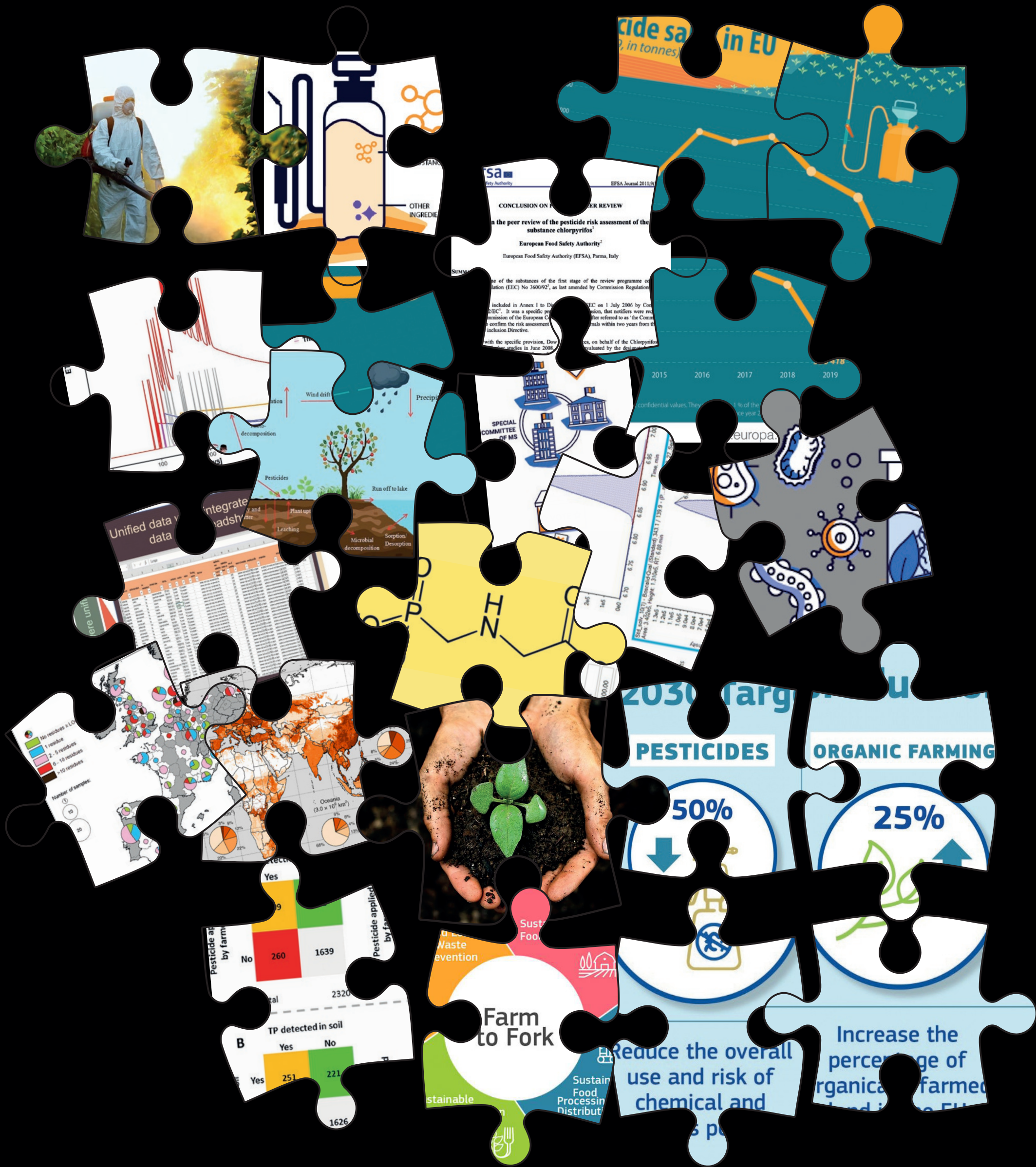
Pesticide residues in EU soils and related risks



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Pesticide residues in EU soils and related risks

Vera Alexandra Félix da Graça Silva

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Chapter 1

General introduction

1.1 The good, the bad, and the ugly part of pesticides

A pesticide is any substance of chemical or biological nature used to prevent, control or kill pests. The term pesticide is rather broad covering 455 approved active substances in Europe (DGSanté, 2019), and 600 worldwide (McDougall, 2018). These substances are very diverse being often classified based on their function, chemical composition, mode of entry, mode of action, hazard, formulation, or source of origin (Akashe et al., 2018). Around 90% of pesticide sales are linked to the agriculture sector (Antier et al., 2020). The pesticides used in agriculture, also known as Plant Protection Products (PPP), are applied to soil to prevent or combat plants that compete for resources with the crops, and/or to crops to combat organisms that damage the crops and agricultural commodities. Between 26-40% of the world's potential crop production is lost due to pests every year; without pesticides, the losses could double (OECD/FAO, 2012). The yield gain by pesticides depends on the crop, management, and environmental factors but can be highly significant: gain of 26% for wheat, 34% for soybeans, 35% for potatoes, 37% for maize, 40% for rice, and 53% for cotton (Oerke, 2006). Besides the farm productivity boost, pesticides have been linked to several other benefits, including long-term and less intuitive ones. Emphasis goes on their contribution to food security and the economy (Cooper and Dobson, 2007; Damalas, 2009).

Pesticides have been used since early times but gained particular relevance in the agricultural sector after the 1940s with the discovery of the insecticide effects of DDT and other organochlorinated compounds. Pesticide sales increased 20-30 fold between the 1960s and the 1990s with the Green Revolution (Carvalho, 2017; Oerke, 2006), and stabilized after that in most developed countries. In most developing countries pesticide sales are still increasing (FAOSTAT, 2021). Currently, global pesticide use exceeds 4 million tonnes per year, with an average of 2.63 kg of pesticides being used per cropland ha (FAO, 2020). Despite their widespread use, pesticide input varies greatly across regions and farming systems. This is due to differences in pest pressure, economic, technological, and regulatory/legislative factors (Delcour et al., 2015; Sharma et al., 2019; Watts, 2019). As pesticide sales increased, so did the concerns about their use and the awareness of their negative effects. The biologist Rachel Carson did one of the first warnings on pesticide side-effects in the landmark book Silent Spring (Carson, 1962). Nowadays countless studies address the environmental and health risks of pesticides (Ali et al., 2021;

Buckwell et al., 2020; Geiger et al., 2010; IPBES, 2016; Maggi et al., 2021), the hidden and external costs of pesticides (Bourguet and Guillemaud, 2016), and the pesticide agenda is getting more public and media attention (e.g., The European Citizens' Initiative on glyphosate's ban after confusing news on its carcinogenicity[1]).

The root of the "pesticides problem" lies in two interlinked facts: one, a substantial part of applied pesticides is released into the environment during or after application [(Carvalho, 2017); *Fig. 1.1*)] and two, several pesticides are toxic to non-target-species (Colin et al., 2019; Francisco, 2011; Ullah et al., 2018), persistent in the environment (Masiá et al., 2013; Silva et al., 2019), and/or accumulate through food chains (Goutner et al., 2012; Wang et al., 2011). Pesticide negative effects can be reduced with precision agriculture, facilitated access to low-risk and more specific pesticides, and more regulated pest management (ECA, 2020; Lamichhane et al., 2016). The use of pesticides is justified by the fact that current agricultural yields cannot be maintained without pesticides (de Ponti et al., 2012; Nishimoto, 2019; Seufert et al., 2012). Securing high yields is more important than ever given the projected increases in the human population (United Nations, 2019), the more caloric diets, the increase in degradation and depletion of arable lands, and the predicted climate change impact on agriculture (Jung et al., 2019; Lykogianni et al., 2021). Integrated pest management (IPM) and organic farming, with respectively reduced and no synthetic pesticides input, are felt to be adequate strategies for achieving sustainable food production (Eyhorn et al., 2019). IPM is compulsory in the EU since 2014 (EC, 2009a), and organic production is highly encouraged, and expected to represent at least 25% of the EU's agricultural land by 2030 (EC, 2020c). Nevertheless, even IPM and organically managed areas can be affected by pesticides, due to current and/or past use of pesticides, and off-site contamination (Fagan et al., 2020; Geissen et al., 2021; Riedo et al., 2021). More discussion and insights on this pesticide paradox (benefits vs negative effects) are therefore urgently needed to transition to a safer, more sustainable, and resilient food system (Gladek et al., 2017).

[1] https://www.euractiv.com/section/agriculture-food/news/more-than-1-3-million-demand-eu-glyphosate-ban/

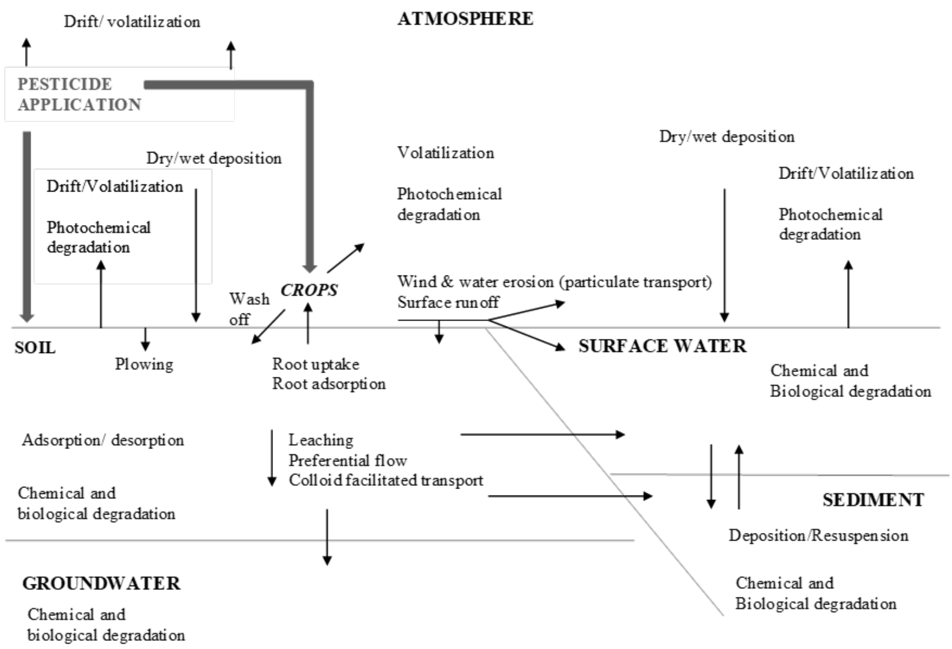


Figure 1.1 – Main pathways and degradation processes of pesticides in the environment.

1.2 The EU pesticides regulatory system

Pre-approval/registration

The high frequency of reports, high diversity, and severity of negative effects of some pesticides raise serious concerns about the protection level of current pesticide regulatory systems. In Europe, pesticides and their residues are governed by the PPP Regulation 1107/2009 (EC, 2009b) and the Maximum Residue Level Regulation 396/2005 (EC, 2005). These regulations aim at high protection of the environment, animal, and human health while safeguarding the competitiveness of EU agriculture. Getting a pesticide in the EU market is a complex and long process that involves multiple actors (see *Fig 1.2* for an overview). The process starts with a pesticide manufacturer applying for the approval of an active substance to an EU country - Rapporteur Member State (RMS). The manufacturer/applicant carries out and informs on the pre-registration assessment studies, which will be the main basis of the RMS report. The RMS report represents the initial risk assessment of the substance and covers information on i) its identity, physical and chemical properties, ii) use details, iii) toxicology and metabolism in "humans" (these studies are typically done in the lab with animals used as a proxy for humans), iv) metabolism and residues in plants and livestock, v) risk for consumers, vi) fate and behavior in the environment, and vii) effects on non-target species. For details on the information in the RMS report, its generation, and its presentation see EU (2013b; 2013c). EFSA (European Food Safety Authority), which guides risk assessment methodologies, performs a peer review of the report and writes a conclusion to the European Commission. The European Commission then drafts an acceptance/rejection proposal, and a special Member States Regulatory Committee votes on it. This process involves weighing policy alternatives, risk assessment, and other legitimate factors (EC, 2022). Based on the Committee voting, the European Commission decides on the approval of the active substance and sets its MRLs. Member States evaluate and decide on PPPs containing EU-approved substances (EU, 2013b; EU, 2013c). PPPs are evaluated on a zonal basis (i.e. North, Central, and South Europe), and once approval is granted, it is common to go for mutual recognition and get authorization for other countries with comparable agricultural conditions.

<u>Post-approval/registration</u>

Approved substances are re-evaluated by the EC after a maximum of 10 or 15 years (for new or already existing active substances, respectively), using the pre-approval procedure. Restrictions to substances may occur before that if enough evidence justifies it (EU, 2013a). The Member States are responsible for preparing national action plans on the correct use of PPP, in line with the Sustainable Use of Pesticides Directive (EC, 2009a) and other relevant legislation (see *Table 1.1* for an overview), and for the verification of their enforcement. These should cover monitoring activities, training programs on the safe use of pesticides, licensing of pesticide handlers, and control measures. Various monitoring activities are recommended for proper evaluation of policy implementation and PPP real risks: quality of PPPs, PPP use in accordance to approved label, pesticide residues in food, environmental and biological matrices, and accidental poisoning cases (FAO, 1988). Most post-approval surveillance data is however linked to residues testing in food (Zeitlin et al., 2021). Verification of real risk and reporting of new effects has relied mostly on scientific research.

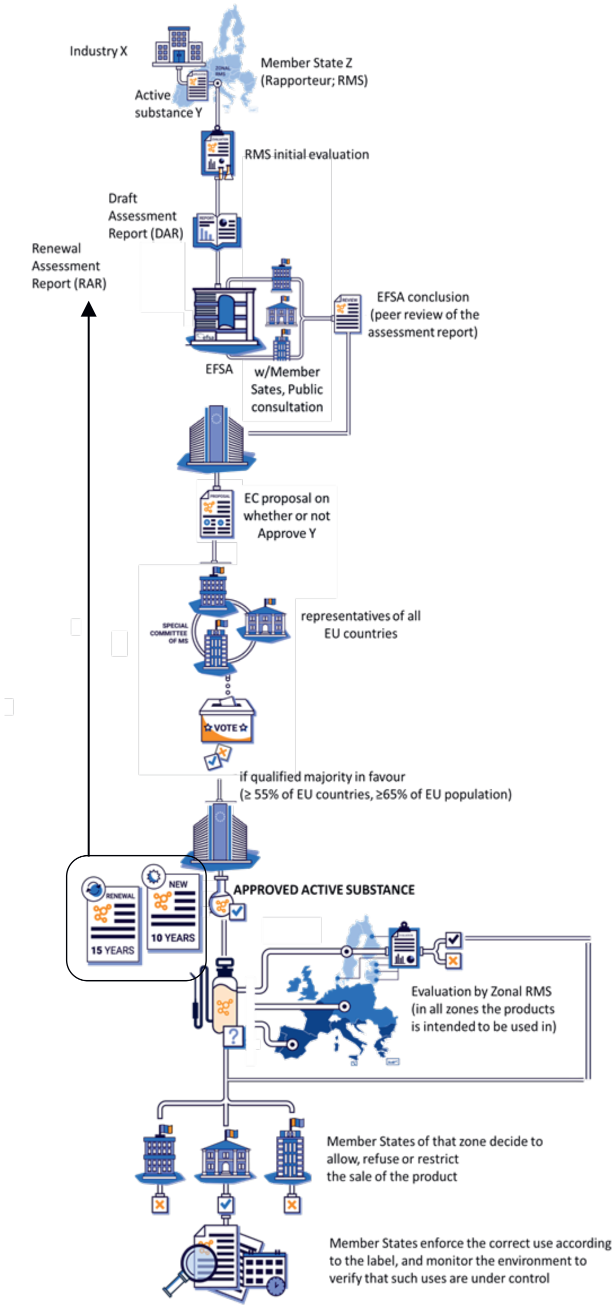


Figure 1.2 - Overview of the pesticides approval and authorization process in the EU. Adapted from: https://ec.europa.eu/assets/sante/food/plants/pesticides/lop/index.html

Table 1.1 - Main pesticide-related conventions, codes, and legal instruments.

International conventions	
Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposals (adopted in 1989)	Purpose: reduce hazardous waste generation and the promotion of environmentally sound management of hazardous wastes; restrict transboundary movements of hazardous wastes.
Rotterdam Convention on Prior Informed Consent Procedure for Certain Hazardous Chemicals and Pesticides in International Trade (adopted in 1998)	Purpose: promote shared responsibility and cooperative efforts in the international trade of certain hazardous chemicals; facilitate information exchange about characteristics of such chemicals, for the decision-making process on import and export decisions.
Stockholm Convention on Persistent Organic Pollutants (adopted in 2001)	Purpose: restrict or eliminate the production and use of persistent organic pollutants (POPs); stockpiles and wastes consisting of or contaminated by POPs are managed in an environmentally sound manner
International agreements	
International Code of Conduct on the Distribution and Use of Pesticides (adopted in 1985)	Purpose: guidance on pesticide management for public and private entities linked with the distribution and use of pesticides.
Intergovernmental Forum on Chemical Safety (established in 1994)	Purpose: promotion of chemical risk assessment and the environmentally sound management of chemicals.
International Code of Conduct on Pesticide Management (adopted in 2013)	Purpose: regulate and control the quality and suitability of pesticide products; ensure that pesticides are used effectively and efficiently in a sustainable manner to minimize adverse effects on human health and the environment while contributing to the sustainable improvement of agriculture.
Codex Maximum Residue Limits (adopted in 2017)	Purpose: establish internationally agreed food standards covering pesticide residues in or on food and feed.
EU legal frameworks	
Registration, Evaluation, Authorisation, and Restriction of Chemicals (REACH regulation) (adopted in 2007)	Purpose: regulate the registration, evaluation, and authorization of dangerous substances and the restrictions applicable to them.
Regulation (EC) No 1107/2009 of the European Parliament and of the Council of 21 October 2009 concerning the placing of plant protection products on the market. (consolidated version: 27/03/2021)	Purpose: ensure a high level of protection of both human and animal health and the environment and at the same time safeguard the competitiveness of Community agriculture.
Regulation (EC) No 396/2005 of the European Parliament and of the Council of 23 February 2005 on maximum residue levels of pesticides in or on food and feed of plant and animal origin. (consolidated version: 10/10/2021)	Purpose: ensure a high level of consumer protection and harmonized Community provisions relating to maximum levels of pesticide residues in or on food and feed of plant and animal origin.

Table 1.1 (cont.) - Main pesticide-related conventions, codes, and legal instruments.

Directive 2009/128/EC of the European Parliament and of the Council of 21 October 2009 establishing a framework for Community action to achieve the sustainable use of pesticides. (consolidated version: 26/07/2019)	Purpose: reduce the risks and impacts of pesticide use on human health and the environment and promote the use of Integrated Pest Management (IPM) and alternative approaches or techniques such as non-chemical alternatives to pesticides.
Regulation (EU) No 528/2012 of the European Parliament and of the Council of 22 May 2012 concerning the making available on the market and use of biocidal products. (consolidated version: 10/06/2021)	Purpose: improve the functioning of the internal market through the harmonization of the rules on the making available on the market and the use of biocidal products, whilst ensuring a high level of protection of both human and animal health and the environment.
Regulation (EC) No 1185/2009 of the European Parliament and of the Council of 25 November 2009 Concerning Statistics on Pesticides. (consolidated version: 09/03/2017)	Purpose: establish a common framework for the systematic production of Community statistics on the placing on the market and use of those plant protection products.
Directive 2009/127/EC of the European Parliament and of the Council of 21 October 2009 amending Directive 2006/42/EC with regard to machinery for pesticide application. (adopted in 2009)	Purpose: introduce requirements for the inspection and maintenance to be carried out on machinery for pesticide application.
Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labeling, and packaging of substances and mixtures. (consolidated version: 01/10/2021)	Purpose: ensure a high level of protection of human health and the environment as well as the free movement of substances, mixtures, and articles.
Regulation (EU) 2018/848 of the European Parliament and of the Council of 30 May 2018 on organic production and labeling of organic products. (consolidated version: 14/11/2020)	Purpose: establish the principles of organic production and lay down the rules concerning organic production, related certification, and the use of indications referring to organic production in labeling and advertising, as well as rules on controls additional to those laid down in Regulation (EU) 2017/625.
EU Action Plan: 'Towards Zero Pollution for Air, Water and Soil' (adopted in 2021)	Purpose: reduce air, water, and soil pollution to not harmful levels, thus creating a toxic-free environment, by 2050.
A Farm to Fork Strategy for a fair, healthy, and environmentally-friendly food system (COM/2020/381 final)	Purpose: reduce pollution from pesticides in air, water, and soil by cutting by 50% their overall use and risk, including the most hazardous ones, by 2030. Other goals focus on the excess of nutrients, antimicrobial resistance, and organic farming area.
Chemicals Strategy for Sustainability (COM(2020) 667 final)	Purpose: better protect citizens and the environment, and boost innovation for safe and sustainable chemicals.

Limitations and ongoing/planned activities to address them

Although considered the strictest pesticide regulatory system in the world (Handford et al., 2015), even the European pesticide system has shortcomings (Buckwell et al., 2020; EC-SAM, 2018; Neumeister and Reuter, 2015; Zeitlin et al., 2021). The main ones relate to:

i) Low representativity of pre-approval risk assessments. EFSA risk assessment reports are prepared for single substances, a limited number of endpoints, and a low number of species. Farmers, however, use multiple pesticides, as tank mixtures and/or via sequential applications, which can lead to a cumulative increase or changes in toxicity (Zeitlin et al., 2021). The effects of such mixtures should be explored (also) in non-standard eco-toxicological species, endpoints, and setups (Hernández et al., 2020; ITPS, 2017; Topping et al., 2020).

ii) High level of protection vs acceptable protection. Despite the precautionary principle foundation of the EU regulation, there are high-risk substances in the EU market (candidates for substitution), as well as substances with known data gaps. In addition, the number of special use or emergency authorizations of banned or not yet approved pesticides is increasing over the years (PAN, 2011), suggesting misuse of the derogation clause.

iii) Limited post-approval monitoring on PPP use and risks. The EU statistics on pesticide use and sales are of limited value. This is mostly because of confidentiality issues or highly aggregated data. Furthermore, the enforcement of IPM principles at the farm level is not always monitored, nor are IPM/pesticide records. Biomonitoring and environmental monitoring data of pesticides could provide some insights on use and risk, but data are limited to certain matrices and substances (ECA, 2020). Environmental risk characterization in RMS/EFSA reports is performed with exposure proxies missing field validation [e.g., predicted environmental concentrations in soil, PECs; (Neumeister and Reuter, 2015)].

