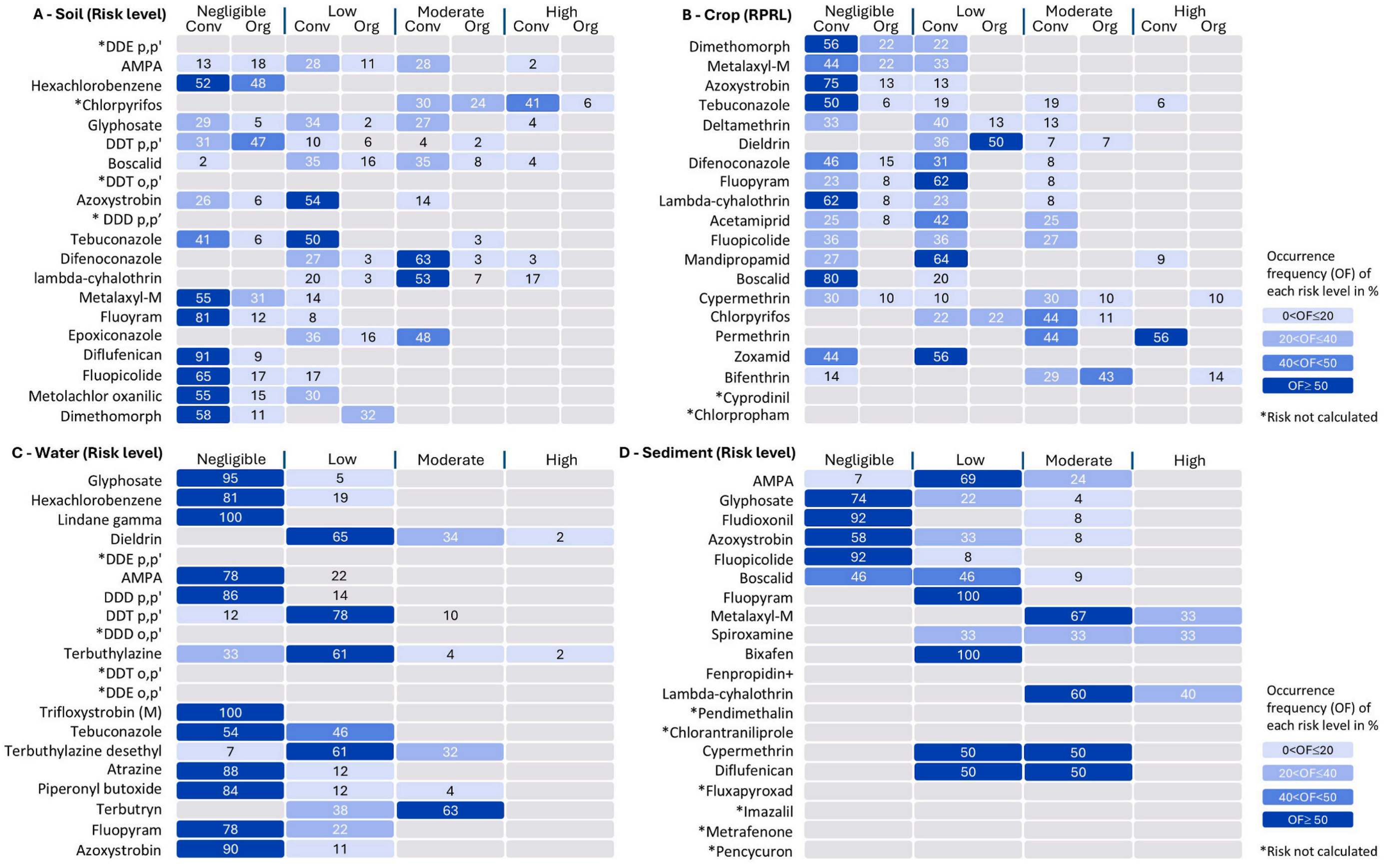
For the low and negligible risk levels, the corresponding frequencies were always higher for conventional farms than for organic farms except for DDT pp, which posed a negligible risk (47% in organic and 31% in conventional). It posed a low risk of 32% in organic soils and 0% in conventional soils (Fig. 4A).