These points were corroborated by the REFIT (Regulatory Fitness and Performance programme) evaluation of EU pesticide legislation (EC, 2020b). The EC is investing in research, guidance documents, and targeted legal instruments to address them. The EC adopted resolutions on endocrine disruptors (EU, 2018), and new risk indicators, tools, methods, and species are being explored by EU and EFSA funded projects for integrated and more realistic assessments (see for instance the H2020 SPRINT project global health approach, https://sprint-h2020.eu/, or the PERA project on next-generation, systems-based approach, https://www.efsa.europa.eu/sites/default/files/2021-12/PERA_FINAL.pdf). Furthermore, EFSA published a guidance document on risk assessment of mixtures (EFSA Scientific Committee et al., 2019), which triggered the recently published EC-EFSA action plan on cumulative risk assessment (EFSA, 2021). This plan focuses on prioritization and elaboration of new cumulative assessment groups, retrospective and prospective cumulative risk assessment, and integration of non-dietary exposure. Also recently, the Farm to Fork Strategy (EC, 2020c) set the first pesticide reduction targets at the EU level: a 50% reduction in overall use and risk of chemical pesticides, and a 50% reduction in the use of more hazardous pesticides; both targets should be achieved by 2030. The two EC Harmonised Risk Indicators published in 2019 (EU, 2019) will help monitor the progress. Finally, pesticide distribution datasets are increasing, via higher integration of pesticides in EU/national monitoring programs and research initiatives (e.g., Water Framework Directive (EC, 2000), LUCAS survey (EC, 2020g), HBM4EU project, https://www.hbm4eu.eu/), and centralized at the IPCHEM portal (Information Platform for Chemical Monitoring, https://ipchem.jrc.ec.europa.eu/). Other studies and works, including the present PhD thesis, can contribute to filling knowledge gaps, connecting different pieces of the pesticide pre- and post-registration puzzle, and ultimately improving pesticide regulatory systems.

1.3 Soil contamination by pesticide residues – a great unknown

This PhD thesis focuses mostly on shortcoming iii mentioned above: limited post-approval monitoring on PPP use and risks, more specifically on the occurrence and levels of pesticides in soil, a compartment where pesticide data is particularly scarce and fragmented. This is because until now Europe did not have a soil Directive nor soil-specific protection and monitoring instruments. A Soil Framework Directive was proposed in 2006 (COM(2006) 232) but was withdrawn in 2014 since there was no agreement among the Member States. A new EU Soil Strategy, published in November 2021, sets out a framework and concrete measures for the protection, restoration, and sustainable use of EU soils (EC, 2021b). A linked EU Soil Health Law is expected in 2023 (EC, 2021b). During the last years, EU soil protection has been done indirectly, via soil embracing and soil-related directives, Member States' national policies, and regulatory guidance values (FAO and UNEP, 2021; Frelih-Larsen and Bowyer, 2022; Pérez and Eugenio, 2018b). The "monitoring" of pesticides in EU soils has been made via specific studies (Bermúdez-Couso et al., 2007; Ene et al., 2012; Orton et al., 2013; Pose-Juan et al., 2015; Qu et al., 2016), which often cover a limited number of pesticides and/or a relatively small area (*Fig. 1.3*). These studies vary greatly on sampling time (year and season), sampling strategy (soil depth), and analytical methods (scope, extraction, and limits of detection and quantification), hampering an overview of occurrence and levels of the residues across EU agricultural soils. Differences in currently used pesticides studies are presented in Sabzevari and Hofman (2022). It is estimated, though, that 62% of European agricultural land is at high risk of pesticide pollution (Tang et al., 2021). Unraveling and monitoring soil contamination by pesticide residues are therefore urgently needed to assess and monitor EU soil quality and health (Bach et al., 2020). Pesticide distribution data in EU soils are also highly valuable for the validation of environmental fate models such as PEARL (Pesticide Emission Assessment at Regional and Local scales), and of the PECs values used on EC's soil risk assessments, to complement pesticides datasets of other environmental matrices, to assess consequences/efficacy of pesticide use and regulatory measures (including restrictions and bans of substances), and to support decisions on land use and agricultural practices (Hvězdová et al., 2018).

Soil is often the first recipient of pesticides (on fields with more mature crops, the crop is the first), and becomes a repository and a source of these residues (Al-Wabel et al., 2016; Holoubek et al., 2009; Tudi et al., 2021). The fate of pesticides is governed by physical, chemical, and biological processes (Alekseeva et al., 2014; Arias-Estévez et al., 2008), with the pool of pesticides in the soil being a dynamic balance between the number and amount of pesticides reaching the soil, and the degradation and export rates of residues. Although predictions can be done in this regard, measurement of pesticide residues in soil samples will always be preferable and more realistic. This is because:

i) there are limitations on pesticide use data, which become more evident if a high temporal and spatial resolution is required
ii) there are no records, or at least no harmonized and public access repository, on the timing, crop growth stage, methods, and environmental conditions at pesticide application time, leading to high uncertainty on the amounts

reaching the soil

iii) repeated applications of pesticides may affect their half-life times (Pose-Juan et al., 2015), and even lead to the accumulation of non-/moderately-persistent residues (Hvězdová et al., 2018)

iv) despite the high susceptibility of European soils to wind and water erosion (Borrelli et al., 2014; Panagos et al., 2015), field data quantifying and explaining particulate export is still missing, and particulate export is not fully covered in the current pesticide fate models.

Background contamination from very persistent pesticides plays an important role in the equation too. Some authors found pesticides in soil months or even years after their last application (Chiaia-Hernandez et al., 2017; Orton et al., 2013). This happens because some pesticides can adsorb particularly strongly to soil particles, in particular organic matter, clays, oxi-hydroxides of iron, and manganese (García-Delgado et al., 2020), but also to plastic debris in soil (Beriot et al., 2020), and form long-term bound residues. See Arias-Estévez et al. (2008) for an overview of the factors influencing the persistence of pesticides in soil.

Adsorbed pesticides are usually less mobile and less bioavailable than residues in solution (Arias-Estévez et al., 2008). This has complex implications: the mobility aspect of the distribution and chemical degradation rates of pesticides, the bioavailability of their toxicity to terrestrial organisms, and microbiological degradation rates. Water-soluble pesticide residues are known to move easier, especially into surface water bodies, groundwater, and organisms (via runoff, leaching, and uptake, respectively), but residues adsorbed to colloids or soil particles can still be moved and be exported to other areas and compartments (via wind- and water-driven erosion). Pesticides toxicity and risks, in both source and receiving areas, will depend on the hazard of the substances present and the exposure of organisms to them. The former relates to the inherent hazardous characteristics of the pesticides, the latter is a function of dose, length, and/or frequency of exposure, and is highly dependent on the behavior of the organism, pesticides distribution, and bioavailability (Arias-Estévez et al., 2008; Hayes and Laws, 1991).

Adsorbed pesticides are less available for uptake by organisms, and consequently linked to lower or delayed toxicity (van Gestel, 2012), but are also less available to microorganisms, and consequently slower degraded (Guo et al., 2000). Pesticide degradation is mostly microbial and involves often the formation of metabolites, breakdown or reaction products, which may have similar activity and toxicity as the parent compounds (Karas et al., 2018; Vasileiadis et al., 2018). Pesticides and their residues have been associated with several negative effects on soil biota; no significant effects or positive effects are much less likely (Gunstone et al., 2021). The negative effects include reductions in microbial activity and diversity (Puglisi, 2012), alterations in behavior and reduced survival of arthropods (Evans et al., 2010), and reductions in the growth and reproduction efficiency of earthworms (Pelosi et al., 2013). Given the different roles of soil organisms in agricultural landscapes [e.g., drivers of the provision of genetic resources, of nutrient cycling, of pest and diseases control, of soil structure formation and water retention, or food web support (Ockleford et al., 2017)], it is imperative to quantify soil contamination by pesticide residues and assess their risks.

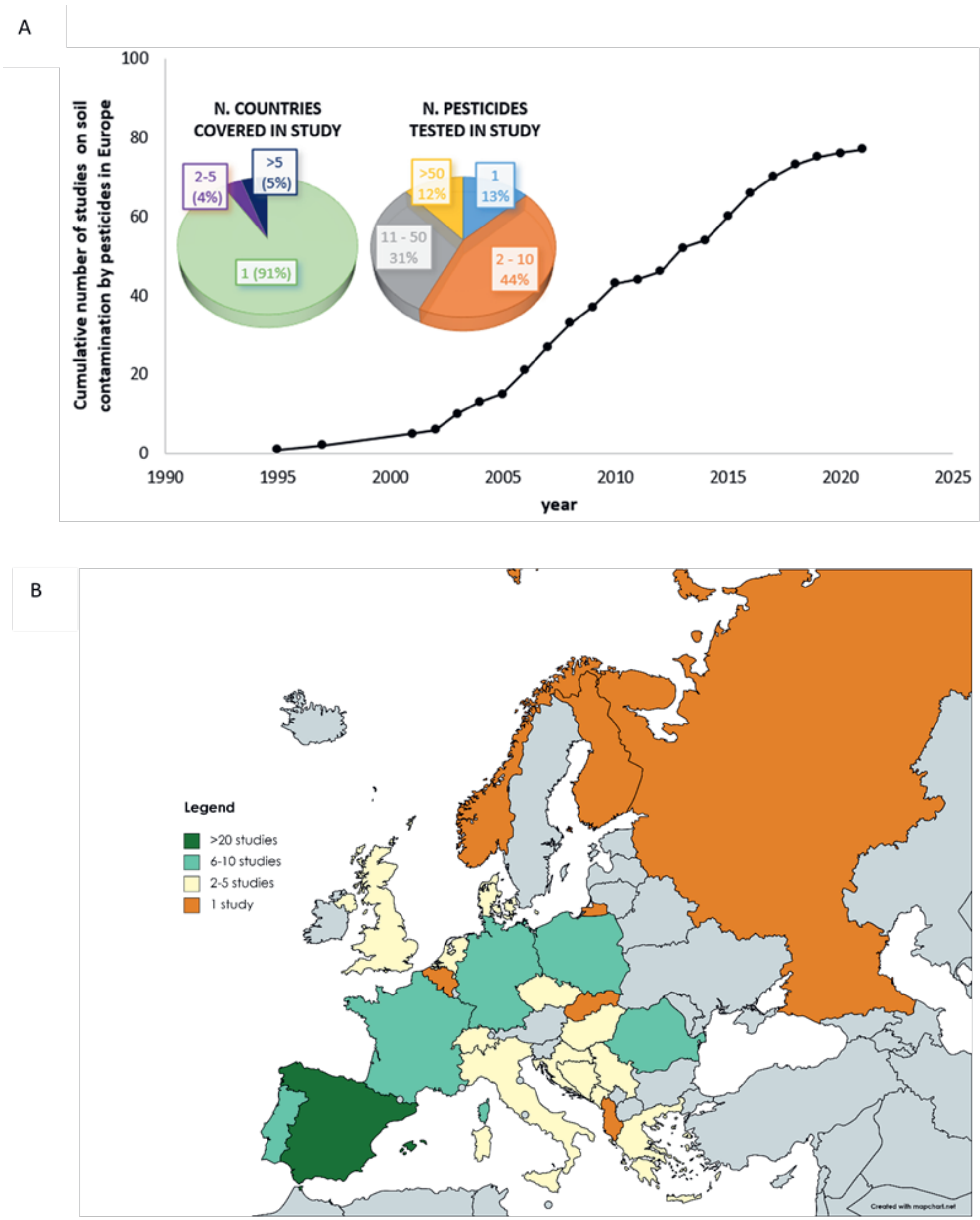


Figure 1.3 – Overview of the European studies on soil contamination by pesticide residues. A – number of studies over the years, number of pesticide residues and countries covered; B – map on number of soil-pesticide studies across EU countries.

1.4 Objectives

This PhD project adds to the discussion on pesticides use and risks and aims to improve the knowledge on the EU agricultural soils contamination status, and the science of environmental risk assessment. In this thesis, particular attention is given to the EU scale, mixtures of pesticide residues, and soil and pesticide agenda. The outline of the thesis is shown in *Fig. 1.4*, and the research objectives are listed below:

1. Assess the distribution of prioritized pesticide residues in EU agricultural soils, covering different geographic regions and different crops.
2. Determine the occurrence and levels of glyphosate and its main metabolite AMPA in the same EU soils, and estimate their potential export rates by wind- and water-driven erosion.
3. Compare the mixtures of pesticide residue in soils of organic and conventional farms in different regions of Europe, and explore the implications of the findings on the transition to organic farming.
4. Establish an EU pesticide use and risk baseline, and explore the potential of different pesticide reduction scenarios to achieve the 50% reduction goals of the Farm to Fork Strategy.

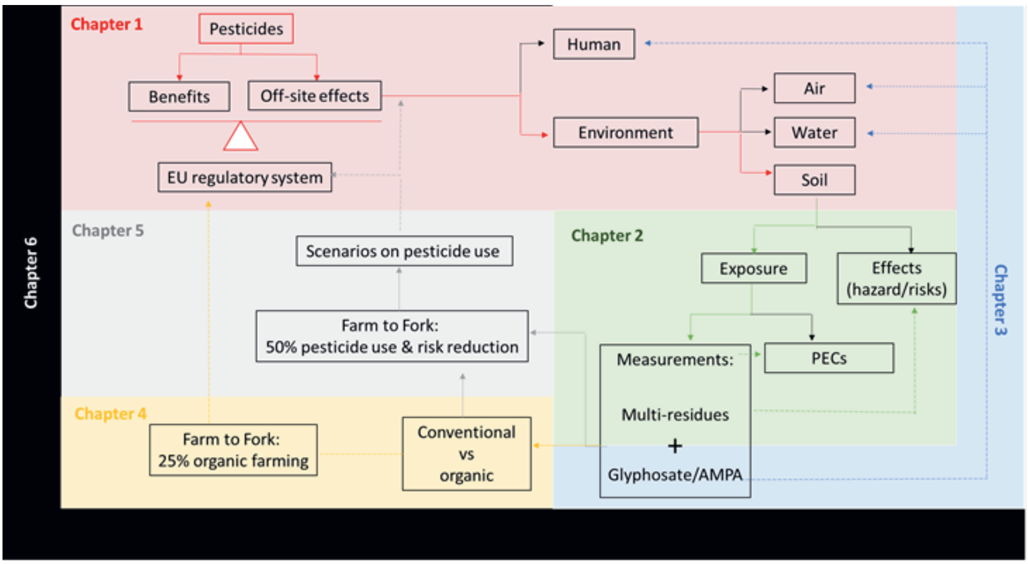


Figure 1.4 – Outline of the thesis. Colored lines indicate addressed links, full lines indicate drivers of the conducted research, and dashed lines implications of the findings.

1.5 Outline of the thesis

This thesis includes six chapters: the first gives a general introduction to pesticides, the EU regulatory framework, and the knowledge gap regarding soil contamination; chapters 2 to 5 address the research objectives of the PhD project; and the last chapter discuss the main findings and implications of the work.

Chapter 1 sets the context of the thesis, stressing the social, political, and environmental complexity of pesticides, exploring the main steps, actors, and limitations of the EU pesticide regulatory system, and finally presenting current knowledge on pesticides in soils.

Chapter 2 identifies the pesticide mixtures in EU agricultural soils. It is the first assessment at the EU level and covers 76 prioritized pesticide residues and 317 soil samples. This chapter includes details on the mixtures found in soil, comparisons between measured and predicted levels of pesticides in soil, and a discussion of the possible risks of the findings for soil health.

Chapter 3 focuses on glyphosate and its main metabolite AMPA since those results could contribute to the ongoing debate on the approval of glyphosate use in the EU. Chapter 3 also includes estimates on potential off-site transport/export of glyphosate and AMPA by wind- and water-driven erosion, and a discussion on potential implications to connected environments, organisms, and human health.

Chapter 4 compares pesticide contamination in conventional and organic farming systems, in four EU case study sites (340 soil samples analyzed in total). The mixtures found in soil are evaluated based on pesticide use interviews, and time since transition to organic farming. Discussion focuses also on the Farm to Fork Strategy 25% organic farmland goal, and food safety.

Chapter 5 presents the first quantitative overview of the characteristics, recommended use, and hazard of the pesticides currently approved in Europe. The potential of seven pesticide reduction scenarios (defined based on application rates, pesticide type, persistence, and hazard) to achieve the Farm to Fork 50% pesticide reduction targets are also investigated.

Chapter 6 summarizes the major outcomes of this PhD project and respective implications on exposure and risk assessment of pesticide residues, and on the Farm to Fork and Soil Strategies for 2030. This chapter concludes with recommendations on these areas and directions for future work.

1.6 Study Areas

Although Europe is the primary study area of this thesis, four areas were explored in more detail in chapter 4: the São Lourenço catchment in Portugal, Carcaixent and the Cartagena region in Spain, and the Groningen region in The Netherlands.

The São Lourenço catchment is integrated into the Bairrada region, an important wine-growing region in central Portugal (*Fig. 1.5*). The São Lourenço catchment has an area of 620 ha, 273 ha of which is occupied by vineyards. This catchment presents three main soil types (calcic cambisols, humic cambisols, and chromic luvisols), gentle slopes (<10%), and a temperate/humid Mediterranean climate [mean annual rainfall of 925 mm, average temperature of 16^{o}C; (Serpa et al., 2015)]. In this catchment, the majority of farmers follow integrated production, with regulated application of pesticides and minimum tillage. Pesticides are applied in spring and summer, and tillage is performed in autumn, at approximately 10-15 cm deep, in alternate inter-rows strips (Ferreira et al., 2018a). Previous studies in this catchment showed the presence of different pesticide residues in surface water, and erosion rates in these vineyards of up to 29 Mg/ha/year (Ferreira et al., 2018a).

Carcaixent is located in Eastern Spain (*Fig. 1.6*), and presents a big surface of both conventionally and organically managed orchards, and a long tradition of intensive orange production. Spain is one of the EU Member States with the biggest use of PPPs (FAOSTAT, 2016), and the largest organic area (Willer and Lernoud, 2015). Citrus is the second crop type with the highest dose of pesticides in Europe, after vineyards (EUROSTAT, 2007). Carcaixent has a hot/semi-arid Mediterranean climate, with average annual rainfall and temperature of 355 mm and 18.7^{o}C, respectively. The west zone of Carcaixent, close to the river, is a flood-prone zone with clay-rich soils. The east zone uses drip irrigation and has sand-rich soils. The main soil type is the same in both zones: cambisols. Information on land operations is not available. In these orchards, most pesticides are applied in spring-summer, according to the guidelines of the local agricultural cooperatives. Some organic fields have bamboo fences, but often there is proximity and absence of a fence between conventional and organic orchards. Previous pesticide studies in the area focused on groundwater quality (Hernández et al., 2008) or bee mortality (Calatayud-Vernich et al., 2016).

Cartagena is located in Southeast Spain, in the region of Murcia (*Fig. 1.7*). Cartagena agricultural region has 28 000 ha, 66% of this area is used for intensive vegetable production (Fulgencio Pérez Hernández et al., 2021). Diversification patterns include commonly two crops per year, usually melons, pumpkins, or maize in summer and lettuces, cabbages, broccoli, or celery in winter. The intensive production originates mostly from conventional farms, supported by the use of pesticides. Organic agriculture represents 22% of the cultivated area in the region[2] and organic output is increasing steadily[3]. Cartagena has a semi-arid climate with a mean annual temperature of 17.5ºC, and mean annual precipitation of 280 mm. Due to the (semi-)arid climate, all the vegetable production in Murcia is irrigated, and plastic mulch is often used by farmers to increase water use efficiency. Soil contamination by plastic debris in this area is presented in Beriot et al. (2021). The main soil type in the region is Haplic Calcisol, with a loamy texture. After harvest, the soil is usually plowed until 30 cm to prepare the field for the next crop.

The province of Groningen is located in the north of The Netherlands (*Fig. 1.8*), where around 70% of the land use is agriculture (Ministerie van LNV, 2019, agrifood Groningen). Potato is one of the dominant crops (cereals is the other), with this region contributing significantly to the global export of seed potatoes[4]. Groningen, presents a Humid Atlantic climate, with a mean annual rainfall of 826 mm and a mean annual temperature of 9.2ºC. Groningen province encourages farmers financially to adopt more environment-friendly farming practices, yet most of the farms are still under conventional management, with large amounts of pesticides being used to protect crops from weeds and diseases (Bin, 2019). Preliminary findings in the area indicated high levels of pesticides and plastic debris in the soil.

[2] https://econet.carm.es/web/crem/inicio/-/crem/sicrem/PU590/Indice1.html

[3] http://www.frutas-hortalizas.com/pdf_uk09/142_153.pdf

[4] https://climateinitiativenoordnederland.nl/en/projecten/the-potato-valley/

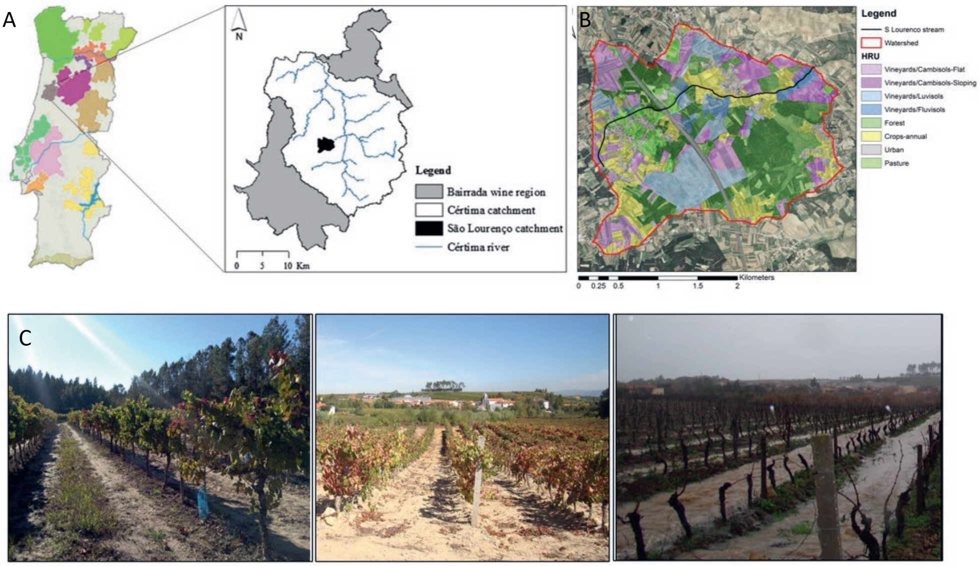


Figure 1.5 – Location of the Portuguese study area. A) Main wine regions in Portugal including the Bairrada region, Cértima and São Lourenço catchment; figure from Ferreira et al., (2018); B) detail of crop and soil type in São Lourenço catchment; C) pictures from São Lourenço vineyards, including during rainfall events.

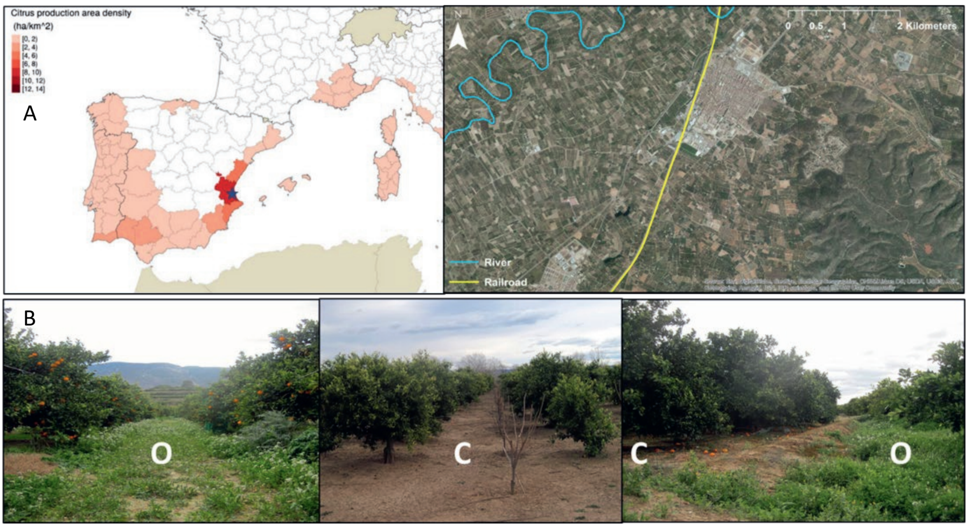


Figure 1.6 – Location of the Carcaixent study area. A) Main Citrus production in Europe, figure from EFSA,2016; the blue star marks Carcaixent; B) pictures from conventional (C) and organic (O) orange orchards in Carcaixent.

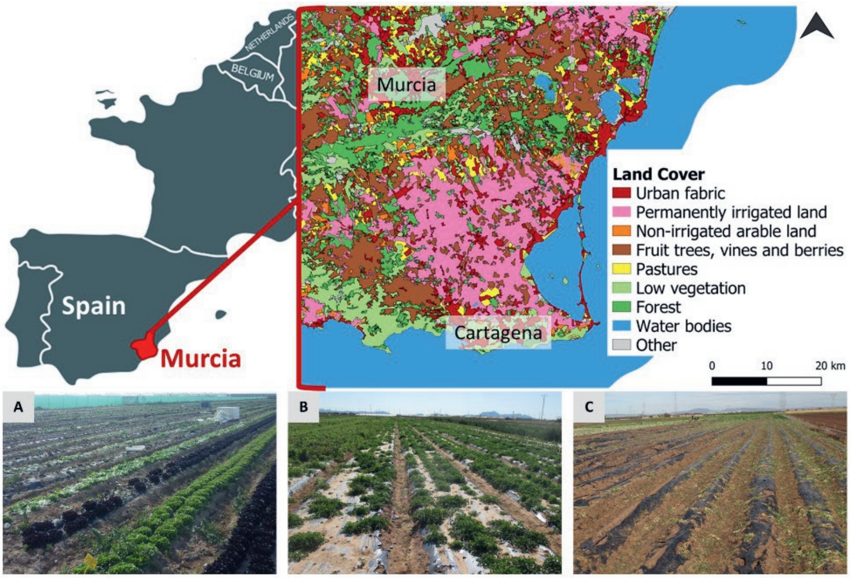


Figure 1.7 – Location and land cover of the countryside of Cartagena. A) picture of fields cultivated with lettuces; B) with parsnip and C) and a field covered with plastic mulch after the harvest.

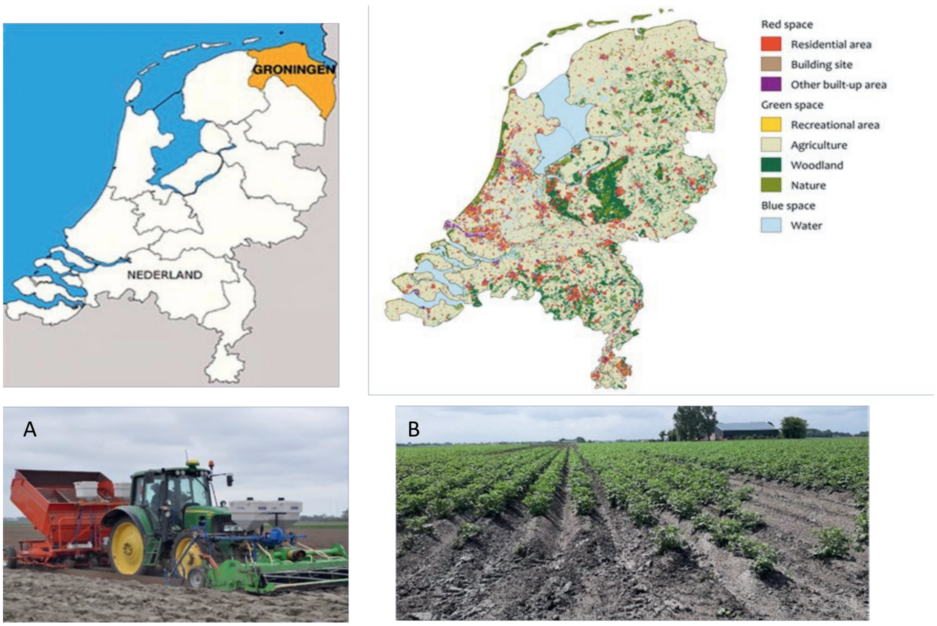


Figure 1.8 – **Location and land cover of the Groningen study area.** A) and B) pictures of current land operations and soil coverage at a conventional field.

Chapter 2

Pesticide residues in European agricultural soils – a hidden reality unfolded

Abstract: *Pesticide use is a major foundation of the agricultural intensification observed over the last few decades. As a result, soil contamination by pesticide residues has become an issue of increasing concern due to some pesticides' high soil persistence and toxicity to non-target species. In this study, the distribution of 76 pesticide residues was evaluated in 317 agricultural topsoil samples from across the European Union. The soils were collected in 2015 and originated from 11 EU Member States and 6 main cropping systems. Over 80% of the tested soils contained pesticide residues (25% of samples had 1 residue, 58% of samples had mixtures of two or more residues), in a total of 166 different pesticide combinations. Glyphosate and its metabolite AMPA, DDTs (DDT and its metabolites), and the broad-spectrum fungicides boscalid, epoxiconazole, and tebuconazole were the compounds most frequently found in the soil samples and the compounds found at the highest concentrations. These compounds occasionally exceeded their predicted environmental concentrations in soil but were below the respective toxic endpoints for standard in-soil organisms. The maximum individual pesticide content assessed in a soil sample was 2.05 mg/kg, the maximum total pesticide content was 2.87 mg/kg. This study reveals that the presence of mixtures of pesticide residues in soils is the rule rather than the exception, indicating that environmental risk assessment procedures should be adapted accordingly to minimize related risks to soil life and beyond. This information can be used to implement monitoring programs for pesticide residues in soil and to trigger toxicity assessments of mixtures of pesticide residues on a wider range of soil species to perform more comprehensive and accurate risk assessments.*

Based on:

Silva V, Mol HGJ, Zomer P, Tienstra M, Ritsema CJ, Geissen V. Pesticide residues in European agricultural soils – A hidden reality unfolded. Science of The Total Environment 2019; 653: 1532-1545.

2.1 Introduction

Pesticides have strongly contributed to the increased food production observed over the last few decades. Since 1960, world average yields of rice, wheat, and maize more than doubled as pesticide use increased by 15 to 20 fold, and as fertilizer use, irrigated land and cultivated land increased by 7, 2, and 1 fold, respectively (Oerke, 2006). Globally, around 3 million tons of pesticides are applied annually, corresponding to a market value of USD 40 billion (Pimentel, 2009). In the European Union (EU), there are almost 500 active substances approved for use in pesticides (EC, 2018b), with annual sales of 374 000 tons of pesticides [average data 2011-2016 for the EU-28; (EUROSTAT, 2018)].

Despite the benefits of pesticides on crop yields and their relevance to the economy, intensive and widespread pesticide use raises serious environmental and health concerns. Diffuse pollution by agrochemicals has become a major soil threat (Stolte et al., 2016), and as such, it may affect several of the United Nations Sustainable Development Goals linked with the soil environment (Keesstra et al., 2016; Pérez and Eugenio, 2018b). Soil contamination raises concerns on soil functions, soil biodiversity, and food safety but also on the off-site transport of contaminants via wind and water-driven erosion. Such off-site transport may impair sink ecosystem functioning and represent additional exposure routes to soil contaminants for humans and other non-target organisms (FAO and ITPS, 2017; Pérez and Eugenio, 2018b).

Despite the several implications of soil contamination, the monitoring of pesticide residues in the soil is not required at the EU level, in contrast to the water monitoring regulated by the EU Water Framework Directive. Moreover, large-scale international studies on soil contamination by pesticide residues are scarce and often limited to one single pesticide, or only a few compounds (Covaci et al., 2013; Silva et al., 2018). Several studies have already characterized the distribution of currently used and of no-longer approved pesticides in soil at the national or regional level (Chiaia-Hernandez et al., 2017; Hvězdová et al., 2018; Masiá et al., 2015; Orton et al., 2013; Pose-Juan et al., 2015; Qu et al., 2016), but the different sampling periods, different sampling strategies, different analytical methods, and different analyte lists among these studies prevent a comprehensive overview of the distribution of pesticides residues in EU soils.

Reference or maximum levels in soils for no-longer approved, highly persistent, obsolete pesticides, such as DDTs, HCHs, atrazine, and dieldrin, are included in the legislation of some European countries (Carlon, 2007). However, although a couple of these countries' regulations include admissible levels for unspecified "other pesticides" (Carlon, 2007), thresholds for approved, currently used pesticides do not exist. Concentrations/content of approved pesticides in soil are often interpreted based on their predicted environmental concentrations for this matrix (PECs). Such PECs are calculated based on worst-case conditions and are used in the review process of individual active substances. PECs are calculated for the main crops to which the substance is applied, considering recommended application rates (highest dose per application, highest number of applications and the lowest applications interval), a default soil bulk density (1.5 g/cm^3) and tillage depth (5 cm for permanent crops and 20 cm for annual crops), typical interception fractions by plants, and the longest degradation rates of the substance in soil from laboratory or field studies (Ockleford et al., 2017). The conclusion report of each approved active substance includes the initial PECs (immediately after pesticide application), short and long-term PECs (1–4 and 7–100 days after application, respectively), and PECs accumulated (sum of PECs initial and plateau concentrations). Plateau concentrations, only calculated for substances with a 90% degradation time above 365 days, refer to the background levels in soils after multi-year pesticide applications.

Current pesticide risk assessment relies on the comparison of toxicity exposure ratios (TERs) and trigger values. TERs are calculated for single residues by dividing ecotoxicologically relevant concentrations for indicator organisms by the residue's highest PECs (PECs initial or PECs accumulated). The ecotoxicologically relevant concentration is the LC_{50} (concentration resulting in the mortality of 50% of the exposed individuals) or the NOEC (highest No Observed Effect Concentration), in the case of acute/short-term toxicity or chronic/reproductive toxicity assessments, respectively. The in-soil indicator organisms are the earthworms *Eisenia fetida* and *E. andrei*, the springtails *Folsomia candida* and *F. fimetaria*, the mite *Hypoaspis aculeifer* and nitrogen transformation microorganisms (Ockleford et al., 2017). TERs lower than 10 or 5, the trigger values for, respectively, acute and chronic exposures of earthworms and other soil macroorganisms (EC, 2011), indicate an unacceptable risk for such organisms. The risk for soil microorganisms is not based on TERs but in the percentage of effect compared to control; an effect above 25% after 100 days of exposure represents an unacceptable risk (Ockleford et al., 2017). Despite the clear importance of PECs on the risk assessment procedure, their validation with field data from pesticide monitoring programs is still missing.

As a first approach to address these data gaps, we analyzed 76 prioritized pesticide residues (of current use and no-longer approved pesticides) in 317 agricultural topsoils, originating from 11 EU countries and 6 cropping systems. Different geographical regions were expected to represent different pesticide application patterns (from different incidence of pests, non-chemical pest management costs, and pesticide products applied) as well as different environmental and edaphic conditions (factors with great impact on pesticide persistence in soils). Different crops were expected to represent different susceptibilities to pests and, therefore, different pesticide application patterns too. Data on the frequency of occurrence and concentrations of pesticide residues in soil could provide valuable information on the geographical areas or crops of higher concern as well as on the usefulness of existing PECs. The adequacy of current pesticide risk assessment for in-soil organisms is also discussed.

2.2 Materials and methods

2.2.1 Soil samples

The presence and the concentration of multiple pesticide residues were analyzed in 317 topsoil samples; 300 agricultural topsoil samples were selected from the pool of topsoils collected during the Land Use/Cover Area Frame Survey (LUCAS) 2015 survey [see Tóth et al. (2013) and Orgiazzi et al. (2017) for more information on LUCAS surveys] and 17 topsoil samples from Portuguese vineyards, where we were studying the transport of pesticide residues by surface runoff (Silva et al. in prep).

The LUCAS topsoil samples originated from 10 European Union (EU) Member States and 6 main crop classes. The selected Member States/countries have the highest agricultural area and pesticide use in arable land and permanent croplands of the Northern (United Kingdom and Denmark), Southern (Italy, Greece, Spain), Eastern (Hungary and Poland), and Western EU regions [The Netherlands, France and Germany; (FAO, 2013; FAO, 2014)]. In each of these countries, the crops with the highest pesticide use per hectare or the highest cultivated area were selected (Muthmann, 2007). The selected soil samples included soils used in the production of (i) cereals, (ii) permanent crops, (iii) root crops, (iv) non-permanent industrial crops, (v) dry pulses, flowers and fodder crops, and (vi) vegetables. Some extra samples from bare soils previously used as croplands (EUROSTAT, 2009; EUROSTAT, 2012) were selected and categorized as class (vii) others. The main crop classes (i-vi) were defined according to the classification adopted in the LUCAS 2015 survey (E4 LUCAS (ESTAT), 2015b). The land cover types included in each crop class are presented in *Table S2.1*. We then selected soil samples from different NUTS 2 regions [EU territorial units of regional level; see EUROSTAT (2015a) for information on the Nomenclature of Territorial Units for Statistics (NUTS) classification system] and with different soil properties [data retrieved for each sampling point from the LUCAS survey 2009 topsoil dataset; (ESDAC, 2009; Panagos et al., 2012)].

The number of topsoil samples used in this study is listed by EU region, country, NUTS 2 region, and main crop class in *Table S2.2*. The number of topsoil samples collected in Portugal was lower than it was in the other countries (17 versus 30 samples per country) and all samples belonged to the same crop class (permanent crops) and NUTS 2 region (PT16). Portuguese data were integrated into the Southern EU results.

Each LUCAS topsoil sample was a mixture of five subsamples (0–15/20 cm): four subsamples collected at 2 meters north, south, east and west of a central LUCAS subsampling point. For crops planted in rows, the subsamples were collected along a linear transect in an inter-row strip (between two crop rows), with a 2-meter distance between each two subsamples (E4 LUCAS (ESTAT), 2015a). The Portuguese samples were collected following these LUCAS sampling procedures. The 317 topsoil samples were collected between April and October of 2015, air-dried at ambient temperature for at least one week until the final soil moisture content was below 6 % (w/w). The dried samples were sieved with a 2-mm sieve and frozen at -20 ^{o}C until chemical determinations could be carried out.

2.2.2 Selection of the pesticide residues

An initial list of the pesticide residues of interest was obtained based on the active substances most often applied to the selected crops (Muthmann, 2007) and on the findings of previous studies concerning the distribution of pesticide residues in EU agricultural soils (Covaci et al., 2013; Masiá et al., 2015; Orton et al., 2013; Pose-Juan et al., 2015; Qu et al., 2016; RůŽičková et al., 2007). Additionally, considering their high soil persistence, the pesticides banned by the Stockholm Convention were also included in the list. Finally, the major metabolites of the selected active substances (of both currently used pesticides and of banned pesticides) were added to the list too.

Due to logistical and financial limitations, some compounds on this initial list were not analyzed. To start, inorganic compounds, plant growth regulators, and botanical agents were excluded from this study. Then, priority was given to compounds that could be analyzed by a multi-residue method, excluding compounds such as mancozeb, fosethyl, metiram or thiram. Nevertheless, considering the high use and relevance of glyphosate-based herbicides, we used a single residue method for the determination of glyphosate and its main metabolite aminomethylphosphonic acid (AMPA). Finally, some compounds were excluded due to analytical limitations, namely by poor recoveries (<70%).

The final list consisted of 76 pesticide residues (34 insecticides, 27 fungicides and 15 herbicide residues; *Table S2.3*), from now on called analytes, which were analyzed in each of the 317 topsoil samples. A subset of the analysis, namely the glyphosate and AMPA results, has been recently published in Silva et al. (2018). Nevertheless, as glyphosate and AMPA significantly contribute to the total pesticide load in soils, we considered these compounds in the current study as well.

2.2.3 Chemicals and reagents

The reference standards of glyphosate (98%) and AMPA (98%) and the isotope-labeled internal standards of glyphosate (1, 2–^{13}C ^{15}N; 100 µg/ml, 1.1 ml) and AMPA (^{13}C, ^{15}N; 100 µg/ml, 1.1 ml) were obtained from Dr. Ehrenstorfer (Germany). The reference standards of the other analytes were purchased from Dr. Ehrenstorfer (Germany) or Riedel-de Haen (Germany). $^{13}C_3$-labeled caffeine and PCB-198 were purchased from Sigma-Aldrich (USA) and Dr. Ehrenstorfer (Germany), respectively. C_{18} (40 µm, Prep LC) was purchased from J.T. Baker (The Netherlands). Sodium tetraborate decahydrate ($Na_2B_4O_7 \cdot 10H_2O$; 99.5% ACS reagent) and ammonium acetate (NH_4Ac; ~98%) were obtained from Sigma-Aldrich (USA). Potassium hydroxide (KOH; 85%) and magnesium sulfate ($MgSO_4$; ≥99.8%) were purchased from Sigma-Aldrich (France) and Sigma-Aldrich (Japan), respectively. Ammonium formate (HCO_2NH_4; 99%) and 9–fluorenylmethoxycarbonyl chloride (FMOC-Cl; ≥99.0%) were purchased from Sigma-Aldrich (Switzerland). Hydrochloric acid (HCl; 37%), formic acid (CH_2O_2; 98-100%), and ammonia solution (NH_3; 25%) were purchased from Merck (Germany). Acetic acid (CH_3COOH; ≥99.8%) was obtained from Biosolve BV (The Netherlands) and sodium acetate (CH_3COONa; 99%) from Alfa Aesar GmbH & Co KG (Germany). Acetonitrile (C_2H_3N; 99.95% LC grade) and methanol (MeOH; 99.98%) were purchased from Actu-All Chemicals (The Netherlands). Primary secondary amine sorbent (PSA) was purchased from Agilent Technologies Netherlands B.V. (The Netherlands).

2.2.4 Chemical determinations

The topsoil samples were thawed the day before the extraction of pesticide residues was carried out. The samples were then stirred with a spoon until visually homogenous samples were obtained. Four aliquots were taken from each sample: two aliquots of 5 g (air-dry weight) for the multi-residue method and two aliquots of 2 g (air-dry weight) for the determination of glyphosate and AMPA.

For the determination of multi-residues, the QuEChERS approach was adapted for soil samples, using a methodology similar to the one described by Anastassiades et al. (2003) and Mol et al. (2008). Briefly, each 5 g soil aliquot was spiked with 50 µl of ^{13}C3-caffeine 10 µg/ml [used as a surrogate standard to check the overall procedure in the liquid chromatography-tandem mass spectrometry (LC-MS/MS) analysis, not used for quantification] and mixed with 5 ml Millipore water and 10 ml of acetonitrile containing 1% acetic acid (ACN 1% HAc; extraction solvent) within a 50 ml Greiner tube. The tube with this mixture was agitated (end-over-end) for 60 minutes, after which, 1 g of sodium acetate and 4 g of magnesium sulfate were added to the tube. The tube was then vortexed and centrifuged (5 minutes; 3,500 rpm) and the supernatant was collected: part to be analyzed using LC-MS/MS, with electrospray ionization (ESI) in positive mode, and part to be analyzed using gas chromatography-high-resolution mass spectrometry (GC-HRMS). For the LC-MS/MS analysis, 125 µl of the supernatant, 125 µl of ACN 1% HAc, and 250 µL of Millipore water were added directly into an LC filter vial to be analyzed. For the GC-HRMS analysis, there was an extra clean-up step: 1500 µl of the supernatant were transferred into an Eppendorf tube containing 38 mg of primary secondary amine (PSA), 38 mg of C18, and 250 mg of magnesium sulfate. Then, 38 µl of PCB-198 1 µg/ml (used as injection standard in the GC-HRMS analysis) was added to the

Eppendorf. The Eppendorf was then centrifuged (15 minutes; 13,000 rpm) and 200 µl of the cleaned supernatant was transferred into an amber glass vial to be analyzed.

Glyphosate and AMPA analyses were conducted following the procedure described by Bento et al. (2016) and Yang et al. (2015). In short, each 2 g dry weight aliquot was mixed with 10 ml of potassium hydroxide 0.6M (extraction solvent) within a 50 ml Greiner tube. The tube was agitated (end-over-end) for 60 minutes and centrifuged (30 minutes; 3,500 rpm). Then, 1 ml of the supernatant was transferred into a 10 ml centrifuge tube to which was also added 80 µl of hydrochloric acid 6M (obtaining a pH of approximately 9), 40 µl of a mix solution of glyphosate and AMPA isotopically labeled internal standards 5 µg/ml, 0.5 ml of borate buffer 5% and 0.5 ml of 9-fluorenylmethoxycarbonyl chloride 6.5 mM (FMOC-Cl; derivatization agent). The tube was briefly vortexed (10-15 seconds) and then allowed to react for 30 minutes. After this time, the reaction was stopped by adding 50 µl of formic acid 98-100% to the tube. The tube was briefly vortexed again and 0.5 ml of the derivatized extract was transferred into an LC filter vial to be analyzed through LC-MS/MS with ESI in negative mode.