3.2.2. Level of contamination of crops and the potential toxicological effects

For the crops from conventional farms, a high RPRL was recorded for 3 substances: tebuconazole with 6%, mandipropamid with 9%, and permethrin with 56%. Two residues had a high RPRL in crops from organic farms: cypermethrin with 10%, and bifenthrin with 14% (Fig. 4B). A moderate RPRL was observed for 12 substances in the conventional farms: Tebuconazole (19%), Deltamethrin (13%), Dieldrin (7%), Difenoconazole (8%), Fluopyram (8%), lambda-cyhalothrin (8%), Acetamiprid (25%), Fluopicolide (27%), Cypermethrin (30%), Chlorpyrifos (44%), Permethrin (44%), and Bifenthrin (29%), and for 4 substances in the organic farms: Dieldrin (7.1%), cypermethrin (10%), chlorpyrifos (11.1%), and bifenthrin (42.9%). For the low RPRL, the DF of the corresponding level was always higher in conventional farms than in organic farms except for dieldrin (36% in conventional farms and 50% in organic farms for low risk) and chlorpyrifos with the same frequency (22%). For the negligible level, the values for the frequencies were much higher in conventional farms than in organic farms.

3.2.3. Risk assessment in water

Fig. 4C shows that high risk only occurred for two substances: dieldrin (1.6%) and terbuthylazine (2.2%). Moderate risk occurred in 6



A - Soil (Risk level)	Negligible Conv	Negligible Org	Low Conv	Low Org	Moderate Conv	Moderate Org	High Conv	High Org
*DDE p,p'								
AMPA	13	18	28	11	28		2	
Hexachlorobenzene	52	48						
*Chlorpyrifos					30	24	41	6
Glyphosate	29	5	34	2	27		4	
DDT p,p'	31	47	10	6	4	2		
Boscalid	2		35	16	35	8	4	
*DDT o,p'								
Azoxystrobin	26	6	54		14			
* DDD p,p’								
Tebuconazole	41	6	50			3		
Difenoconazole			27	3	63	3	3	
lambda-cyhalothrin			20	3	53	7	17	
Metalaxyl-M	55	31	14					
Fluoyram	81	12	8					
Epoxiconazole			36	16	48			
Diflufenican	91	9						
Fluopicolide	65	17	17					
Metolachlor oxanilic	55	15	30					
Dimethomorph	58	11		32				

B - Crop (RPRL)	Negligible Conv	Negligible Org	Low Conv	Low Org	Moderate Conv	Moderate Org	High Conv	High Org
Dimethomorph	56	22	22					
Metalaxyl-M	44	22	33					
Azoxystrobin	75	13	13					
Tebuconazole	50	6	19		19		6	
Deltamethrin	33		40	13	13			
Dieldrin			36	50	7	7		
Difenoconazole	46	15	31		8			
Fluopyram	23	8	62		8			
Lambda-cyhalothrin	62	8	23		8			
Acetamiprid	25	8	42		25			
Fluopicolide	36		36		27			
Mandipropamid	27		64				9	
Boscalid	80		20					
Cypermethrin	30	10	10		30	10		10
Chlorpyrifos			22	22	44	11		
Permethrin					44		56	
Zoxamid	44		56					
Bifenthrin	14				29	43		14
*Cyprodinil								
*Chlorpropham								

Occurrence frequency (OF) of each risk level in %
0<OF≤20
20<OF≤40
40<OF<50
OF≥ 50
*Risk not calculated

C - Water (Risk level)	Negligible	Low	Moderate	High
Glyphosate	95	5		
Hexachlorobenzene	81	19		
Lindane gamma	100			
Dieldrin		65	34	2
*DDE p,p'				
AMPA	78	22		
DDD p,p'	86	14		
DDT p,p'	12	78	10	
*DDD o,p'				
Terbuthylazine	33	61	4	2
*DDT o,p'				
*DDE o,p'				
Trifloxystrobin (M)	100			
Tebuconazole	54	46		
Terbuthylazine desethyl	7	61	32	
Atrazine	88	12		
Piperonyl butoxide	84	12	4	
Terbutryn		38	63	
Fluopyram	78	22		
Azoxystrobin	90	11		