2.2.5. Quality control

The chemical determinations and the quality control of the analytical results were performed according to the guidance document on analytical quality control and method validation procedures for pesticides residues analysis in food and feed (EC, 2015a). Briefly, 3 sets of multi-pesticide calibration standards were prepared for LC-MS/MS-based multi-method, GC-HRMS-based multi-method, and glyphosate/AMPA analysis, respectively. Each set of calibration standards was prepared from a mix solution that combined the reference standards of all compounds that were going to be analyzed by the respective analytical method. The 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. In the LC-MS/MS analysis, a calibration curve of calibration standards (multi-method: 1.25, 3.125, 6.25, 12.5 and 50 ng/ml; glyphosate/AMPA: 0.005, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1 and 2 µg/ml) was injected at the start, middle and end of each sample sequence. For GC-HRMS analysis, as the sample sequences were shorter, a calibration curve (2.5, 10, 25, 50, and 100 ng/ml) was injected only at the start and at the end of each sequence. The calibration curves presented satisfactory linearity of response versus concentration, with correlation coefficients above 0.99 and residuals of response lower than ± 20%.

Each sample sequence included also 3 to 6 fortified blank soils (i.e., agricultural soils from a previous study that were tested during the method development and that did not contain any of the tested residues) and 3 to 6 fortified soil samples (a 5th aliquot was randomly taken from 3 to 6 EU agricultural topsoil samples). These soils were spiked with the mix solutions of the reference standards and analyzed as the EU agricultural topsoil samples. For the LC-MS/MS-based multi-method the spiking levels were 0.01 and 0.05 mg/kg, for the GC-HRMS-based multi-method, 0.005 and 0.05 mg/kg, and for glyphosate and AMPA determinations, 0.05 and 0.25 mg/kg. The recoveries obtained in the fortified soils were between 70 and 120%.

The lowest calibration level included in the analysis was used as the reporting limit, i.e. the threshold for reporting results. Such reporting limits were equal to the limits of quantification (LOQ) of the compounds. To facilitate further comparisons on the occurrence of pesticide residues in soil, there was a single LOQ for all the compounds analyzed by the same method. A LOQ of 0.01 mg/kg was achieved for the pesticide residues measured by the LC-MS/MS-based multi-method while for the compounds measured by GC-HRMS this LOQ was 0.005 mg/kg, and for glyphosate and AMPA this was 0.05 mg/kg. The list of compounds analyzed by LC-MS/MS-based multi-method and by GC-HRMS is presented in *Table S2.4* and *Table S2.5*, respectively. The LC-MS/MS and GC-HRMS apparatus and conditions are described in *Table S2.6* and *Table S2.7*, respectively.

Each of the 76 analytes was identified according to (i) the retention time and peak shape of the respective reference standard (or of the isotopically labeled internal standard, in the case of glyphosate and AMPA), and (ii) the ion ratio, with ratios between the quantification and confirmation transitions within ± 30% of the average ion ratio of the calibration standards. The response of the GC-HRMS analytes was normalized according to the response of PCB-198, and the glyphosate and AMPA response was normalized according to the response of the isotopically labeled analogs. The concentration of the analytes was calculated based on bracketing calibration, with a matrix-matched calibration standard (LC-MS/MS-based multi-method 3.125 ng/ml; GC-HRMS-based multi-method 10 ng/ml) or with a solvent standard containing the labels for glyphosate and AMPA (0.1 µg/ml) analyzed every 10–15 injections/samples.

As each compound was analyzed in duplicate (two soil aliquots for the multi-residue method and two aliquots for glyphosate and AMPA determinations), the mean content of both aliquots was considered to be the content in the sample. The content in each of the two aliquots was within ± 35% of the mean content of both aliquots. In the few cases (<2% of all positive results) where the compound content was equal to or above the LOQ in just one of the aliquots, the ≥LOQ value was assumed as the content of the sample (conservative approach). This was only done because the values <LOQ and the values ≥LOQ were very close to the LOQ value.

2.2.6 Data analysis

Only pesticide residue content equal to or above the respective LOQs was considered in data analysis (data entries where the analyte content was below the LOQ were left empty). Due to the analytical method chosen, and as the results for phthalimide may not originate only from folpet (Lach and Bruns, 2016), only qualitative results are provided for this compound and no concentrations in soil are given. As a result, phthalimide was considered in the number of residues present in the soil but it was not considered in the total pesticide content.

Due to privacy issues, the number of pesticide residues in soil and the total pesticide content in soil (i.e. sum of the content of the individual pesticide residues ≥LOQ per soil sample) could not be given for the individual sampling points, instead, this information is presented at the EU region, country, NUTS 2 region and cropping system level. Normal distribution and homogeneity of variances of the number of residues and the total pesticide content in soil were tested using the Shapiro-Wilk and Levine's tests, respectively. As parametric assumptions were not satisfied, even after $\log_{10}$, $\log_{10}$ (x+1), ln, square root, or exponential data transformation, non-parametric Kruskal-Wallis tests were used to compare the number of residues in soil and the total pesticide content in soil among different EU regions, countries, and cropping systems. In the presence of significant effects ($p<0.05$), Bonferroni-corrected Mann-Whitney tests were performed to test differences between each two EU regions, countries or crop systems. Statistical analyses were not performed at the NUTS 2 level due to the very reduced number of samples in some NUTS 2 regions (*Table S2.2*).

Principal Component Analysis (PCA) and spearman's rank correlations were used to explore possible relationships between the content of pesticides in soil and the pesticide and soil properties. The pesticide properties, obtained from the Pesticide Properties Database (PPDB, 2017) or the PAN Pesticide Database (PAN Pesticide Database, 2017), included: half-life time in soil (DT_{50}, days; an indicator of soil persistency), solubility in water at 20°C (Sw, mg/L), octanol-water partition coefficient (Log P, at pH 7 and 20 °C; an indicator of bioaccumulation potential), vapor pressure at 25°C (Vp, mPa; an indicator of volatility), GUS index (an indicator of leaching potential), and organic carbon-water partition coefficient (Koc, ml/g; an indicator of soil adsorption and mobility). The basic soil properties (pH, organic carbon content, % silt, and % clay) were extracted for the 317 individual sampling points, from the LUCAS survey 2009 topsoil dataset (ESDAC, 2009). The statistical analyses, the PCAs and spearman's correlations analysis were performed using SPSS 22.0.

In the figures, to simplify comparisons, the number of pesticide residues in soil and the total pesticide content in soil were aggregated by classes: "0, 1, 2–5, 6–10, >10 residues" and "No residues ≥LOQ, ≥LOQ–0.05, ≥0.05–0.15, ≥0.15–0.5, ≥0.5–1, ≥1 mg/kg", respectively. The class thresholds of 0.05, 0.15, 0.5 and 1 mg/kg correspond, respectively, to the 22nd, 50th, 81st and 93rd content percentile of the samples containing quantifiable pesticide residues (nq; nq is the number of samples containing pesticide residues minus the number of samples with just phthalimide). The NUTS 2 maps using these classes were produced in ArcGIS 10.4.

The measured content of the most common pesticide residues in soil (i.e. present in >10% of tested soils) was compared with their predicted environmental concentrations in soil (PECs from the EFSA conclusion reports of these substances), or in the case of the banned DDTs, with national soil screening values. Additionally, the maximum measured content of each of these residues was used to calculate a second set of TER values for in-soil organisms, where TER=(LC_{50} or NOEC)/maximum measured content. The NOECs and LC_{50} values for in-soil organisms were also obtained from the EFSA conclusion reports. As the content of DDE pp and DDTs (sum of DDT and its metabolites) in soil were very similar, and considering the higher availability of DDTs screening values than of DDE screening values, only DDTs levels were explored. The screening values of DDTs in European countries are compiled in Carlon (2007).

2.3 Results

2.3.1 Number of pesticide residues in soil

Overall, only in 17% of the tested agricultural topsoils no pesticide residues were detected (i.e. glyphosate and AMPA content <0.05 mg/kg, the content of the 46 compounds measured by the LC-MS/MS-based multi-method <0.01 mg/kg, and the content of the 28 compounds analyzed by GC-HRMS <0.005 mg/kg). In 25% of the topsoils, a single pesticide residue was quantified while 58% of the topsoils had multiple residues present. Results indicate a predominance of mixtures of a few residues in soil (2–5) relative to mixtures of moderate (6–10) or large numbers of residues (>10; *Fig. 2.1*).

The number of pesticide residues varied significantly within the EU region ($p<0.01$), country ($p<0.01$), and cropping system ($p<0.01$; *Fig. 2.1*). The Southern regions of the EU had the highest frequency of soils with no pesticides (26%), and significantly fewer residues in soil than the Northern, Eastern and Western EU regions. Eastern parts of the EU had the highest frequency of soils with pesticide residues (93%) and the highest frequency of samples with ≥6 residues in soil (23%).

The number of different pesticide residues in soil was significantly lower in Italy than in the other EU Member States (but note that the number of samples by crop varied among countries, *Table S2.2*), with 53% of the soils containing pesticide residues. In the remaining countries, at least 75% of the soils had pesticide residues, with a maximum of 100% in Poland. Portuguese soil samples contained the least complex mixtures, being the only country where all of the samples had less than 6 compounds (*Fig. 2.1*).

None of the soil samples collected from the NUTS 2 regions UKC2, UKH1, DE12, DE13, DE26, ITF1, ITH2, ITI4, EL63 and HU23 contained pesticide residues (*Fig. 2.2*; note that, except for UKH1, these NUTS 2 regions are represented by a single soil sample only). Conversely, the tested soils from the UKF1, UKJ1, UKM5, DE91, DEB1, ITH1, PL21, PL52 and FR22 regions contained mixtures of at least 6 residues (*Fig. 2.2*; just one soil sample was analyzed from each of these NUTS 2 regions).

Soils from root crops had significantly more pesticide residues than the soils from other crops: 100% of the tested soils from root crops contained pesticide residues and 85% of the samples had multiple residues. On the other hand, soils from dry pulses, flowers and fodder crops, with the highest frequency of soils with none (29%) and with a single pesticide residue (38%), had significantly fewer residues than the soils from the other crops (*Fig. 2.1*).

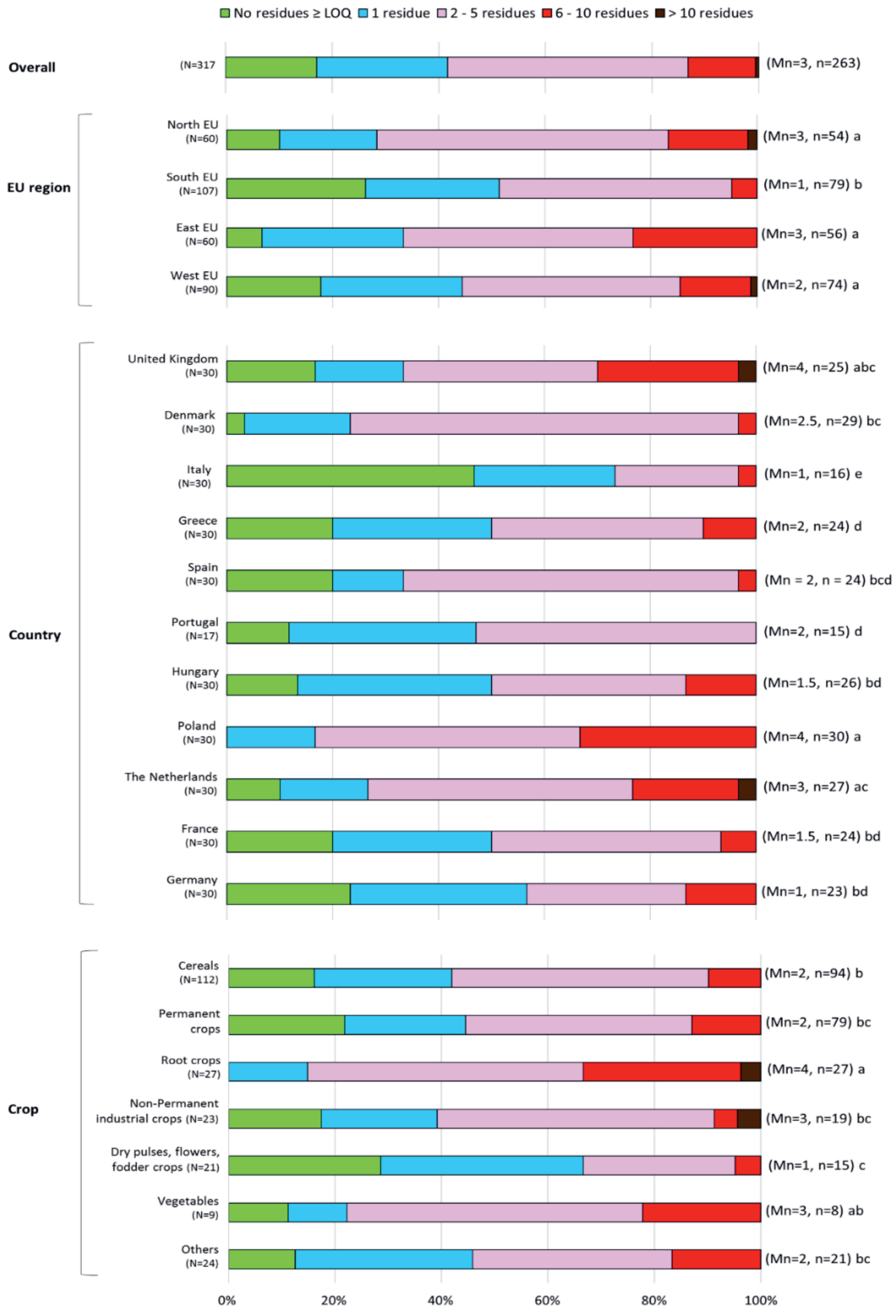


Figure 2.1 – Distribution of the frequency of topsoil samples with no quantified pesticide residues, 1 pesticide residue and multiple pesticide residues by EU region, country and cropping system. N-number of tested samples; Mn-median number of residues in the soils containing pesticide residues; n–number of soils containing pesticide residues. The lowercase letters in the right panel denote significant differences in the number of pesticide residues in soil among EU regions, countries and crops (a>b>c>d>e).

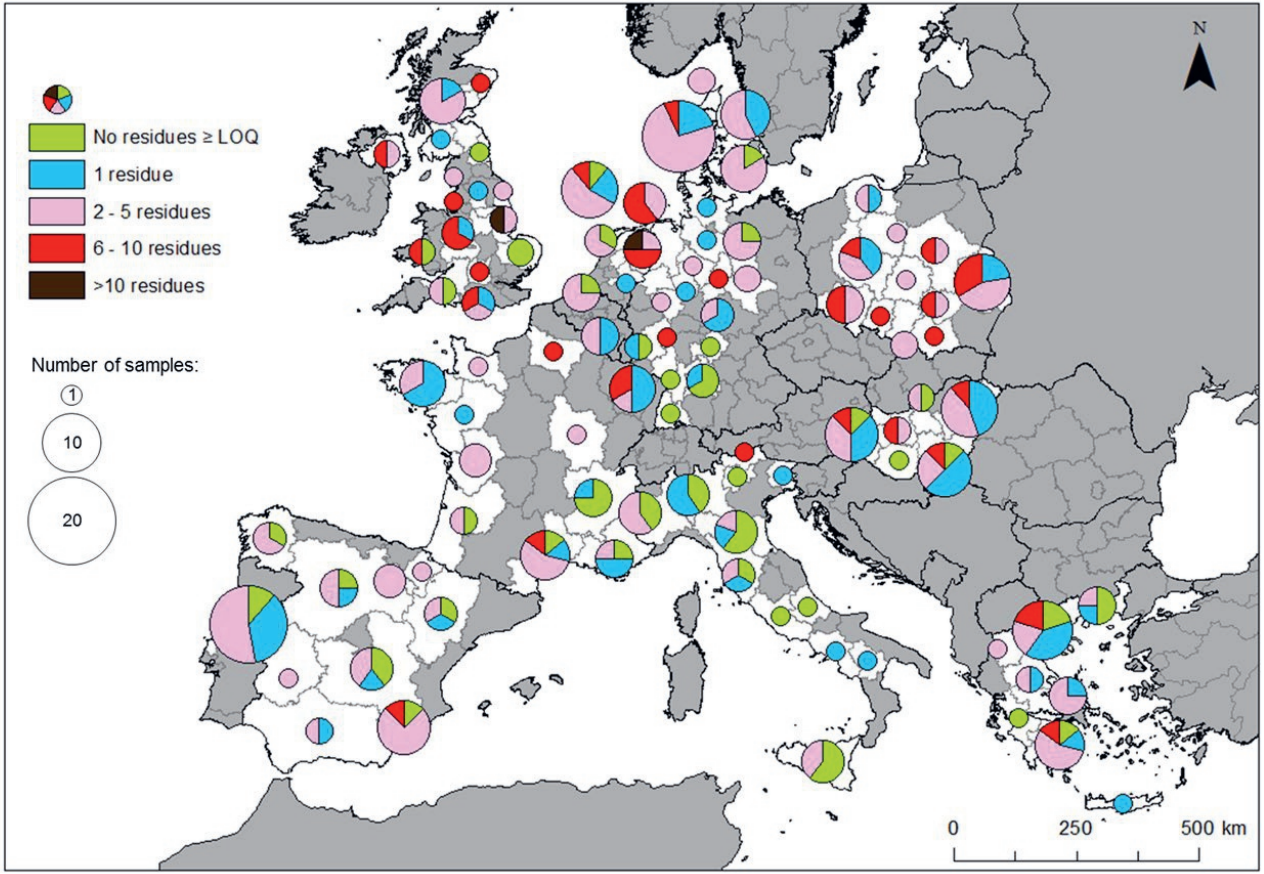


Figure 2.2 – Number of pesticide residues in EU agricultural topsoils at the NUTS 2 level. The pie-charts represents the proportion of soil samples with 0, 1 and multiple pesticide residues (2–5, 6–10, >10) in each NUTS 2 region. The size of the pie-charts represents the sampling effort by NUTS 2 regions, with bigger circles corresponding to a higher number of soil samples. NUTS 2 designations were not included in the map to improve readability, but they are provided in Figure S2.1. The white and grey areas in the map represent sampled and not-sampled NUTS2 regions, respectively.

2.3.2 Type of pesticide residues in soil

Overall, 43 different residues (approximately 57% of the tested analytes) were present in the tested soils (*Table S2.8*). European soils revealed a high diversity of pesticide combinations; a total of 166 pesticide combinations were observed in soils; 150 corresponded to mixtures of ≥ 2 residues (*Table S2.9*). The most common mixtures in soil were glyphosate (GLY) + AMPA and GLY + AMPA + phthalimide (PTI), both present in 2% of the samples (*Table S2.9*). GLY and AMPA were often combined with other pesticide residues; such mixtures corresponded to 25% of pesticide combinations in soil and 18% of the samples. Mixtures of GLY + AMPA + PTI and other residues were way less common, corresponding to 6% of pesticide combinations and 3% of the samples (*Table S2.9*).

Pesticide composition in soil varied among EU regions, countries and cropping systems. In North and East EU, the most common mixtures in soil included an organochlorinated compound (mostly DDE pp) + AMPA or PTI while in South and West EU, they included combinations of AMPA, GLY, PTI and FOLPET (FOL; *Table S2.10*). Country results were in line with respective EU region results (*Table S2.11*). In cereals, the most common mixture was DDE pp + PTI, in permanent crops AMPA + GLY and AMPA + GLY + PTI, and in the remaining classes, each pesticide mixture appeared just once (*Table S2.12*).

The majority (60%) of the pesticide residues present in the EU soils were non-persistent (DT_{50}< 30 days) or moderately persistent compounds (DT_{50}: 30–100 days). Persistent (DT_{50}: 100–365 days) and very persistent compounds (DT_{50}> 365 days) represented 16 and 23% of the residues found, respectively. Fourteen of the compounds present in soils were active substances or metabolites of active substances no longer approved in the EU markets at the time of sampling (e.g. DDTs, dieldrin or procymidone).

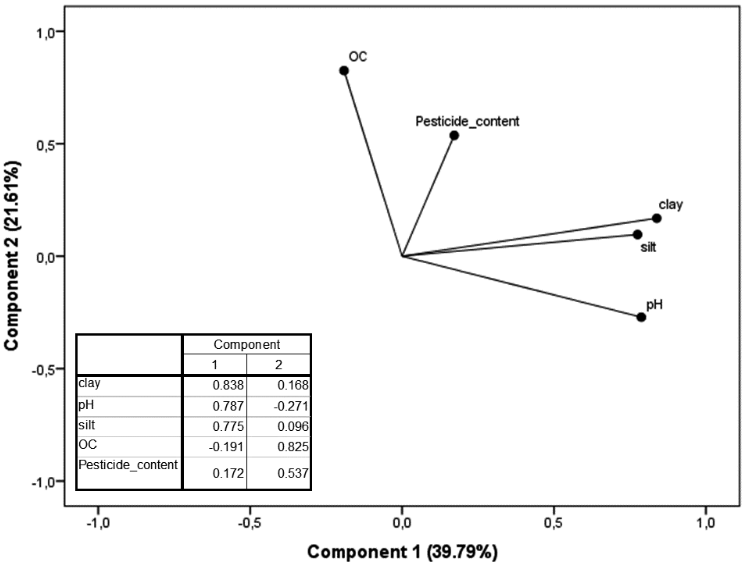
Only 7 compounds were quantified in more than 10% of the soil samples (*Table S2.8*): glyphosate, AMPA, DDE pp (a metabolite of the long since banned DDT), boscalid, epoxiconazole and tebuconazole (all broad-spectrum fungicides), and phthalimide [PTI; metabolite of the broad-spectrum fungicide folpet and a potential artifact; (Lach and Bruns, 2016)] AMPA was the most frequent compound in soils, present in 42% of the samples (*Table S2.8*).

2.3.3 Content of total pesticide residues in soil

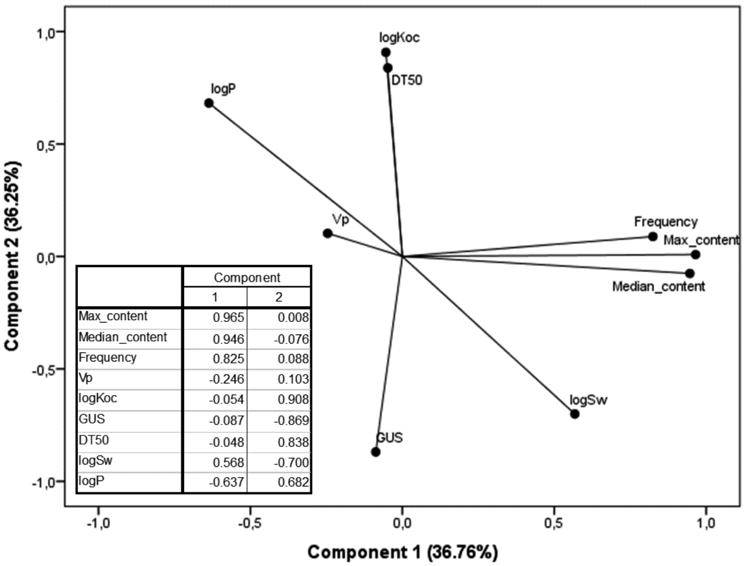
The soils containing quantifiable pesticide residues (246 out of 317) had a median and a maximum total pesticide content of 0.15 and 2.87 mg/kg, respectively (*Table S2.8*). *Fig. 2.3A* indicates that soil properties influence pesticide content in the soil, with organic carbon content showing a strong positive correlation with total pesticide content.

No significant differences were found in the total pesticide content among EU regions ($p=0.51$), but pesticide content varied significantly among EU countries ($p<0.01$) and cropping systems ($p=0.04$; *Fig. 2.4*). Despite having the highest frequency of pesticide-free soils, and significantly fewer pesticide residues in soil than the other EU regions, the Southern EU region had the highest frequency of soils with pesticide contents ≥1 mg/kg (11 versus the 3% of West EU, and the 2% of North and East EU; *Fig. 2.4*). The Portuguese soil samples presented the highest pesticide content by far, mostly attributed to glyphosate and AMPA content, with a median and a maximum total pesticide content of 1.99 and 2.87 mg/kg, respectively. Soils from Greece and Hungary had the lowest pesticide content, with median values of 0.04 and 0.05 mg/kg and with maximum values of 1.06 and 1.32 mg/kg, respectively. Pesticide content was ≥ 0.05 mg/kg in all the topsoil samples collected from the following NUTS 2 regions: UKF1, UKM5, DE91, DE92, DEA5, DEB1, FR22, FR26 and ITH1 (*Fig. 2.5*; but note that just one soil sample was analyzed in each of these regions).

Soils from permanent crops had the highest frequency of soils with total pesticide content ≥ 1 mg/kg (13%), and the highest pesticide content (2.87 mg/kg). Nevertheless, the highest median pesticide content was observed in soils with root crops (0.23 mg/kg; permanent crops had a median content of 0.19 mg/kg). Soil samples from dry pulses, flowers and fodder crops had the lowest median and the lowest maximum pesticide content, 0.09 and 0.36 mg/kg, respectively (*Fig. 2.4*).



	Component	
	1	2
clay	0.838	0.168
pH	0.787	-0.271
silt	0.775	0.096
OC	-0.191	0.825
Pesticide_content	0.172	0.537



	Component	
	1	2
Max_content	0.965	0.008
Median_content	0.946	-0.076
Frequency	0.825	0.088
Vp	-0.246	0.103
logKoc	-0.054	0.908
GUS	-0.087	-0.869
DT50	-0.048	0.838
logSw	0.568	-0.700
logP	-0.637	0.682

Figure 2.3 - Principal component analysis (PCA) of the frequency of detection and pesticide content in soil, and soil and pesticide properties. In (A), the total pesticide content is represented along with basic soil properties (number of soils containing quantifiable pesticide residues, Nq =246). In (B), the frequency and the median and maximum contents of the different pesticide residues quantified in soil are related to their pesticide properties (N pesticides=42). DT_{50}-soil half-life time; Koc-organic carbon-water partition coefficient (ml/g); LogP-octanol-water partition coefficient at pH 7 and 20 ºC; Sw-solubility in water at 20 ºC (mg/L); Vp-vapor pressure at 25ºC (mPa); GUS leaching potential index.

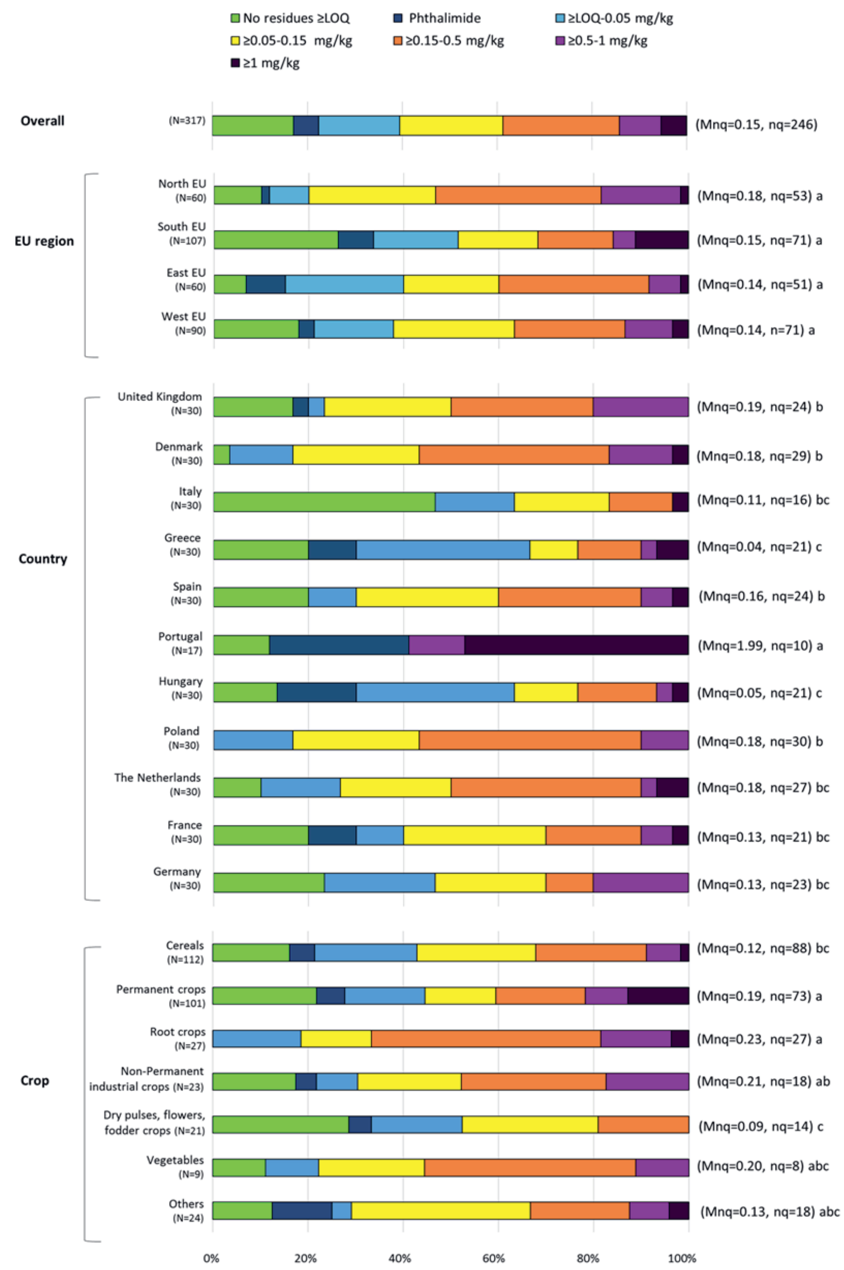


Figure 2.4 – Distribution of total pesticide content in the topsoil samples from different EU regions, countries and cropping systems, by content classes. The pesticide content classes thresholds of 0.05, 0.15, 0.5 and 1 mg/kg correspond, respectively, to the 22nd, 50th, 81st and 93rd content percentile of the samples containing quantifiable pesticide residues (nq=246). N number of tested samples; Mnq-median pesticide content in the soils containing quantifiable pesticide residues; nq–number of soils containing quantifiable pesticide residues. The lowercase letters in the right panel denote significant differences in pesticide content among EU regions, countries and crops.

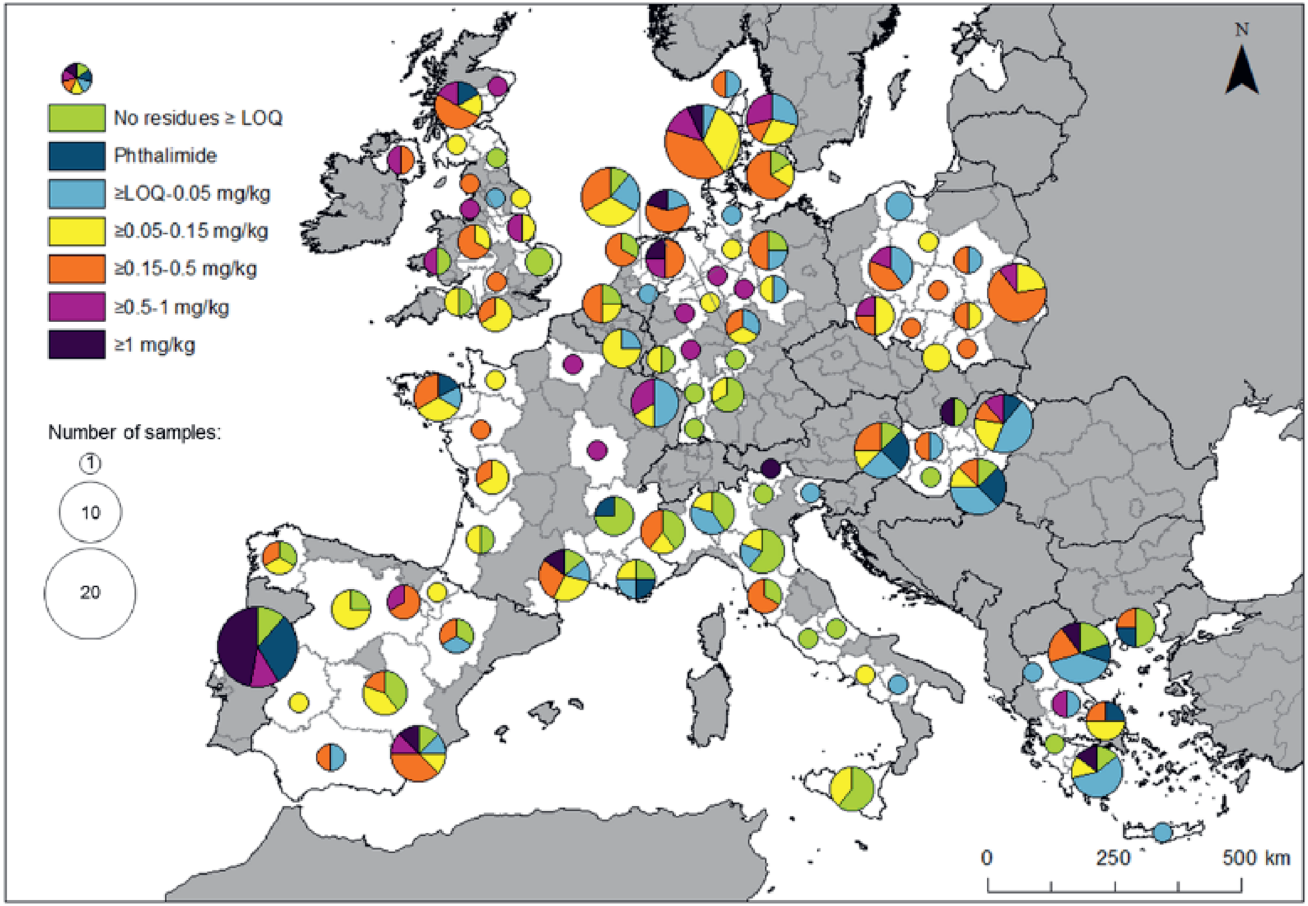


Figure 2.5 – Distribution of total pesticide contents in EU agricultural topsoils at the NUTS 2 level. The pie-charts represents the proportion of soil samples from each NUTS 2 region with pesticide content in each content class. The pesticide content class thresholds of 0.05, 0.15, 0.5 and 1 mg/kg correspond, respectively, to the 22nd, 50th, 81st and 93rd of the overall pesticide content in contaminated samples (nq=246). The size of the pie-charts represents the sampling effort by NUTS 2 regions. The number of topsoil samples tested in each NUTS 2 region is provided in Table S2.2.

2.3.4 Contribution of individual pesticide residues

The most common compounds in soils (present in >10% of soil samples), AMPA, boscalid, epoxiconazole, DDE pp, glyphosate and tebuconazole, also had the highest content in soil (*Table S2.8*). The levels of these pesticides in soil were weakly correlated with both soil and pesticide properties (*Table S2.13* and *Fig. 2.3B*, respectively).

Glyphosate and AMPA contributed the most to the total pesticide content in soils (*Fig. 2.6*), with a maximum content of 2.05 and 1.92 mg/kg, respectively (*Table S2.8*). Boscalid levels in soil were 3 to 5 times lower than those of glyphosate and AMPA, with a median and a maximum content of 0.04 and 0.41 mg/kg, respectively. DDE pp, epoxiconazole and tebuconazole had a median content of 0.02 mg/kg, with maximum values ranging from 0.16 to 0.31 mg/kg. The content of some less common compounds such as prothioconazole, azoxystrobin, linuron, difenoconazole, cymoxanil, chlorpyrifos and penconazole were comparable to those of DDE pp, epoxiconazole and tebuconazole (*Table S2.8*).

The measured content of the most common compounds in soil was often within or below their respective PECs range (i.e. initial PECs, long-term PECs and the accumulated PECs). Nevertheless, occasionally the measured content of glyphosate, epoxiconazole and of tebuconazole exceeded the respective PECs accumulated (*Fig. S2.2*, *Table S2.12*). Measured levels of glyphosate and epoxiconazole exceeded predicted levels for cereals (GLY: 0.34 and 0.60>0.03 mg/kg; EPI: 0.16>0.13 mg/kg), while for tebuconazole it occurred in samples from vineyards (0.19>0.12 mg/kg) and from oilseed rape (0.18>0.14 mg/kg). For both epoxiconazole and tebuconazole, the maximum measured values exceeded the PECs used in the TERs calculations for in-soil organisms. Nevertheless, as the maximum measured content of these residues in soil was very close to their highest PEC, the TERs from the approval reports of these substances and the TERs calculated with measured levels are very similar (*Table S2.15*).

Furthermore, measured DDTs' contents occasionally exceeded the screening values for DDTs (*Fig. S2.3*), namely the Italian limit for residential/public use (0.015 and 0.016 > 0.01 mg/kg), the Dutch target value (0.07, 0.05 and 0.04>0.01 mg/kg) and the permissible concentration for Polish agricultural topsoils (0.12, 0.06, 0.06, 0.05, 0.04, 0.04 and 0.03> 0.025 mg/kg).

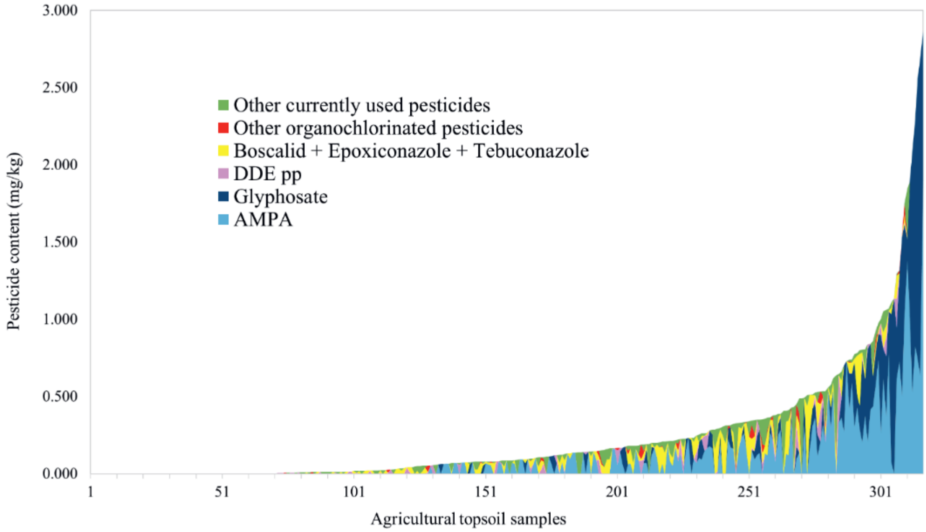


Figure 2.6 – Pesticide distribution across the 317 EU agricultural topsoil samples. Topsoil samples (numbered from 1 to 317) were organized by increasing total pesticide content.

2.4 Discussion

2.4.1. Pesticide residues in EU agricultural soils

The soils from the Southern EU regions presented the lowest number of pesticide residues and the highest pesticide content. The available data on pesticide use in arable land and on permanent crops in EU countries indicate that southern countries apply more pesticides than countries from other EU regions (FAO, 2014). Nevertheless, these data correspond to pesticide use from 2005-2009, and use patterns may have altered since then. Pesticide sales data from 2014-2015 [the year of the soils sampling and the year before that; (EUROSTAT, 2018)] indicate that Spain, Italy and France had some of the highest pesticide use in Europe, which might be a result of their larger agricultural area (FAO, 2014) and not of higher application rates in agricultural sites per se. As information on pesticide application is not available for the soil sampling points, and as other factors might have affected the pesticide results by country/region (e.g. different number of soil samples selected per crop system, different climate and soil conditions), no clear conclusions can be drawn between the diversity of products and pesticide use in the different EU regions and the occurrence and measured content of pesticide residues in soil.

The tested soils from root crops and permanent crops presented the highest pesticide contents, which is in line with the reported intensive pesticide use in these crops (Muthmann, 2007). However, more recent detailed data on pesticide use are required for robust interpretations of pesticide content in the soils of different crop systems. The production of food on soils containing pesticide residues is a concern with respect to the possible uptake of residues by the (following) crop. Although this is an aspect covered in pesticide registration requirements (rotational crop studies need to be carried out in certain cases), it may increase residue burden and is an issue in organic farming. According to the EFSA report (EFSA, 2018), 6.5% of the organic food samples analyzed during 2013-2015 from the EU Member States, Iceland and Norway contained pesticide residues. For conventionally produced food samples, this value was 44.5%. In total, 184 different pesticide residues were detected in the food samples (out of the 213 tested residues), including long since banned pesticides such as DDT, dieldrin, chlordane, heptachlor and hexachlorobenzene; residues which are also present in agricultural soils of the EU (this study).

As total pesticide content in soils is highly dependent on the number and type of residues analyzed, only the content of the individual pesticide residues was compared with other studies. Glyphosate and AMPA had the highest content in soil by far, with maximum values of 2.05 and 1.92 mg/kg, respectively. Our glyphosate measurements were in agreement with the range of concentrations observed in other European soils while our AMPA measurements were higher than those noted in the literature (see the range of other studies in *Table S2.14*). The predominance of glyphosate and AMPA in the tested soils is probably the result of the popularity of glyphosate-based herbicides and the higher application rate of these herbicides compared to other pesticides (*Table S2.14*).

Fungicide residues were also common in agricultural soils of the EU, namely boscalid, epoxiconazole, tebuconazole and phthalimide (> 10% of soils). The presence of boscalid, epoxiconazole and tebuconazole in soils is not unexpected since they are approved, broad-spectrum and moderately persistent or persistent fungicides. The content of these 3 compounds was below 0.5 mg/kg, corroborating the range of concentrations found in previous studies (see ranges in *Table S2.14*). As mentioned above, phthalimide is not only a metabolite of the approved broad-spectrum fungicide folpet but may also originate from other sources, e.g. a reaction product of phthalic anhydride with primary amines (Lach and Bruns, 2016). Therefore, interpretations of its presence in soil should be performed carefully.

The main insecticides detected in soils were DDTs. Soil contamination by DDTs has been widely studied in Europe (*Table S2.14*), with a maximum reported content of 5.83 mg/kg in topsoils from Romania (Ene et al., 2012), a much higher value than the maximum content of 0.31 mg/kg measured in this study. DDTs are some of the few pesticide residues for which screening values are available for almost all European countries. Nevertheless, the type of screening values and the admissible DDTs content in soil is country-specific (Carlon, 2007), hindering comparisons and generalizations on the extent of soil contamination. Neonicotinoid insecticides are highly discussed due to their negative effect on bees, and their use has recently been banned in the EU. Imidacloprid, the only neonicotinoid analyzed in this study, was present in 7% of the EU topsoil samples at a maximum content of 0.06 mg/kg.

2.4.2. Main limitations of the current risk assessment procedure

Pesticide risk assessment, performed according to EFSA regulations, is based on the comparison of toxicity exposure ratios (TERs) and trigger values. The adequacy of current TERs is discussed here by closely examining the two components of this ratio: the ecotoxicologically relevant concentrations for indicator species and the PECs values.

The potential toxic effects of single active substances and metabolites on in-soil organisms are evaluated in a limited number of standard tests, for the maximum exposures of 56 days. The indicator organisms [*Eisenia fetida, E. andrei, Folsomia candida, F. fimetaria, Hypoaspis aculeifer* and N transformation microorganisms; (Ockleford et al., 2017)] represent less than 0.005% of the more than 1 million species living in soil (FAO and ITPS, 2017). Ockleford et al. (2017) compared the sensitivity of current standard species to several pesticides with the sensitivity of other species from the same taxonomic group and concluded that standard species might not always be the most sensitive, resulting in an underestimating of pesticide toxicity in the EFSA procedures. This uncertainty should be accounted for in the risk assessment procedure, and an increase in the current trigger values for soil organisms should be considered.

Furthermore, community shifts are not addressed by EFSA, although changes in community structure are known to be the most significant effects of some pesticides (FAO and ITPS, 2017). The equilibrium between the organisms beneficial for plant growth and soil pathogens can be easily disturbed in cases where the two groups of organisms have different sensitivities to pesticide residues. For example, the abundance of *Pseudomonas fluorescens* diminishes after the application of glyphosate-based herbicides, which results in a dominance of the root pathogen *Fusarium* spp (Kremer and NE., 2009; Zobiole et al., 2011). Such community imbalances might adversely affect crop health and soil ecosystem services (Zobiole et al., 2011).