D - Sediment (Risk level)	Negligible	Low	Moderate	High
AMPA	7	69	24	
Glyphosate	74	22	4	
Fludioxonil	92		8	
Azoxystrobin	58	33	8	
Fluopicolide	92	8		
Boscalid	46	46	9	
Fluopyram		100		
Metalaxyl-M			67	33
Spiroxamine		33	33	33
Bixafen		100		
Fenpropidin+				
Lambda-cyhalothrin			60	40
*Pendimethalin				
*Chlorantraniliprole				
Cypermethrin		50	50	
Diflufenican		50	50	
*Fluxapyroxad				
*Imazalil				
*Metrafenone				
*Pencycuron				

Occurrence frequency (OF) of each risk level in %
0<OF≤20
20<OF≤40
40<OF<50
OF≥ 50
*Risk not calculated

Fig. 4. Risk assessment in (A) soil, B) crop, C) water, and D) sediment based on risk quotient RQ and its corresponding occurrence frequency (OC) in %; *No risk calculated; RPRL: Relative pesticide residue level.

cases and the highest DF was seen for terbutryn (62.5%) followed by dieldrin (33.9%), Terbuthylazine desethyl (32.1%), DDT pp (10.2%), terbuthylazine (4.3%), and finally piperonyl butoxide (4%). For the low risk, the highest frequency was recorded for DDT.p,p (77.6%), dieldrin (64.5%), and tebuconazole (46.4%). For the negligible risk, for the majority of the substances, the frequencies exceed 50%. There was no risk calculated for DDE.p.p, DDT.o.p., or DDE.o.p.

3.2.4. *Risk assessment in sediment*

For sediments, high risk was recorded for 3 substances: metalaxyl M. (33 %), spiroxamine (33%), and lambda cyhalothrin (40%) (Fig. 4D). For moderate risk, the highest frequency was recorded for metalaxyl M. (67%), followed by lambda cyhalothrin (60%), cypermethrin and diflufenican (50%), and spiroxamine (33%), as well as glyphosate, Fludioxonil, Azoxystrobin, and boscalid with a frequency varying between 4% and 9%. There was no risk calculated for pendimethalin, chlorantraniliprole, fluxapyroxad, imazalil, or metrafenone. Additional figures of the PNEC analysis of water based on the RQs obtained from measurements of the concentrations above LOD are given in **SM12**.

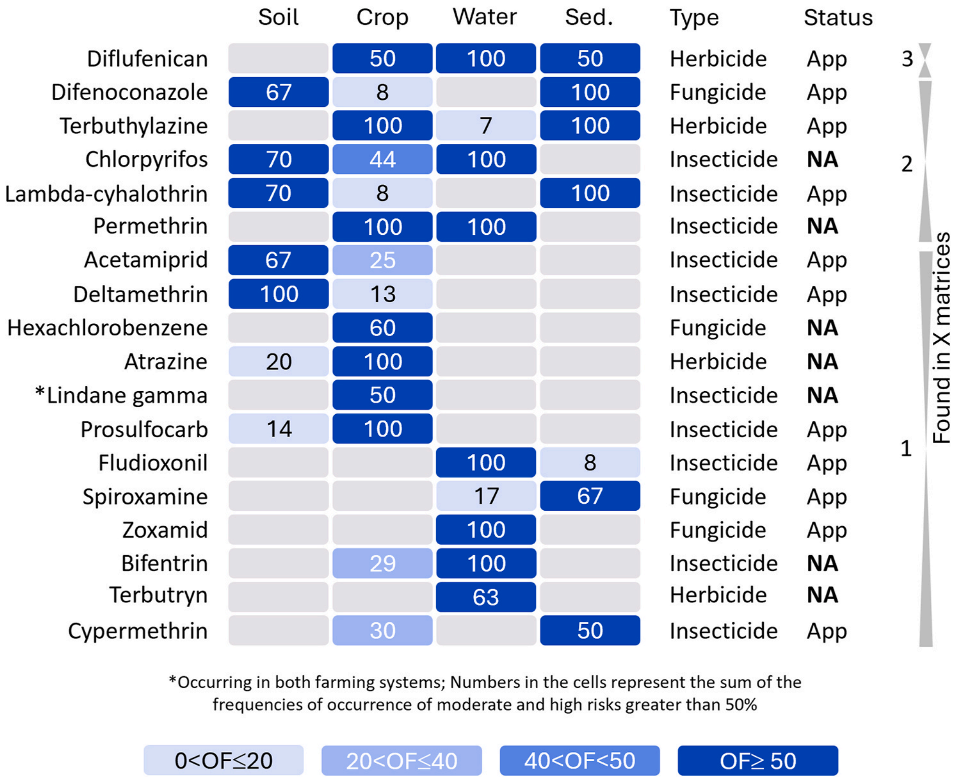
3.3. *Most frequently detected compounds in all matrices*