As shown by this study, the presence of multiple residues in the soil is the rule rather than the exception. However, no ecotoxicological endpoints are presented for mixtures in EFSA conclusion reports. Urgent attention is required to address the toxicity of the mixtures of residues present in the soil, especially considering the possibility of combined effects of different residues on different taxa, resulting in indirect effects on the structure and functioning of the community (SCHER et al., 2012).

Regarding the exposure assessment, PECs are calculated based on recommended application rates, which may not necessarily be the actual application rates. Actual application rates are often not available, especially for individual substances, and a validation of the PECs by field data is lacking. Some of our measurements exceed the highest PECs, which could be a result of the over-application of pesticides or the deposition of contaminated soil particles eroded from surrounding areas, a factor not considered in the PECs calculation. Such underestimations on levels of pesticide in soil translate into TER overestimations, and potentially into risk underestimations. In this study, as the measured concentrations of the most common pesticide residues in soil were almost always below or within the respective PECs range, the TER values from EFSA were the most conservative approach. In the few situations where the PECs used in TER calculations were exceeded by our pesticide measurements (namely for epoxiconazole and tebuconazole), the highest measured concentrations of these pesticides were very close to the highest PEC. Therefore, no major impact would be expected on the risk assessment of these substances. Nevertheless, since the application data in the sampling points were not available, the measured values in this study may or may not correspond to the highest field levels, immediately after pesticide application.

2.4.3. Limitations of this study and recommendations for future research

Using topsoil samples from an existing monitoring program, initially not focused on pesticides, brought some limitations to this study. For instance, information on farming systems is not available for the LUCAS soil sampling points, and was not a criterion in the sample selection. Such information could have provided interesting insights into the extent of soil contamination by pesticide residues for different farming systems.

The measured pesticide concentrations are average concentrations of the topsoil layer (0-15/20 cm). However, pesticide residues often accumulate on the soil surface. For example, the levels of AMPA and glyphosate can be up to 2 to 3 times higher in the top 1-2 cm of the soil surface layer than deeper in the profile (Laitinen et al., 2006; Yang et al., 2015). Underestimations of soil surface pesticide content will lead to underestimations of the potential export of pesticide residues to the surrounding environment by water and wind erosion processes and of the risk to soil quality (Silva et al., 2018). This limitation of average content for the top 15/20 cm soil layer is also common to EFSA predictions. PECs' initial values refer to the average content of the substance in the upper 5 cm of soil, while for background values it relates to a soil depth of 5 (permanent crops) or 20 cm (annual crops). Future assessments (field monitoring programs and PECs calculations) should consider residue distribution at different topsoil depths and should focus on the uppermost 1 cm of the soil surface layer, in particular.

As our soil sampling period (April-October) coincides with the recommended application period of several pesticides, the measured contents of currently applied pesticides may correspond to background levels (in case the pesticide was applied just after sampling), to the contents after a single or multiple pesticide applications (which could explain the big proportion of non-persistent compounds found in soils) or even to the accumulated content (in case of very persistent compounds). For this reason, the measured contents were compared against all the PECs values included in the respective active substances reports: PECs initial, long-term PECs and accumulated PECs. In future works, sampling in early spring, right before the first pesticide applications, should provide a better indication of background values of currently used pesticides (Hvězdová et al., 2018), an information that might be highly relevant for soil management.

Since measured pesticide data results of a single sampling time in 2015, the representativeness of data should be addressed. First, considering the large spatial scale covered in this study (and all the variability associated with it), it is unlikely that pesticide results are occasional or accidental. Then, as pesticide patterns are usually very similar among consecutive years our assessment of 2015 is most probably typical for the years immediately before and after the sampling. The plateau level of persistent and very persistent substances might oscillate slightly though: it is expected to increase with time for currently applied compounds, and to reduce for banned compounds. Another reason to believe that our results could be extrapolated for the current soil situation is the fact that none of the most relevant pesticides of this study (in terms of frequency and concentration in soil) was banned from EU markets since the sampling time. And the ones that had their approval extended in the meantime (glyphosate) kept the same recommended application rates. Of course, some very recently approved substances might have replaced some of the older approved ones but, as the use of individual active substances is not available in EU databases, it would be too speculative to assume significant changes in the pesticide products used by EU farmers in such a short period.

Despite the criteria used in sample selection intended to represent a realistic worst-case scenario, the selected samples represent most probably a mixture of field conditions. Although the samples originated from countries and crops with reported high pesticide use in the past, there is no certainty on how intensive pesticide application in the sampling points was. Furthermore, as information on farming systems is not available, some samples may have been collected in organic fields, with no or very regulated pesticide applications. Therefore, it is likely that some of the samples might have originated from agricultural fields with more intensive pesticide use and others from fields with less intensive use. Application data would be necessary to evaluate if the lower pesticide concentrations (at least of currently applied compounds) and the less complex mixtures correspond to fields with less intensive pesticide use.

The 76 prioritized pesticides residues analyzed in the EU agricultural topsoils correspond to less than 20% of the active substances available on the EU market, indicating that the total amount of pesticide residues in EU soils might even be higher than presented in this study and the actual residue mixtures even more extensive and complex, also with regard to possible effects on soil life.

Finally, harmonized EU soil protection policies are required to achieve sustainable food production. Such policies should not only address the introduction of a pesticide to the market (EC, 2009b) and the reduction of pesticide inputs (EU, 2009), but also the monitoring of actual pesticide residue content and pesticide composition in soils as well as the establishment of well-founded soil quality standards. For this purpose, the effects of mixtures of pesticide residues on soil biota require more attention and preferably should become one of the important indicators for approval of new products to the market. Additionally, more sustainable agronomic practices should be adopted to reduce pesticide applications and prevent further soil contamination. Erosion-related transport of contaminated soil particles to other areas, water bodies and the atmosphere requires particular attention. Pesticide residues should be also monitored in dust since contaminated small particle soil fractions, once emitted into the atmosphere, can be inhaled by humans and animals (Bento et al., 2017).

2.4.4. Main findings and implications

- A total of 76 pesticide residues (active substances and metabolites) were analyzed in 317 European agricultural topsoil samples; of those, 43 residues were detected (57%). Considering that we tested less than 20% of the active substances currently approved in the EU markets, pesticide residue occurrence in soils might be higher.

- Pesticide residues were present in 83% of the tested agricultural soils and 58% of the soils contained multiple residues. The presence of multiple pesticide residues in the soil environment is the rule rather than the exception.

- Pesticide composition varied greatly among individual soil samples, with a total of 166 different pesticide combinations. The toxic effects of actual pesticide mixtures on soil life are virtually unknown.

- Maximum total pesticide content in soil was 2.87 mg/kg. Glyphosate and its main metabolite AMPA contributed the most to the total pesticide content in soil. The measured content of individual pesticide residues in soil occasionally exceeded the related predicted environmental levels (PECs) from EFSA, raising concerns about whether PECs are realistic or conservative enough.

- Soil contamination by pesticide residues should be an integral aspect in the characterization of overall soil quality. Yet, so far, there is no EU legislation for thresholds or quality standards for total or individual pesticide residues in soil, accounting for potential effects on soil biota in the widest possible sense. Unfortunately, no adequate soil protection policies are yet in place to combat and reverse this hidden threat.

See supplementary materials on pages 177-224.

Acknowledgments

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Chapter 3

Distribution of glyphosate and aminomethylphosphonic acid (AMPA) in agricultural topsoils of the European Union

Abstract: *Approval for glyphosate-based herbicides in the European Union (EU) is under intense debate due to concern about their effects on the environment and human health. The occurrence of glyphosate residues in European water bodies is rather well documented whereas only a few, fragmented and outdated information is available for European soils. We provide the first large-scale assessment of the distribution (occurrence and concentrations) of glyphosate and its main metabolite aminomethylphosphonic acid (AMPA) in EU agricultural topsoils and estimate their potential spreading by wind and water erosion. Glyphosate and/or AMPA were present in 45% of the topsoils collected, originating from eleven countries and six crop systems, with a maximum concentration of 2 mg/kg. Several glyphosate and AMPA hotspots were identified across the EU. Soil loss rates (obtained from recently derived European maps) were used to estimate the potential export of glyphosate and AMPA by wind and water erosion. The estimated exports, the result of a conceptually simple model, clearly indicate that particulate transport can contribute to human and environmental exposure to herbicide residues. Residue threshold values in soils are urgently needed to define potential risks for soil health and off-site effects related to export by wind and water erosion.*

Based on:

Silva V, Montanarella L, Jones A, Fernandez-Ugalde O, Mol HGJ, Ritsema CJ, Geissen V. Distribution of glyphosate and aminomethylphosphonic acid (AMPA) in agricultural topsoils of the European Union. Science of the Total Environment 2018; 621: 1352-1359.

3.1 Introduction

Glyphosate (N-phosphonomethylglycine), the active substance in glyphosate-based herbicides (GlyBH), is up for renewal in the European Union (EU) as an ingredient in Plant Protection Products. All the active substances approved by the European Commission are re-evaluated after a certain period and the authorization for its use must be renewed for selling and application again. Within this context, an important prerequisite is that glyphosate should not adversely affect the environment and human and animal health (EC, 2009a). Currently, there is strong debate about the potential harmfulness of glyphosate [e.g., (EFSA, 2015a; IARC, 2015a; Myers et al., 2016a)], with some studies associating its use with cancer and endocrine disruption in humans and acute and chronic toxicity to aquatic species (Annett et al., 2014; Gasnier et al., 2009; Guyton et al., 2015; Mesnage et al., 2015; Thongprakaisang et al., 2013). The European Chemical Agency (ECHA) prepared a scientific opinion on the harmonized classification of glyphosate (ECHA, 2017), to be used as a decision base by the European Commission. According to ECHA (2017), glyphosate is not proven to be carcinogenic, mutagenic or negatively affect reproduction (e.g., reduction of fertility or occurrence of malformations), but it can cause serious eye damage and exert toxicity on aquatic biota, with long-lasting effects. ECHA's opinion is based on evaluating only glyphosate's hazardous properties, not addressing its levels in the different environmental compartments (atmosphere, aquatic and terrestrial ecosystems) or the likelihood of exposure and associated risks for humans and wildlife. Hazardous properties, potential exposure and risks of glyphosate's main metabolite aminomethylphosphonic acid (AMPA) have not been considered in the ECHA study at all.

GlyBH are intensively applied to agricultural fields, before planting the crop, pre- or post-harvest, in both conventional and in reduced/no-till farming, to control the growth of annual and perennial weeds. Minor non-agricultural applications (< 10% of global GlyBH use) include weed control in railway lines, parks and home gardens. The large fields of genetically modified soybeans, maize, canola, cotton and corn tolerant to glyphosate in the USA, Argentina and Brazil strongly contribute to the high amounts of GlyBH applied every year worldwide (Benbrook, 2016). In Europe, where no genetically modified crops are used, GlyBH are mainly applied to cereals (wheat, rye, triticale, barley and oats), oilseeds (rapeseed, mustard seed and linseed) and orchards and vineyards. Here GlyBH are usually applied one (cereals and oilseeds) to three times a year (orchard crops and vines), at recommended rates between 0.72 and 2.88 kg glyphosate/ha per treatment, and at a maximum annual application rate of 4.32 kg glyphosate/ha (EFSA, 2013; EFSA, 2015d).

Numerous laboratory and field studies have been performed to investigate glyphosate and/or AMPA behavior in more detail, especially their transport to the aquatic environment (Al, 2014; Borggaard and Gimsing, 2008; Daouk et al., 2013; Laitinen et al., 2009; Laitinen et al., 2006) indicating some recognition and concern that these substances can move towards surface waters. At the same time, glyphosate and AMPA are only sporadically detected in deep groundwater systems and at low concentrations (Battaglin et al., 2014; Horth, 2012; Poiger et al., 2016) indicating that the leaching of these compounds is generally unlikely and probably negligible. Although GlyBH use is almost limited to terrestrial application, information regarding the occurrence and cumulative and/or background levels of glyphosate residues in soils has received less attention, especially at the European scale. In fact, despite some recent studies on the distribution of glyphosate and AMPA in soils from Argentina (Aparicio et al., 2013; Lupi et al., 2015; Primost et al., 2017), U.S.A. (e.g., (Battaglin et al., 2014; Scribner et al., 2007) or Australia (Todorovic et al., 2014), in Europe, where the approval for GlyBH use will be decided by the end of 2017, information on occurrence and levels of these substances in the soil is still very limited and out of date (Grunewald et al., 2001; Laitinen et al., 2009; Laitinen et al., 2007; Laitinen et al., 2006). The European long-term use of GlyBH, as the most sold herbicide in Europe, urgently requires monitoring of residues in agricultural soils.

The lack of information on soil residues prevents proper evaluation of on-site soil pollution and proper risk estimation of potential particulate transport of these compounds by soil erosion processes to surrounding environments. Therefore, the main objective of this study is to evaluate the distribution (occurrence and concentrations) of glyphosate and its main metabolite AMPA in several agricultural topsoils across the EU, covering different locations and crop systems. Concentration data were also used for estimating potential export rates of these compounds by wind and water erosion, based on recently derived European soil loss maps (Borrelli et al., 2016; Panagos et al., 2015).

3.2 Materials and methods

3.2.1 The soil samples

Glyphosate and AMPA distributions were assessed in 317 topsoil samples: 300 samples from the LUCAS 2015 survey – Land Use/Cover Area Frame Survey, a harmonized assessment of topsoil characteristics across the EU Member States (Tóth et al., 2013), and 17 samples from three independent vineyards in north-central Portugal, where a parallel study on the transport of pesticide residues by water erosion was conducted (Zuilhof, 2016).

The samples from the LUCAS 2015 survey were collected between April and October of 2015 as described in ESTAT (2015a), and represent the uppermost 15/20 cm of soil. The samples selected for this work followed two main criteria: they were collected in i) the countries of each EU region with the highest percentage of agricultural area and pesticide use per hectare of arable and permanent croplands (FAO, 2013; FAO, 2014) and ii) the crops with the highest pesticide use per hectare or highest extension of cultivated area in those countries (Muthmann, 2007). Pesticide use included, but was not restricted to, GlyBH use since other pesticide residues were also analyzed in the samples. These sample selection criteria provide a worst-case estimate of the distribution of multiple pesticide residues in EU agricultural topsoils.

The countries selected by EU region were, from largest to smallest in order of pesticide dosage, in the northern region: United Kingdom (UK) and Denmark (DK); southern region: Italy (IT), Greece (EL) and Spain (ES); eastern region: Hungary (HU) and Poland (PL); western region: The Netherlands (NL), France (FR) and Germany (DE). The crops selected were: cereals (wheat, barley, rye, maize, triticale, oats), root crops (potatoes, sugar beet), non-permanent industrial crops (sunflower, rapeseed), dry pulses and fodder crops (floriculture, alfalfa, temporary grassland), permanent crops (citrus, vines, olives, other fruit trees and berries), vegetables (tomatoes, other fresh vegetables). Additionally, some bare soils which were croplands in the previous LUCAS 2009 and 2012 surveys were included in the category others. The exhaustive list of crops within each LUCAS category is available in (E4 LUCAS (ESTAT), 2015b). Not all the crops of each category were covered by the samples selected for this study; the covered ones are listed between brackets. Preference was then given to samples having the same land cover in previous

LUCAS surveys and from different regions. All EU Member States are subdivided into regions, according to the Nomenclature of Territorial Units for Statistics (NUTS) classification, to ensure comparable regional statistics. The NUTS classification includes three hierarchical levels: NUTS 1 - major socio-economic regions, NUTS 2 - basic regions for the application of regional policies, and NUTS 3 - small regions for specific diagnoses (EUROSTAT, 2015b). In this study, results are presented for basic regions (NUTS 2), defined according to the NUTS 2013 classification. The distribution of samples by country, NUTS 2 region and crop system is present in *Table S3.1*.

The samples from the LUCAS 2015 survey were air-dried and stored in the Joint Research Centre (JRC) installations in Ispra, Italy. The 300 LUCAS samples selected for this study were homogenized (by stirring the soil with a spoon until obtaining a visually homogeneous sample) and sub-samples (of approximately 50 grams dry weight) were collected for pesticide analysis. The sub-samples were sieved with a 2-mm sieve and frozen until chemical analysis. The Portuguese (PT) soil samples were collected in September of 2015, also following the method described in ESTAT (2015a), and treated as the LUCAS (sub-)samples, i.e. air dried, 2-mm sieved and frozen until chemical analysis.

3.2.2. Glyphosate and AMPA analysis

The day before the analytical determinations, the soil samples were thawed and homogenized as described above for the selected LUCAS samples. Two aliquots of 2 grams were collected from each sample. Glyphosate and AMPA concentrations were determined in the aliquots through HPLC-MS/MS using the same extraction and derivatization method, chemicals, mobile phases, column characteristics and instrumentation conditions as described in Bento et al. (2016) and Yang et al. (2015).

All the validation parameters and quality control criteria were in line with those described in the guidance document for pesticides residues analysis in food and feed (EC, 2015a). Briefly, glyphosate and AMPA analytes were identified according to the retention time and peak shape of isotopically-labeled internal standards, glyphosate (1,2-^{13}C,^{15}N) and AMPA (^{13}C,^{15}N). Two transitions were measured by analyte [the quantification (Qn) and confirmation transitions (Ql)], and all positive results/samples presented an ion ratio of the two transitions within ± 30% of the mean ion ratio of the solvent standards. The responses of the analytes were normalized according to the response of the isotopically-labeled internal standards. Glyphosate and AMPA concentrations were calculated based on one-point calibration, the solvent standard of 0.1 μg/ml, which was analyzed every 10–15 injections/samples. A calibration curve (of the solvent standards 0, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1 and 2 μg/ml) was injected at the start, middle and end of the sample sequences. All calibration curves presented satisfactory linearity of response versus concentration, with correlation coefficients ≥0.99 and individual residuals within ± 20%. Blank soil standards fortified with a mixture of glyphosate and AMPA standards (0.25 μg/g) presented a recovery of both analytes between 70 and 120%. Similar recovery values (75–120%) were observed in soil samples fortified with the same mixture of glyphosate and AMPA standards (a third aliquot was prepared from approximately 10% of the soil samples). The concentration of glyphosate and AMPA measured in each of the two aliquots (replicates) collected per sample was typically within ± 30%, and always within ± 35%, the mean concentration of both aliquots. The mean concentrations of glyphosate and AMPA of aliquots were adopted as the concentrations of the sample. The limit of detection (LOD) of glyphosate and AMPA were 0.02 and 0.03 mg/kg, respectively, while the limit of quantification (LOQ) of both compounds was 0.05 mg/kg.

3.2.3. Data analysis

Only measurements/samples with glyphosate or AMPA (≥ the LOQ 0.05 mg/kg) were considered in the data analysis. Distribution of the concentrations of glyphosate and AMPA in the soils were presented in box-and-whisker plots per country and crop systems. Normality and homogeneity of variances of glyphosate and AMPA concentrations were tested with, respectively, Shapiro-Wilk W and Levine's tests. As the parametric assumptions were not met, even after log, ln, square root or arcsine transformation, differences among EU regions, countries and crop systems were tested with Kruskal-Wallis H tests. In the presence of significant differences ($p < 0.05$), a Pairwise Mann-Witney U test with Bonferroni corrections was performed to test differences between each two EU regions, countries or crop systems. The box-and-whisker plots and the statistical analyses were performed using SPSS 22.0.

Wind erosion rates in European agricultural soils were estimated by Borrelli et al., (2016) using a GIS version of the Revised Wind Erosion Equation model (GIS-RWEQ) while Panagos et al. (2015) used a modified version of the Revised Universal Soil

Loss Equation (RUSLE) model to estimate water erosion rates in Europe. The complete wind and water erosion datasets are available via the European Soil Data Centre (ESDAC, 2017). Glyphosate and AMPA concentration data is represented at the basic region NUTS2 level and not on exact locations due to privacy issues, and plotted together with erosion rates (although the different time scales; the erosion maps are annual maps and the soil samples were from a single time point) to indicate immediately if high concentrations in soil appear in areas vulnerable to wind and water erosion, to present a first idea of the dimension of the potential problem which was relevant to be further studied. Since the application pattern of GlyBH in croplands is similar each year, it is expected that concentration data is representative of the normal, recurrent soil situation. The maps of frequency of detection and maximum concentration of glyphosate and AMPA by NUTS 2 region were produced in ArcGIS 10.4.1.

To estimate the potential export of glyphosate and AMPA to other locations, glyphosate and AMPA concentrations in topsoils were multiplied by the potential annual soil loss rates from wind and water erosion at the sample collection points (extracted with ArcGIS from soil loss by wind and water erosion datasets). Export values were obtained for individual soil sampling points, if glyphosate or AMPA concentration in soil was ≥ 0.05 mg/kg and wind or water erosion > 0 Mg/ha/year. Export rates of individual soil sampling points were then aggregated by (i) content of residues in soil, i.e. low to medium (defined in this study as 0.05 – 0.5 mg/kg) or high glyphosate or AMPA contents (> 0.5 mg/kg), (ii) EU region, (iii) country, (iv) NUTS 2 region and (v) crop system. The threshold of 0.5 mg/kg used in this work corresponds to the 80th and 85th percentile of glyphosate and AMPA overall concentrations, respectively. The proportion of AMPA to glyphosate in soil was determined for each sample containing glyphosate and/or AMPA (≥ 0.05 mg/kg), as the ratio of AMPA concentration in soil to the combined glyphosate and AMPA concentration in the soil, [AMPA / (Glyphosate + AMPA)]*100.

3.3 Results and discussion

3.3.1. Overall distribution of glyphosate and AMPA in topsoils

Glyphosate and/or AMPA were present (≥ 0.05 mg/kg) in nearly half (45%) of the soil samples, with 18% of the tested soils containing both compounds. AMPA was the predominant form, being present in 42% of the soils while glyphosate was present in 21%. Both compounds were present at higher frequencies in northern soils, while eastern and southern regions generally had the most glyphosate- and AMPA-free soils (< 0.05 mg/kg), respectively. At national levels, the frequency of soils with glyphosate ranged from 7% in Poland to 53% in Portugal, while the frequency of soils with AMPA ranged from 17% in Italy and Greece to 80% in Denmark (*Fig. 3.1A* and *Table S3.2*). Samples from permanent crops and root crops had the highest frequency of soils with glyphosate and AMPA (30 and 52%, respectively), and dry pulses and fodder crops had the lowest for both compounds (5 and 29%, respectively, see *Fig. 3.1B* and *Table S3.2*).