The substance most frequently detected in all matrices (soil, crop, water, and sediment) are ranked according to the number of matrices where they were found (first vertical column) and according to their different risk classes (negligible, low, medium, and high; horizontal cells) (**SM13). The** substances detected in all 4 matrices are: azoxystrobin, boscalid, difenoconazole, diflufenican, dimethomorph, fludioxonil, fluopicolide, fluopyram, glyphosate, mandipropamid, metalxyl-M, spiroxamine, tebuconazole, and terbuthylazine. The risks are variable and range from negligible to high. The substances detected in 3 matrices are: AMPA, chlorpyrifos, acetamiprid, DDT pp, dieldrin, hexachlorobenzene, lambda cyhalothrin, atrazine, lindane gamma, prosulfocarb, bixafen, and zoxamide. The ones detected in 2 matrices are: epoxiconazole, terbuthylazine desethyl, permethrin, deltamethrin, bifenthrin, cypermethrin, metolachlor S, and metolachlor oxanilic. Finally, the substances detected in 1 matrix are: DDD pp, trifloxystrobin, terbutryn, and piperonyl buroxide.

3.4. *Short list of compounds having moderate or high risk*

For the 38 substances with a moderate to high risk (sum of the frequencies of occurrence of moderate and high risks greater than 50%) most frequently detected across all matrices (**SM12**), 18 substances have been highlighted and discussed according to their health risk (Fig. 5) and their related hazard category and level **(SM14)**.

Only established hazards with a level high/yes have been considered. Among the 18 substances selected for their risk profile, 12 compounds with high hazard levels in multiple categories, for the environment and humans, are listed below. In water, diflufenican is hazardous for algae (acute and chronic). Chlorpyrifos is hazardous for earthworms (chronic) in soil, and in water and sediment, it is hazardous for fish (acute and chronic), aquatic invertebrates (acute and chronic), aquatic crustaceans (acute) and ground-dwelling organisms (acute and chronic). Permethrin is hazardous for fish and algae (acute and chronic) as well as aquatic invertebrates and aquatic crustaceans (acute). Acetamiprid is hazardous for earthworms (acute). Fludioxonil and zosamide have highly severe effects on aquatic invertebrates (chronic) and fish (chronic), respectively. Bifenthrin is hazardous for fish and aquatic invertebrates (acute and chronic) and for aquatic crustaceans (acute). Cypermethrin has a highly severe effect on ground-dwelling organisms (acute). Among the substances with a moderate hazard level on the environment, 16 out of the 18 affect earthworms (Difenoconazole, chlorpyrifos, lambda-cyhalothrin, acetamiprid, and deltamethrin), and aquatic organisms (diflufenican, chlorpyrifos, permethrin, fludioxonil, zoxamide, bifenthrin, and terbutryn). Five are hazardous for sediment-dwelling organisms (diflufenican, difenoconazole, terbuylazine, chlorpyrifos, and spiroxamine).



	Soil	Crop	Water	Sed.	Type	Status
Diflufenican		50	100	50	Herbicide	App
Difenoconazole	67	8		100	Fungicide	App
Terbuthylazine		100	7	100	Herbicide	App
Chlorpyrifos	70	44	100		Insecticide	**NA**
Lambda-cyhalothrin	70	8		100	Insecticide	App
Permethrin		100	100		Insecticide	**NA**
Acetamiprid	67	25			Insecticide	App
Deltamethrin	100	13			Insecticide	App
Hexachlorobenzene		60			Fungicide	**NA**
Atrazine	20	100			Herbicide	**NA**
*Lindane gamma		50			Insecticide	**NA**
Prosulfocarb	14	100			Insecticide	App
Fludioxonil			100	8	Insecticide	App
Spiroxamine			17	67	Fungicide	App
Zoxamid			100		Fungicide	App
Bifentrin		29	100		Insecticide	**NA**
Terbutryn			63		Herbicide	**NA**
Cypermethrin		30		50	Insecticide	App

*Occurring in both farming systems; Numbers in the cells represent the sum of the frequencies of occurrence of moderate and high risks greater than 50%

Fig. 5. List of substances with the sum of the frequencies of occurrence for moderate and high risks greater than 50%; this concerns only the conventional fields except in the case of lindane gamma; last column gives the number of matrices where the substances met the requirement.

Six compounds detected in crops are potentially hazardous to humans: diflufenican, permethrin, hexachlorobenzene, atrazine, lindane gamma, and prosulfocarb. Diflufenican is hazardous for humans because it is an endocrine disrupter and neurotoxicant. Permethrin has a high hazard level for humans when consumed in crops. It is a carcinogen, an endocrine disrupter, and a neurotoxicant and it also has detrimental effects on reproduction and development. Hexachlorobenzene has highly severe effects on humans as it is classified as a carcinogen, endocrine disrupter, and neurotoxicant. Atrazine and lindane gamma are both hazardous for humans and act as endocrine disrupters. Lindane gamma and Prosulfocarb are neurotoxicants.

4. Discussion

4.1. Occurrence of pesticide residues

Examination of the substances most frequently detected in the 4 matrices shows that of the 20 ranked substances, fungicides had much higher occurrence rates than insecticides and herbicides in soil, crops, and sediment. For water, insecticides had the highest occurrence among the 20 substances listed. This pattern has also been seen in European surface waters from rivers, streams, and channels (Moschet et al., 2014; Papadakis et al., 2015; Schreiner et al., 2016; Casado et al., 2019). Fungicides are mainly used in agricultural settings, accounting for about 35% of the global market share for pesticides. Europe is thought to be the leading market for fungicides, which are mostly used on vegetables, fruits (especially in viticulture), grains, and cereals (e.g., wheat) (Research and Markets, 2014).

Moreover, fungicides are low to moderately persistent in water (median 50% dissipation time (DT50): 5 days; also referred to as the half-life), and moderate to highly persistent in soil (median DT50: 54 days). The high DF of fungicides in soil as shown in this study can be explained by their intensive application on crops, especially on trees and vine branches which may drastically increase the drift distances with the higher nozzle height increasing the risk of transport to adjacent soil and aquatic systems (Lefrancq et al., 2013; Zubrod et al., 2019). When considering the cumulative frequency of product usage in our CSS, we recorded an annual average of 50 applications in apple crops, followed by pears, wine grapes and cherries. Potatoes required extensive fungicide and insecticide treatment, but PPPs in cereals, oilseed crops, and some vegetables were restricted to five applications. Fungicides were the most used in perennial crops (apple, pears, wine grapes, cherry, strawberries, plums and olives), and insecticides were mostly used for vegetable crops (pepper, potatoes, cabbage, radicchio), whereas herbicides were more commonly used in arable crops. The number of substances measured above the LOD was consistently higher in soil and crop samples from conventional fields compared with soil samples from organic fields. Similarly, for both matrices, high risk was recorded more frequently for substances in samples from conventional fields than for substances from organic fields.