The highest concentrations of glyphosate and AMPA in soil were observed in southern parts of the EU (*Fig. 3.1C* and *Table S3.2*), suggesting higher application rates of GlyBH in this region. Nevertheless, only concentrations of glyphosate were significantly higher in this region [glyphosate: Kruskal-Wallis (H) = 3.03, degrees of freedom (df) = 3, $p < 0.001$, n = 67; AMPA: H = 20.50, df = 3, $p = 0.387$, n = 133]. Soils from southern parts of the EU also presented the lowest proportion of AMPA (*Table S3.2*), suggesting more recent GlyBH applications and/or slower degradation of glyphosate into AMPA under drier conditions. Portuguese topsoils (all from vineyards) presented significantly higher amounts of glyphosate (H = 31.97, df = 10, $p < 0.001$, n = 67) and AMPA (H = 27.73, df = 10, $p = 0.02$, n = 133) than the other countries, with both compounds reaching concentrations as high as 2 mg/kg (*Fig. 3.1* and *Table S3.2*). NUTS 2 regions such as FR71, EL51, NL23, ES24 or ITC4 seem to contain low herbicide residues or be residue-free (< 0.05 mg/kg). Other NUTS 2 regions, including DK04, HU10, ES62, PT16 and ITH1, appear to have hotspots of glyphosate and/or AMPA contamination (> 0.5 mg/kg; *Fig. 3.2* and *Table S3.3*).

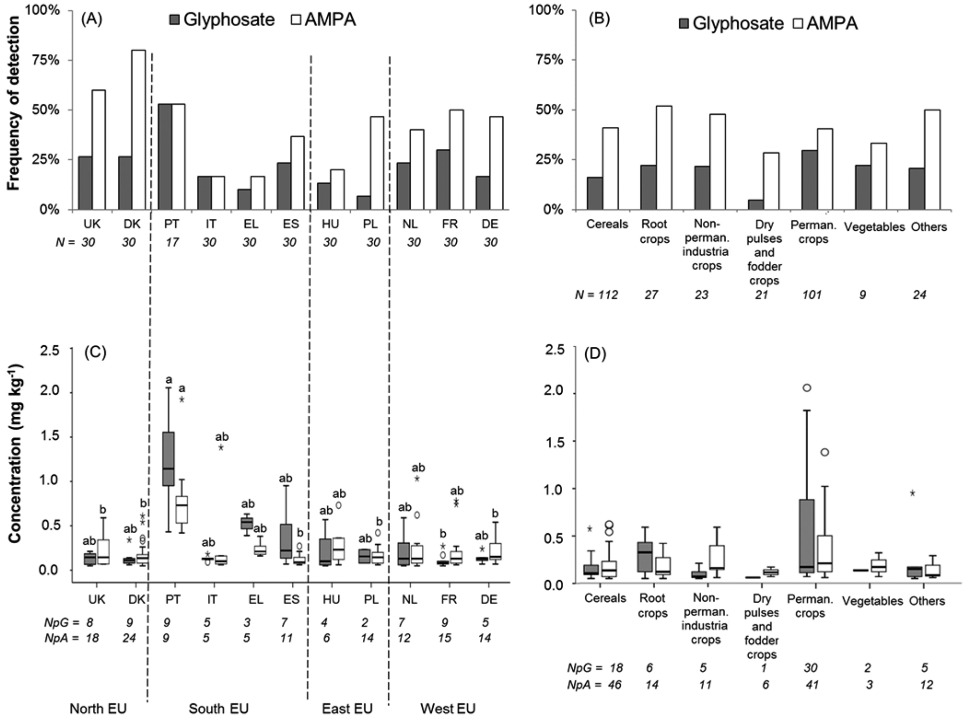

Figure 3.3 - Overall distribution of glyphosate and AMPA in EU topsoils (0-15/20 cm). Frequency of detection of glyphosate and AMPA (≥ 0.05 mg/kg) in soils from different (A) EU countries and (B) crop systems. Box-and-whisker plot representation of the distribution of glyphosate and AMPA contents in soils by the same factors: (C) country and (D) crop system. Only measurements ≥ 0.05 mg/kg were considered in the box-and-whisker plots. Each box represents the 25th percentile, median and 75th percentile. Whiskers represent 1.5 times the interquartile range or minimum and maximum concentrations of glyphosate or AMPA. Outliers (1.5 – 3 times the interquartile range) are marked with points and extreme outliers (> 3 times the interquartile range) with asterisks. Different letters represent significant differences [($p < 0.05$): a>b] in glyphosate or AMPA concentrations between countries or crop systems. N – number of samples tested, Np= number of positive samples ≥ 0.05 mg/kg, G – glyphosate, A – AMPA.

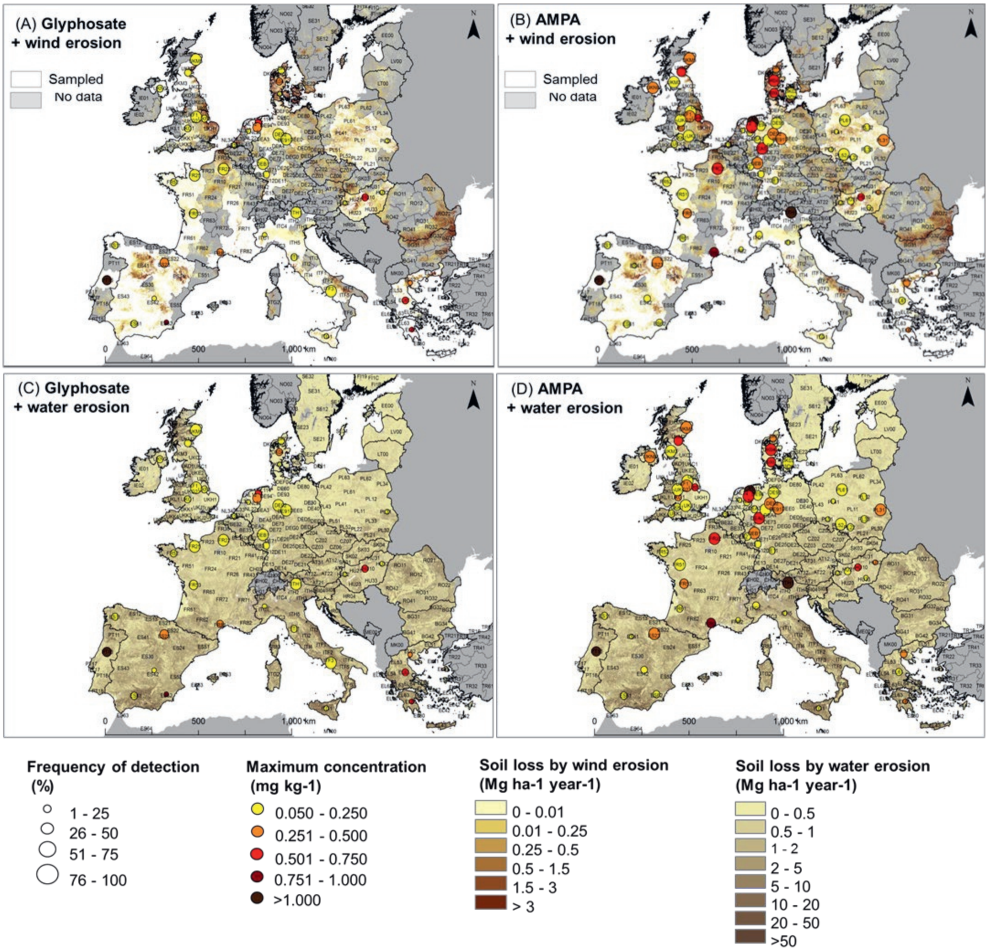

Figure 3.4 - Frequency of detection of glyphosate and AMPA and respective maximum concentrations in EU agricultural topsoils (0-15/20 cm) by NUTS 2 region, imposed on maps of soil loss by wind and water erosion. Circles in a NUTS 2 region indicate at least one soil sample containing glyphosate or AMPA (≥ 0.05 mg/kg).

Glyphosate and AMPA contents in soil were highest under permanent crops and lowest with dry pulses and fodder crops (*Fig.3.1D* and *Table S3.2*), yet no significant effect of the crop system was observed (glyphosate: H = 10.29, df = 6, p = 0.113, n = 67; AMPA: H = 11.57, df = 6, p = 0.72, n = 133).Vineyards presented the highest concentrations of glyphosate, yet at lower levels than those expected in the soil of this crop, with a maximum predicted environmental concentration (PEC) of 3.06–4.60 mg/kg. On the other hand, the measured glyphosate concentrations in cereals occasionally exceed the respective maximum PECs value of 0.30 mg/kg (EFSA, 2013). Maximum PECs values for AMPA, of 3.08–6.18 mg/kg, available only for the worst-case scenario of a single application of 4.32 kg glyphosate/ha, were never exceeded. Discrepancies between field-measured concentrations and maximum PECs values probably result from an application regime by the farmers different from the recommended (in terms of the number of treatments and the amounts applied), of the growth stage (and interception) of the crop, or different edaphic, management or environmental conditions. In the calculation of PECs values, a worst-case interception of 90% (cereals) and 0% (orchards and vineyards), a fixed bulk density of 1.5 g/cm^3, a tillage depth of 5 cm (permanent crops) or 20 cm (annual crops) and a half-life time (DT_{50}) of 143.3 days for glyphosate and of 514.9 days AMPA are assumed (EFSA, 2013).

3.3.2. Off-site transport by wind and water erosion

In areas with low to medium glyphosate or AMPA contents in soil (0.05–0.5 mg/kg), estimated glyphosate and AMPA removal by wind erosion reaches 1.9 g/ha/year, while in areas with contents in soil > 0.50 mg/kg export could exceed 3.0 g/ha/year. Water erosion could lead to higher potential losses/exports of glyphosate and AMPA, with estimated maximum exports of 9.8 g/ha/year in soils with low to medium herbicide contents, and of 47.7 g/ha/year in soils with higher contents (*Fig.3.3A* and *Tables S3.4* and *S3.5*). The highest export potentials are observed in Southern parts of the EU (*Fig. 3.3B* and *Tables S3.4–S3.7*), in areas highly vulnerable to water erosion. Different crop systems, with different soil covers, lead to different transport potentials of glyphosate and AMPA: non-permanent industrial crops and root crops show the highest potential exports through wind erosion, while permanent crops and cereals present the highest exports through water erosion (*Fig. 3.3C* and *Tables S3.4* and *S3.5*).

A ratio between these potential exports and the typical GlyBH application rates (the exact application rates in the soil sampling points are not known) could indicate the % of the initially applied products lost by erosion processes, potentially reaching water systems and the atmosphere. The highest estimated potential export of glyphosate by water erosion (5.7 g/ha/year; *Table S3.4*), for example, would correspond to a loss of 0.13% of the recommended maximum application rate of 4.32 kg glyphosate/ha/year. As only glyphosate is applied to fields, no ratio can be calculated for AMPA, the most common compound in soils. Furthermore, such ratio can lead to misleading results because glyphosate and AMPA are persistent compounds in soil, and their concentrations in soil (the ones used to estimate the potential exports by wind and water erosion) often result of more than one year of treatments. Therefore, the ratio should consider not only the amount applied but also the amount accumulated from previous treatments.

Recent experimental and monitoring studies confirm wind-driven transport of glyphosate and AMPA (Bento et al., 2017; Farenhorst et al., 2015; Lamprea and Ruban, 2011; Quaghebeur et al., 2004). Bento et al. (2017) demonstrated in a wind tunnel experiment that contents of AMPA and especially of glyphosate were particularly high (respectively > 0.6 and > 15 µg/g) in the finest soil particle fractions (< 10 µm), which can be inhaled by humans directly. In addition, both glyphosate and AMPA were often (>50%) detected in air samples collected from agricultural areas in the U.S.A, reaching concentrations of respectively 9.1 and 0.97 ng/m^3 (Chang et al., 2011). The presence of glyphosate in the atmosphere can result of spray drift during the application and/or wind erosion of contaminated soil particles. However, for AMPA, which is formed in soil, wind erosion is the only source. The contribution of wind erosion to the atmospheric concentration of glyphosate is still unknown. In a comprehensive environmental survey conducted in the U.S.A., Battaglin et al. (2014) observed the presence of glyphosate and AMPA in over 70% of the precipitation samples analyzed, at maximum concentrations of respectively 2.5 and 0.5 µg/L. In Europe, lower frequencies of detection are reported, with glyphosate and AMPA present in respectively 10 and 13% of the rainwater samples, but with higher maximum concentrations, 6.2 and 1.2 µg/L, respectively (Quaghebeur et al., 2004). Glyphosate is supposed to degrade rapidly in the atmosphere by photochemical oxidative degradation (EFSA, 2013), but the results from air and rain analyses indicate that glyphosate and AMPA can persist in the atmosphere and can be washed out and redistributed by rain (wet deposition).

Particulate transport via water erosion is an important pathway for glyphosate and AMPA toward surface water bodies (Todorovic et al., 2014; Yang et al., 2015). In fact, after a 60 minutes rain simulation at a rain intensity of 1 mm/min, Yang et al. (2015) observed that 4-5% of the initially applied glyphosate was lost/transported by runoff in the dissolved phase while 8-11% of the applied glyphosate was transported by the suspended load. Glyphosate and AMPA are frequently detected in U.S. large rivers (53-89%, respectively), streams (53-72%, respectively), lakes, ponds and wetlands (34-30%, respectively) at maximum levels of respectively 300 and 48 µg/L (Battaglin et al., 2014). In Europe, glyphosate and AMPA have been analyzed in respectively 75,350 and 57,112 surface water samples and detected in

33 and 54% of the samples at levels up to 370 µg/L and >200 µg/L (Horth, 2012). Correlations between these concentrations in waters and the concentrations measured in this study in soils would be too speculative given the different time collection and location between the information that is available for glyphosate in streams and the soil samples analyzed for this study. However, the spatial relationship between erosion rates and pesticide distribution in soils and water bodies should be further explored. Particulate transport processes are particularly important for the off-site transport of pesticides strongly adsorbed to soil particles, just like glyphosate and AMPA. Quantification of the extent of transport off the field to surface waters (or to the atmosphere) should be explored, too. It should be noted that current EU legislation presents environmental quality standards in the field of water policy for only some pesticides, not including glyphosate or AMPA (EC, 2013).

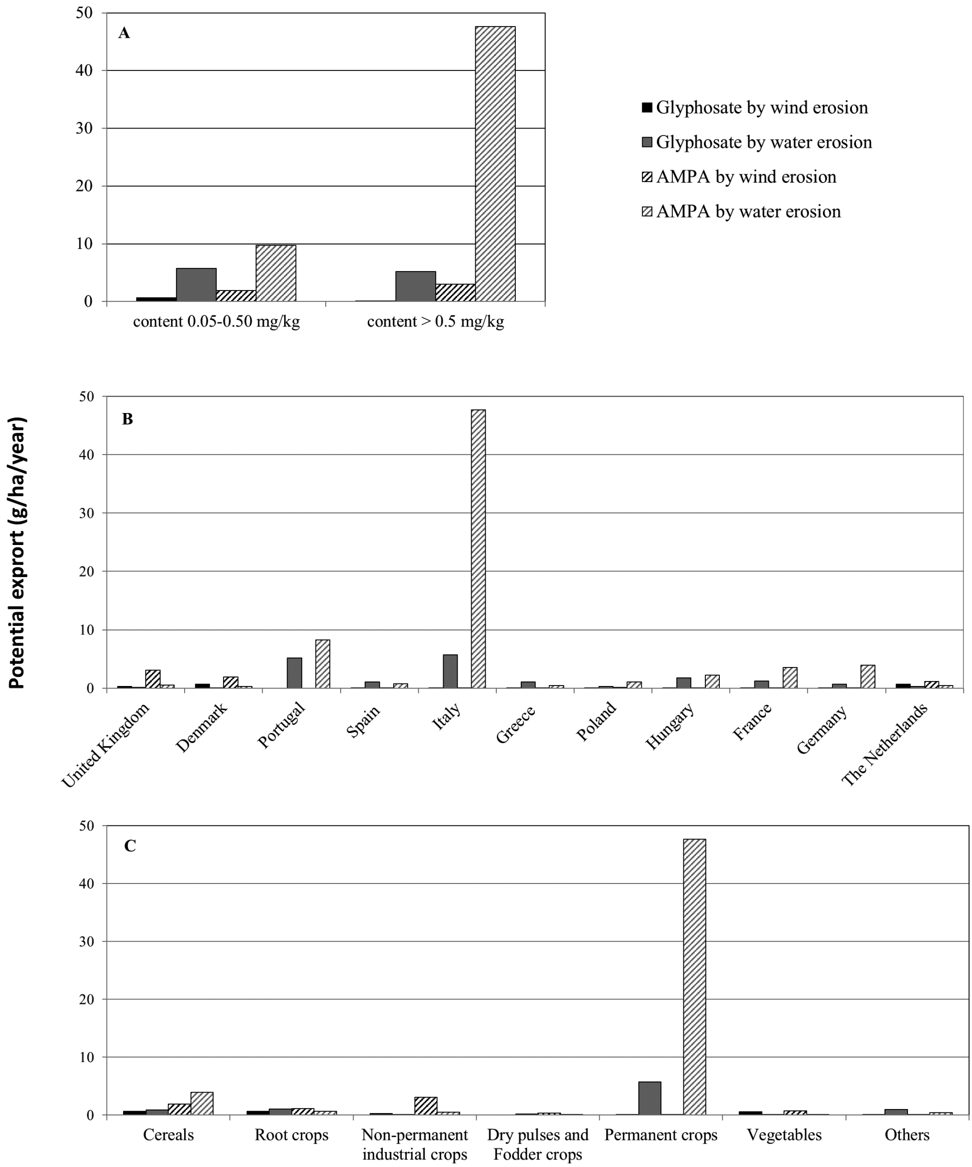

Figure 3.5 - Potential export of glyphosate and AMPA by wind and water erosion. Maximum export estimations according to (A) glyphosate or AMPA content in topsoil, (B) country and (C) crop system. Perm. – Permanent.

3.3.3 Implications for exposure and risk assessment

Within the context of this study, some considerations can be made. First, soil samples used in this study were collected during the spring and summer of 2015. No information is available regarding prior GlyBH application dates and rates per sample location, indicating that the 317 samples represent a mixture of real-field conditions, ranging from samples with no trace of glyphosate and/or AMPA to samples with very high levels. Despite the EC recommendations on the frequency of treatments and application rates, information on the actual use/sales of GlyBH in the EU, or of the active substance glyphosate, is not available and the amounts applied per crop system is confidential in almost all countries (Muthmann, 2007).

The half-life times of glyphosate and AMPA, also of importance in the respect of the amounts found in soils, are highly variable, ranging from a few days up to one or two years, depending on edaphic and environmental conditions, namely temperature and soil moisture (Bento et al., 2016; EFSA, 2013). AMPA is more persistent than glyphosate, and the degradation of both compounds is slower in colder and dryer conditions (Bento et al., 2016). The drier soils in the southern EU might then explain the higher glyphosate ratio found there.

Second, it is well-known that glyphosate and AMPA strongly adsorb and accumulate in the top centimeter(s) of soils (Laitinen et al., 2006; Okada et al., 2016; Yang et al., 2015). As glyphosate and AMPA contents determined in this study are average values for entire topsoil layers up to 15/20 cm depth (a consequence of using topsoil samples from an already established survey), actual contents in the surface layer could be higher than the determined average, implying that the presented potential erosion-driven transport rates of glyphosate and AMPA could be underestimated. The distribution of glyphosate and AMPA at the surface layer (the region most prone to soil erosion) and within topsoil should be considered in future work and should cover different soil management practices, as tillage results in the incorporation of contaminants accumulated on soil surface into deeper layers.

Third, pesticide residues transported by wind and water erosion do not necessarily end up in the atmosphere and surface water systems alone; other land and even ocean regions can be reached by such phenomena, with deposition of transported compounds as a result (DeSutter et al., 1998; Mercurio et al., 2014). This stresses the need for better monitoring of the occurrence and spatial distribution of glyphosate and AMPA across the interlinked environmental domains of soil, water and air.

Fourth, from a regulatory and legislation perspective, greater effort is needed to more thoroughly assess glyphosate and AMPA contents in soils, define critical limits to protect soil quality and soil biodiversity, and minimize the risk of further distribution of these compounds by wind and water erosion. Some EU countries have legislation and screening values for pesticide residues in soil but they are mainly limited to persistent organochloride pesticides (Carlon, 2007). Air quality monitoring programs should also target pesticide residues in transported soil dust, in particular glyphosate and AMPA, and the potential risk of inhalation by humans.

Despite its limitations, the results of this study are concerning; high levels of glyphosate of its main metabolite AMPA have been often detected in agricultural soils across the EU. The presence of glyphosate and AMPA in agricultural soils may not only form a risk for soil health but also a potential risk of further spreading of these compounds across land, water, and air domains. Indeed, besides potential effects on local edaphic communities and humans (that can be exposed to these substances by inhalation of contaminated dust particles, dermal contact or ingestion of contaminated surface water), wind and water erosion have the potential to transport contaminants to all the environmental compartments. This information should be fully accounted for in reconsidering the approval and use of GlyBH. Additional efforts should be made to fully quantify the extent of soil contamination by glyphosate residues in agricultural soils worldwide and to assess the related risk for humans and the environment.

See supplementary materials on pages 225-235.

Acknowledgments

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Chapter 4

Cocktails of pesticide residues in conventional and organic farming systems in Europe: legacy of the past and turning point for the future

Abstract: *Considering that pesticides have been used in Europe for over 70 years, a system for monitoring pesticide residues in EU soils and their effects on soil health is long overdue. In an attempt to address this problem, we tested 340 EU agricultural topsoil samples for multiple pesticide residues. These samples originated from 4 representative EU case study sites (CSS), which covered 3 countries and four of the main EU crops: vegetable and orange production in Spain (S-V and S-O, respectively), grape production in Portugal (P-G), and potato production in the Netherlands (N-P). Soil samples were collected between 2015 and 2018 after harvest or before the start of the growing season, depending on the CSS. Conventional and organic farming results were compared in S-V, S-O and N-P. Soils from conventional farms presented mostly mixtures of pesticide residues, with a maximum of 16 residues/sample. Soils from organic farms had significantly fewer residues, with a maximum of 5 residues/sample. The residues with the highest frequency of detection and the highest content in soil were herbicides: glyphosate and its main metabolite AMPA (P-G, N-P, S-O), and pendimethalin (S-V). Total residue content in soil reached values of 0.8 mg/kg for S-V, 2 mg/kg for S-O and N-P, and 12 mg/kg for P-G. Organic soils presented 70-90% lower residue concentrations than the corresponding conventional soils. There is a severe knowledge gap concerning the effects of the accumulated and complex mixtures of pesticide residues found in soil on soil biota and soil health. Safety benchmarks should be defined and introduced into (soil) legislation as soon as possible. Furthermore, the process of transitioning to organic farming should take into consideration the residue mixtures at the conversion time and their residence time in soil.*

Based on:

Geissen V, Silva V, Lwanga EH, Beriot N, Oostindie K, Bin Z, Pyne E, Busink S, Zomer P, Mol H, Ritsema CJ. Cocktails of pesticide residues in conventional and organic farming systems in Europe – Legacy of the past and turning point for the future. Environmental Pollution 2021; 278.