Surprisingly, in water, there were 12 non-approved substances listed among the top, attesting to a long-term persistence, especially in sediments which may act as a sink and a secondary potential emission source for water (Subrod et al., 2019). Four common substances were found in both water and sediment of which two were found with high DF: AMPA (81% in water and 76% in sediment), and glyphosate (100% in water, and 61% in sediment) (Tables 1C-1D). There were 2 others that were found with lower DF: azoxystrobin (30% in water and 32% in sediment) and fluopyram (36% in water and 24% in sediment). The excessive use of glyphosate in agriculture may increase its concentration in water and sediment due to leaching, explaining the high DF of both glyphosate and AMPA. AMPA, the primary breakdown product of glyphosate, persists in sediments longer than glyphosate itself because AMPA is more resistant to degradation and has a higher sorption affinity to sediments. As a result, even after the parent glyphosate has broken down, AMPA can remain in sediments for a long time (Grunewald et al., 2001). Pesticides may be harmful to toxic to non-target organisms such as bees, birds, fish, and beneficial insects (Mengoni Goñalons and Farina, 2018; Milan et al., 2018). Long-term exposure to these pesticides can disrupt ecosystems, leading to declines in biodiversity, impacting pollination and disrupting natural pest control mechanisms. Therefore, understanding the dynamics and impacts of pesticides in water and sediment is essential to protecting and conserving aquatic ecosystems as well as developing strategies for prevention and remediation.

4.2. Widespread contamination and its consequences

There were 10 substances from the list of 20 that were detected in both soils and crops simultaneously. Eight of the compounds were approved fungicides (dimethomorph, metalaxyl-M, azoxystrobin, tebuconazole, difenoconazole, fluopyram, fluopicolide, and boscalid) and 2 were insecticides, one approved (Lambda-cyhalothrin), and one banned (chlorpyrifos). 31% of the substances were found in higher concentrations in the soils than in the crops, 93% of which were fungicides. The bioavailability of these substances, illustrated by their high concentrations, could be a result of their differing adsorption onto soil particles and the movement of bioavailable fractions into plant roots. Although this association was not supported by information on long-term monitoring and pesticide applications, a link between soils and crops has been reported in other studies (Wang et al., 2021), and others have addressed the risk these crops may pose to humans if their uptake exceeds the threshold values (EFSA et al., 2022a). Wang et al. (2021) showed that all tested pesticides found in soil (imidacloprid, acetamiprid, tricyclazole, azoxystrobin, tebuconazole, and difenoconazole) were taken up by maize after 14 days, respectively. The authors showed that the pesticide accumulation in maize was negatively correlated with the adsorption coefficient. Organic compounds in soil are usually considered to be bioavailable (Van der Wal et al., 2004; Wu and Zhu, 2016). It is worth noting that in certain cases, the number of substances detected in organic crops exceeded the number detected in conventional crops; if we simply look at the 20 compounds most commonly detected in crops, we can see that bifenthrin, chlorpropham, and dieldrin are among them (Fig. 2; **SM9**). Therefore, investigations looking into the land management history of the soils in question are a prerequisite for the adoption of sustainable agricultural management practices to ensure that crops are free of pesticide residues, including those that were banned a long time ago (e.g. chlorpyrifos, and cyprodinil found in both soil and wine grapes from Portugal).

However, only 4 of the 20 substances were detected simultaneously in water and sediment (glyphosate, AMPA, fluopyram, and azoxystrobin), indicating a non-obvious association between the two matrices at least among the top 20. This can be explained by the fact that concentrations of pesticides can differ significantly between seasons in water and space in sediments (Cui et al., 2020). Using the fugacity fraction to assess the exchange behavior of pesticides between the sediment and water for some pesticides, Cui et al. (2020) reported that the sediments may act as a sink and a potential secondary emission source for chlortoluron, isoproturon, and atrazine, while for metaldehyde, the role of sediments as a sink was less relevant. These findings showed the need to assess concurrent seasonal monitoring of pesticides in various matrices including soil, water, sediment, and crops to shed light on the environmental behavior, transport, and fate of these compounds. These processes could affect management practices and mitigate deleterious human and animal exposures (Stehle and Schulz, 2015; Zhang et al., 2016).

From the 20 substances which had moderate to high RQs in different matrices (listed in Fig. 5), 7 have not been approved for use in agriculture and 5 are used for industrial purposes: chlorpyrifos, permethrin, hexachlorobenzene, bifenthrin, and terbutryn. Lindane is used for veterinary drugs, while atrazine is used for both veterinary drugs and industrial purposes. Based on this conservative approach, among the ranked substances, 6 detected in crops may have potential adverse effects on humans: diflufenican, permethrin, hexachlorobenzene, atrazine, prosulfocarb, and zoxamide. There were 2 substances detected in soil that have highly severe effects on earthworms: chlorpyrifos and acetamiprid. Six compounds detected in water are hazardous for aquatic organisms: diflufenican (algae), chlorpyrifos and permethrin (fish, aquatic invertebrates and crustaceans), fludioxonil (aquatic invertebrates), zoxamid (fish), and bifenthrin (aquatic invertebrates and crustaceans). Lastly, 2 substances detected in sediments, chlorpyrifos and cypermethrin, are hazardous for ground-dwelling insects.

Along with the non-approved substances with dual use, many active substances have been banned due to knowledge gained a posteriori concerning their high persistence and/or toxicity to non-target species (EASAC, 2023; OJL, 2023). These substances are widespread and present in all environmental matrices. Their long-term persistence in various ecosystem matrices and the use of mixtures of compounds increase pest resistance, endanger numerous environmental functions globally, and have an impact on food safety (Beketov et al., 2013; Stehle and Schulz, 2015). The effect of cocktails of multiple active compounds has not yet been assessed (Silva et al., 2023).

4.3. *Strength and limitations*

Several studies have focused on the processes controlling the fate and transport of pesticides including runoff and leaching as well as dry and wet deposition from atmospheric transport (Zhong et al., 2014; Carratala et al., 2017). Many initiatives for managing pesticides and monitoring water quality have been established by the EU such as the Integrated Pest Management program (IPM) and the Water Framework Directive (WFD) (EU, 2000; Hillocks, 2012). The European Commission defined two pesticide reduction targets set as part of its Farm to Fork strategy: a 50% reduction in chemical pesticide use and risk by 2030, as well as a 50% reduction in the use of more hazardous pesticides by 2030, compared to the baseline period of 2015–2017 (EC, 2000). Although the EU has a pre-market entry risk assessment process for pesticides, pesticide-related benchmarks and post-market monitoring programs are limited to drinking water and food (e.g., EFSA, 2013; Efsa et al., 2022; EU, 2008). Under EU Regulation 1107/2009, which governs the authorisation process for pesticides, several active substances have been banned in the EU over the last decade. However, the current way of developing and registering active ingredients has shown its limitations, banning active ingredients and the development of new active ingredients lead to the emergence of side effects such as resistance or environmental damage (Carvalho, 2017; Gensch et al., 2024; Siviter and Muth, 2020). This study has shown that banned substances are still present at high frequencies and concentrations, and together with authorised substances they form mixtures with yet unknown risks. The substances ranked in this study will make it possible to identify the mixtures of greatest interest for risk assessment and provide an opportunity for policymakers to update existing legislation.

This study examines prominent crops in both conventional and organic agricultural systems in various climate zones throughout Europe. Standard operating procedures were developed to standardize sample collecting, storage, and shipment techniques. The whole study protocol was published before the start of the fieldwork (Alaoui et al., 2021; Silva et al., 2021). The project aimed to analyze many pesticide residues in a wide range of matrices using standardized methods for treatment and analysis by experienced and reference laboratories (Alaoui et al., 2021; Alaoui et al., 2024). Our analysis is quantitative because it is based on a comparison between measured concentrations and the established PNEC for each substance based on RQ. It allowed us to identify the most harmful substances to the ecosystem and human health.

We used a conservative approach to examine the link between risk and hazard by considering only moderate to high risks on the one hand, and only established hazards with a high hazard level on the other (Fig. 5). In this study, we have shown that humans are mainly exposed to substances in the environment, including dual-use substances, as evidenced by the presence of a set of common pesticide residues across all matrices suggesting exposure to mixtures of multiple pesticides. Further studies are necessary to draw any conclusions concerning the background noise from these compounds. Despite these many advantages, the large-scale and multi-matrix nature of our study imposed several constraints.

First, the unique sampling season reflects only a snapshot, and the picture retrieved may not reflect the history of the cropping system throughout the year. Since the sampling was done after pesticide application, any interaction with the environment, leading to their high mobility and/or persistence, has not been considered and does not reflect the whole story of their application, especially in water. Pesticides detected in soil, sediment, and to a certain extent crops, may reflect the land management history. Secondly, crops differ from site to site and the comparisons of the farming systems was based on the DFs and the MCs in different matrices without considering differences in the crops or the doses applied. However, the occurrence of products in different matrices is more closely linked to the pesticides used during the entire crop rotation, which better reflects the agricultural practices of the FS than those practices used for a single crop. In addition to data heterogeneity, it was not always possible to compare different matrices in terms of DFs and concentrations because not all substances were tested in all matrices. Some matrices, such as water bodies and sediments, are often not directly linked to the fields under consideration, nor to a FS. Third, the estimates were based on average values for each matrix. This was done to avoid biases from individual values as a result of the above limitations. Finally, the hazard information should be regarded as indicative because it was based on (i) detection (>LOD) rather than levels, and on (ii) a conservative approach (hazard was considered when it was reported in the literature) (Silva et al., 2023).

This study provides a useful basis for selecting the pesticide residues to be considered in the investigation of mixtures, as it highlights the most frequently detected substances across all matrices. Apart from this list, additional substances, detected with lower frequencies, could combine to form a mixture of unknown toxicity. Further investigations are still needed to examine the health effects of these mixtures.

5. Conclusions

In this study, we showed that most of the pesticide residues detected in soils, crops, water, and sediment, including banned substances that are still in use for a variety of purposes, have been identified as potentially hazardous to ecosystems and humans. Our study shows that soils are highly polluted and seem to in turn contaminate the crops grown in them. Sediment, among others, can act as a sink and a potential secondary emission source for surface water highlighted by the occurrence of substances banned from use in surface water. More studies are needed to investigate the route of exposure and the interactions of sediments-rivers-groundwater, which are critical for improving the accuracy of the risk assessment of pesticides. Given the extent of pollution generated by all these substances, our findings indicate the need for selecting uncontaminated soil when adopting sustainable agricultural practices. This widespread contamination is evidenced by the presence of a set of common pesticide residues across all matrices suggesting exposure to mixtures of multiple pesticides. The toxic effect of such exposure is unknown, especially over a longer period. Understanding all relevant exposure pathways and related sources of contamination in the environment has the potential to mold management practices to mitigate deleterious human and animal exposures.

CRediT authorship contribution statement

Abdallah Alaoui: Writing – review & editing, Writing – original draft, Project administration, Formal analysis, Data curation, Conceptualization. **Florian Christ:** Writing – review & editing, Investigation,

Data curation. **Nelson Abrantes:** Writing – review & editing, Methodology, Investigation. **Vera Silva:** Writing – review & editing, Project administration, Funding acquisition, Conceptualization. **Neus González:** Writing – review & editing, Investigation. **Lingtong Gai:** Writing – review & editing, Formal analysis, Data curation, Conceptualization. **Paula Harkes:** Writing – review & editing, Investigation, Data curation, Conceptualization. **Irene Navarro:** Writing – review & editing, Investigation. **Adrián de la Torre:** Writing – review & editing, Investigation. **María Ángeles Martínez:** Writing – review & editing, Investigation. **Trine Norgaard:** Writing – review & editing, Investigation. **Anne Vested:** Writing – review & editing, Investigation. **Vivi Schlünssen:** Writing – review & editing, Project administration. **Virginia Carolina Aparicio:** Writing – review & editing, Investigation. **Isabel Campos:** Writing – review & editing, Investigation. **Igor Pasković:** Writing – review & editing, Investigation. **Marija Polić Pasković:** Writing – review & editing, Investigation. **Matjaž Glavan:** Writing – review & editing, Investigation. **Coen Ritsema:** Writing – review & editing, Funding acquisition, Conceptualization. **Violette Geissen:** Writing – review & editing, Writing – original draft, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

The SPRINT project (on Sustainable Plant Protection Transition, https://sprint-h2020.eu/) leading to this publication has received funding from the European Union's Horizon 2020 Programme for research & innovation under grant agreement n∘ 862568. We would like to thank the CESAM (UIDB/50017/2020+UIDP/50017/2020+LA/P/0094/2020) for its financial support".

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2024.125056.

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