4.1 Introduction

Farming systems in Europe rely strongly on the use of pesticides to secure yields in plant production and animal husbandry, with farmers using an average of 340,000 to 370,000 tons of active substances annually (FAOSTAT, 2019). As a result of such intensive pesticide use, multiple pesticide residues are commonly found in soil (Silva et al., 2019), water (Casado et al., 2019), food and feed (EFSA, 2020), and humans (Bevan et al., 2017). Of the 487 active substances approved for sale in the EU market (EU Pesticides database, 2021), almost 50% are bioaccumulative, 25% are persistent in soil [DT_{50}> 100 days; (PPDB, 2021)], 30% have a high acute aquatic toxicity, and 28 are suspected carcinogens (EC, 2008b). These and other related figures raise serious concerns about the impact of pesticides on the health of ecosystems, animals and humans.

The effects of pesticides on organisms are assessed following European Food Safety Authority (EFSA), Organisation for Economic Co-operation and Development (OECD) and International Standards Organisation (ISO) standards and guidance documents, which relate to the direct effects of individual active substances on single species. Similarly, pre-market approval of new pesticides is focused on the risks and impacts of individual active substances and pesticide formulations. Current pesticide approval protocols take into account only a limited range of environmental and health indicators and non-target organisms. A recent EFSA report (2019) describes procedures for the assessment of the effects of mixtures. However, data and procedures relating to the long-term effects of pesticide residues' mixtures on non-standard and native species and communities are not yet available. In the meantime, serious pesticide adverse effects have been observed in different taxa, including beneficial insects and pollinators (Grubisic et al., 2018; Sánchez-Bayo and Wyckhuys, 2019). For example, neonicotinoids have been proven to cause bee mortality (Colin et al., 2019) and are therefore restricted in Europe. Additionally, recent studies have shown that the changes in the gut microbiome of bees following glyphosate exposure reduce resilience, making the bees more susceptible to diseases (Motta et al., 2018). Although scientists have discussed the idea that pesticide use is one of the main reasons for the decline of beneficial insects and pollinators (Lamb et al., 2017), scientific knowledge about the effects of mixtures of pesticides with different modes of action remains very limited.

The effects of mixtures of pesticide residues are even less known for non-target soil organisms. Some studies have raised concerns about the effects of cocktails of pesticides on earthworms by reporting, among others, avoidance behavior (Pereira et al., 2009), DNA damage (Uwizeyimana et al., 2017), and changes in enzymatic activities (Jouni et al., 2021; Tiwari, 2016). Pesticides are also known to have various effects on the soil microbiome (Oyeleke et al., 2011; Wang et al., 2020) with various microorganisms being negatively impacted while others thrive leading sometimes to an imbalance between beneficial and pathogenic microorganisms (Van Bruggen et al., 2018). Earthworms and microorganisms play a key role in soil fertility but the consequences of multiple pesticides contaminating soil remain uncertain. Kosubová et al. (2020) recently suggested a more integrated method for assessing risks in the soil ecosystem.

Considering the high persistence of certain pesticides, including the long-banned organochlorine pesticides like DDT, soil assessments are pertinent not only to conventional farms but also to organic farms. Farms that have converted to organic farming within the last 2 to 3 years can exhibit contamination by pesticides applied while managed conventionally. This can occur because the required 2-3 year transition time for converting to organic farming may not be enough for the complete decay of some residues (EC, 2008a). Furthermore, drift and atmospheric deposition from nearby conventional farms may also contribute to organic soil contamination. Soil contamination assessments are particularly relevant since organic farming areas are rapidly developing in the European Union (EU) in response to higher consumer concerns regarding food and environmental safety, the new Farm to Fork policy, and financial support for organic production (EC, 2020d; Willer, 2019).

Most pesticides are applied during the crops' growing season, resulting in a peak of residues in soils during this period. However, residues may persist long after application, and accumulate in the soil over the years. Pesticide mixtures in soils are usually only evaluated at the case study level (vs. large scale assessments) due to the high analytical costs and the lack of a mandatory post-approval pesticide monitoring system. Silva et al. (2019) provided the first study with a more comprehensive overview of EU soil status, analyzing 76 pesticide residues in 317 agricultural samples from 11 EU countries. They identified 166 different pesticide mixtures, with a maximum of 13 residues (active substances and metabolites) per soil sample. However, we don't know if these findings were a result of short-term contamination or accumulated residues and we don't know which farm management system the results relate to.

The Regulation (EC) No 1107/2009 on the placing of pesticides on the market has acted as a catalyst for the development of more accurate exposure modeling tools and risk-evaluation procedures (EC, 2009c). Actual risk assessment procedures from EFSA are performed based on Toxicity Exposure Ratios (TERs) of single residues in which predicted environmental concentrations of pesticides in soil (PECs) are used as an exposure proxy for soil organisms. These PECs are calculated based on representative pesticide uses and recommended application schemes. Validation of the PECs with field data has not been conducted yet, including predictions for different soils and climatic characteristics. Furthermore, historical contamination due to banned and discontinued pesticides is not considered in the pesticide approval process, which may lead to an underestimation of the real risk. Knowing which pesticide mixtures exist in the soil is a pre-requisite to realistic assessments of pesticide impacts on soil organisms, as well as comprehensive pesticide risk assessments.

The main objectives of this study were to (i) compare the pesticide residue mixtures present in topsoils of organic and conventional farms in different regions of Europe, and (ii) discuss the (need for) regulations related to residue mixtures in soils and for transitioning to organic farming. With this study, we have gained knowledge that will assist in the implementation of the European Green deal, namely the recently published Farm to Fork Strategy and the Zero Pollution Strategy that aim to reduce pesticide use by 50%, eliminate soil pollution and establish a minimum of 25% organic farmland in Europe by 2030 (EC, 2020d; EC, 2020f).

4.2 Methodology

4.2.1 Case study sites overview

For this study, we compiled data collected from 4 Case Study Sites (CSS; *Table 4.1*) from 3 EC funded projects addressing soil quality: RECARE (www.recare-project.eu/), iSQAPER (www.isqaper-project.eu/) and DIVERFARMING (www.diverfarming.eu/). In all three projects, pesticide application patterns and distribution of pesticide residues in agricultural soils were studied at a CSS level. These CSS represented typical cropping systems and covered different climate zones: vegetable production under plastic mulch in Southeast Spain (S-V), orange production in Eastern Spain (S-O), grape production in Northern Portugal (P-G), and potato production in Northern Netherlands (N-P). The CSS included both organic and conventional production systems, except for P-G (organic grape farms were not common in the sampled area of Portugal). The organic fields were converted more than 5 years ago (S-V, S-O) or more than 10 years ago (N-P). The conventional farms were managed as such for at least the last 10 years. Overall, we collected and analyzed 340 topsoil samples (0-10/15 cm depth). Soil samples were collected between 2015 and 2018 at the end of the growing season (S-V, S-O, P-G) or before the growing season (N-P). The characteristics of the CSS and the sampling pattern for each CSS are presented in *Table 4.1*. The soil samples were air-dried (at ambient temperatures, under dark conditions, and for a maximum of 1 week), sieved to 2 mm and frozen (-20 °C) until the extraction and determination of pesticide residues could be carried out.

Table 4.1 - Characteristics of the case study sites (CSS) and respective sampling details. C= conventional, O=organic.

Site code	P-G (P-G-C)	N-P (N-P-C, N-P-O)	S-V (S-V-C, S-V-O)	S-O (S-O-C, S-O-O)
Location	Bairrada, N-Portugal	Groningen, N-Netherlands	Cartagena, SE-Spain	Valencia, E-Spain
Crop	Grapes	Potatoes (in rotation with cereals)	Vegetables	Oranges
Climate	Temperate Mediterranean	Atlantic	Arid Mediterranean	Hot Mediterranean
No. harvests	1 (October)	1 (September)	2 (winter & summer)	1 (December/January)
Soil type; Texture	Cambisols and Luvisols; clay, sandy	Cambisols; sandy loam, clay	Calcisols; sand, clay	Cambisols; Sandy loam
Organic matter (mean ± SDev)	6.2 ± 1.8%	3.6 ± 0.9%	1.1 ± 0.3%	3.5 ± 1.5%
pH in H_2O (mean ± SDev)	7.1 ± 1.3	7.7 ± 0.4	8.4 ± 0.3	8.1 ± 0.2
timing of soil sampling	October 2016	April 2018	February 2018	February 2015
No. of fields sampled	C: 9; O: 0	C: 9; O: 1	C:18; O: 18	C:6; O: 6
No. of samples per field	12	C: 3/4; O: 6;	3	C:9; O: 6
No. of samples per CSS	C: 108; O: 0	C: 28; O: 6	C:54; O: 54	C: 54; O: 36

4.2.2 Selection of the pesticide residues to be analyzed

For each CSS, we carried out interviews with farmers and pesticide retailers and asked which pesticides had been used on the farms during the 2 growing seasons before sampling. Interview questions covered the type of substances applied, the application amounts, and the application timing. The results of the interviews are presented in *Table S4.1*. As we depended upon the willingness of the farmers and retailers to answer the questions, different information was gathered across the study sites:

a) In P-G, all the 9 farmers (9 conventional) replied, giving a shortlist of pesticides used. Detailed application records from 5 of these farmers were later made available to us.
b) In N-P, 10 of the potato farmers (9 conventional and 1 organic) replied, and detailed pesticide application records were gathered from them.
c) In S-V, all the conventional farmers (6) gave the names of applied pesticides. Detailed application records from 3 of these farmers were later made available to us.
d) In S-O, 4 of the farmers (3 conventional and 1 organic) and one pesticide retailer replied, but only the names of the applied pesticides were made available.

The information obtained from the interviews was combined with EUROSTAT data of the most common pesticides used in our crop-country combinations (EUROSTAT, 2017) to define a list of analytes of high interest per CSS. Additionally, in S-O, P-G and N-P, we analyzed obsolete pesticide residues, such as organochlorides and organophosphates that were banned decades ago, to gain insight into long-term soil contamination. The main metabolites of currently used and obsolete pesticides were also added to the list of analytes of high interest (details see *Table S4.1*). The residues that required a specific analytical method (except glyphosate and its main metabolite AMPA), or that did not present satisfactory recoveries (between 80 and 120%) during the validation step of the multi-residue method were excluded. The final list of analytes (i.e. the list of the pesticide residues tested in soil samples) included 47 residues in P-G, 36 in N-P, 38 in S-V and 75 in S-O. Overall, 151 different pesticide residues were tested: 66 approved active substances, 70 non-approved active substances, and 15 metabolites (*Table S4.2).* In this study, we focused only on synthetic pesticide residues.

4.2.3 Analysis of pesticide residues in soil samples

All soil samples were thawed and homogenized (hand-mixed until a visual homogeneous sample was obtained) and split into two aliquots: one for the determination of basic soil properties (pH, organic matter and texture) and one for the determination of pesticide residues. The pesticide residue aliquot was also split into two parts: 2 g for the determination of glyphosate and its main metabolite AMPA (in S-O, P-G and N-P) and the remaining 5 g for the screening of multi-residues (all CSS). Since none of the parties interviewed for this study reported that glyphosate was applied in S-V, it was not analyzed in those samples. Glyphosate and AMPA were determined using the method described by Bento et al. (2016) and Yang et al. (2015) using LC-MS/MS (liquid chromatography-tandem mass spectrometry; Instrument: Quattro Ultima from Micromass (UK) coupled to an Acquity UPLC system from Waters (USA). The other pesticide residues were extracted using an adaptation of the QuEChERS approach to soil samples, as described by Silva et al. (2019) and analyzed by LC-MS/MS (different MS systems: Quattro Ultima from Micromass, Premier, TQ-S and TQ-XS from Waters, all coupled to Acquity UPLC systems from Waters) and GC-MS/MS (gas chromatography-tandem mass spectrometry; Instruments: 300 GC-MS from Bruker, and a 7010B MS coupled to a 7890B GC from Agilent Technologies) or GC-HRMS (gas chromatography-high-resolution mass spectrometry; Instrument: Q-Exactive GC Orbitrap from Thermo Scientific).

Analyses were performed according to the analytical quality control and method validation procedures for pesticides residues analysis in food and feed. The guidelines for the current version, at the time of analysis, of the SANTE document were applied (EC, 2015b; EC, 2017a). Analyses involved the use of calibration standards, reference standards, isotope-labeled internal standards, a surrogate standard (caffeine) and an injection standard (PCB-198). The calibration standards were prepared from a mix solution that combined the reference standards of all the compounds that were going to be analyzed. Isotope labeled internal standards were only used in glyphosate and AMPA determinations, for normalization of the response of these compounds. Caffeine was used as a surrogate to check potential issues in the LC-MS/MS analyses other than glyphosate and AMPA, and PCB-198 for normalization of response in the GC-MS/MS and GC-HRMS analyses. Further details on standards can be found in Silva et al (2019). The reference standards were purchased from LGC Standards (Germany), HPC Standards (Germany) or Sigma-

Aldrich (USA). The isotope-labeled internal standards of glyphosate and AMPA and the PCB-198 were obtained from LGC Standards (Germany) while the caffeine was purchased from Sigma-Aldrich (USA). Limits of quantification (LOQ) were used as reporting limits. The LOQ of glyphosate and AMPA was 0.050 mg/kg while the LOQ of the remaining residues ranged between 0.001 and 0.02 mg/kg (*Table S4.2*).

4.2.4 Data analysis

Interviews

All data (interviews, sampling) were collected using different sampling patterns due to the requirements of the different European projects associated with each CSS. We did not conduct statistical tests on the data derived from interviews because the interviews only resulted in a limited amount of information. However, we used the data from the interviews to give a realistic qualitative overview of the pesticide applications and resulting accumulated residues in soils under different cropping and farming systems. The number and basic characteristics of the active substances identified in the farmers' interviews are presented in *Table S4.1*. When pesticide application rates were available, they were included in the table; when application rates were not available, the substance was listed in the table with no associated application amount.

Residues in soil

We calculated the frequency of detection, the median and the range of concentrations for each compound from each organic and conventional farming system per CSS. The pesticide residues with the highest frequencies (> 50%) and with moderate frequencies in soils (20-50%) are presented in *Table 4.3*. Data from pesticide residues with frequencies below 20% are shown in *Table S4.3*. Furthermore, we present the range and the median number of pesticide residues found in organic and conventional soils for each CSS. We added the content of the different pesticide residues found in each sample to obtain the total residues content per sample. Non-parametric Mann Whitney U tests were used to test significant differences in the number of residues and the total residues content in soils between conventional and organic farms within the same CSS, and between CSS within the same farming strategy. Statistical analyses were performed using STATISTICA, version 12. The significance level was set at 0.05.

4.3 Results

4.3.1 Applications of Pesticides in the CSS

The number of applied pesticides (active substances) varied strongly across conventional farms, and across the CSS (*Fig. 4.1; Table S4.1*). Overall, farmers reported 98 active substances: 69 active substances were applied in only one CSS, 19 active substances were applied in two CSS, and 9 active substances (8 fungicides and 1 insecticide) were applied in three CSS. The compound with the highest input was the insecticide chlorantraniliprole, with around 35 kg/ha/year in S-V-C (*Table S4.1*). A maximum of 11 different active substances were applied per farm per year in S-O-C, between 10 and 18 active substances in P-G-C farms, between 8 and 22 active substances in S-V-C farms, and finally, between 5 and 44 active substances in N-P-C farms (*Fig. 4.1*). In N-P-C, farmers applied mainly herbicides, in P-G and S-V-C fungicides, and in S-O-C mainly insecticides. 44-55% of the active substances applied in the CSS are non-persistent, 26-36% moderately persistent, 0-24% persistent and 4-11% very persistent (*Table 4.2*).

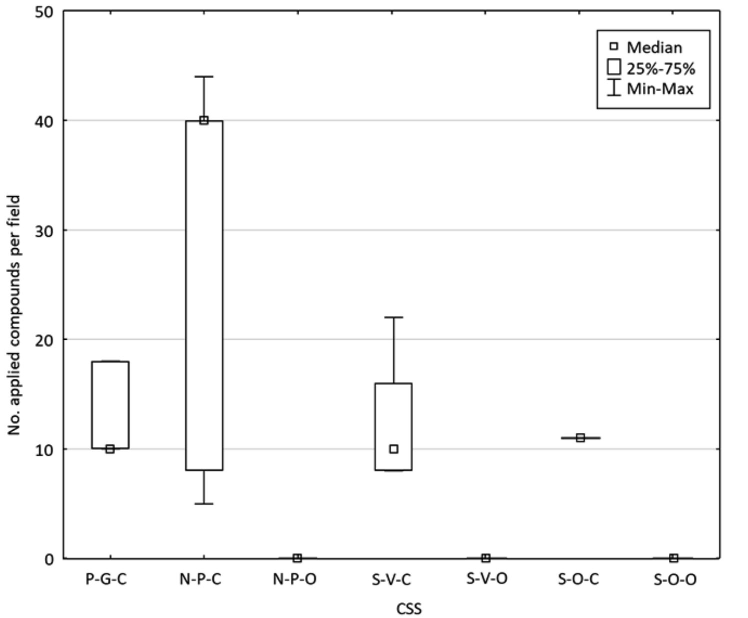

Figure 4.1 - Number of active substances applied per field per year in the different Case Study Sites (CSS). Data based on interviews with farmers and pesticide retailers. Min = minimum; Max = maximum. Vegetable production in Southeast Spain (S-V), orange production in Eastern Spain (S-O), grape production in Northern Portugal (P-G), and potato production in Northern Netherlands (N-P). C=conventional; O=organic.

Table 4.2 - Characteristics of applied compounds per Case Study Site (CSS). Non-persistent: half-life time, DT_{50}<30 days; moderately persistent: 30 days <DT_{50}< 100 days; persistent: 100 days< DT_{50}< 365 days; and very persistent: DT_{50}> 365 days). Persistence data and persistence data classes were retrieved from *PPDB, 2020*. Application data refer to interviews with CSS farmers and pesticide retailers. I = insecticide, F = fungicide, H = herbicide; No. = number of compounds applied per CSS, %= number of non- moderately-very persistent compounds/number of total compounds* 100; S-V = vegetables production in Southeast-Spain, S-O = orange production in Eastern Spain, P-G = grape production in Northern Portugal, and N-P = potato production in Northern Netherlands; C=conventional, O=organic.

CSS	Total No. of compounds applied	Non- persistent compounds No./%	Moderately persistent compounds No./%	Persistent compounds No./%	Very persistent compounds No./%
P-G-C	18 (I:2, F:15, H:1)	8/44%	6/33%	2/11%	2/11%
N-P-C	57 (I:10, F:19, H:28)	25/44%	18/32%	11/19%	3/5%
S-V-C	50 (I:19, F:22, H:9)	23/46%	13/26%	12/24%	2/4%
S-O-C	11 (I:5, F:3, H:3)	6/55%	4/36%	0/0%	1/9%

4.3.2 Pesticide residues identified in the CSS

The number of residues found in EU soil samples ranged between 0 and 16, with significantly more residues discovered in conventional fields than in organic fields (*Fig. 4.2*). The only pesticide residue-free soils under conventional farming were identified in S-O-C (2% of all conventional soils; *Fig. 4.3*); all other soils under conventional farming contained one or more pesticide residues. In P-G-C and S-O-C, more than 80% of the soils contained 2 to 5 residues, while most N-P-C and S-V-C samples contained 6 to 10 different residues (71% and 83%, respectively). A substantial part of N-P-C (25%) and S-V-C (9%) soil samples contained even more complex mixtures, with more than 10 residues. As mentioned above, soils from organic farms contained significantly fewer residues, with 44% of the soils in S-V-O and 11% of the soils in S-O-O being free of tested pesticide residues. However, 100% of N-P-O soils and 72% of S-O-O soils contained mixtures of 2 to 5 residues. In S-V-O, 30% of the soil samples contained 1 residue and 26% of the samples contained 2 to 5 residues (*Fig. 4.3*).

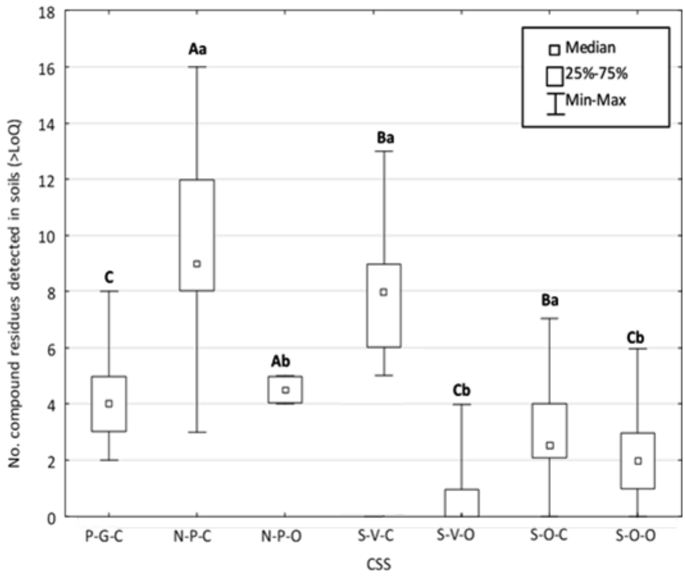

Figure 4.2 - Numbers of pesticide residues identified per soil sample across Case Study Sites, CSS. Significant differences among CSS within the same management system (Mann and Whitney U-Test, $p<0.05$): A>B>C. Significant differences between organic and conventional fields, from the same CSS: a>b. Number of samples, n: P-G-C n: 108, N-P-C n: 28, N-P-O n: 6, S-V-O n: 54, S-V-C n: 54, S-O-O n: 36, S-O-C n: 54. LOQ – Limit of quantification. Vegetable production in Southeast Spain (S-V), orange production in Eastern Spain (S-O), grape production in Northern Portugal (P-G), and potato production in Northern Netherlands (N-P). C=conventional; O=organic

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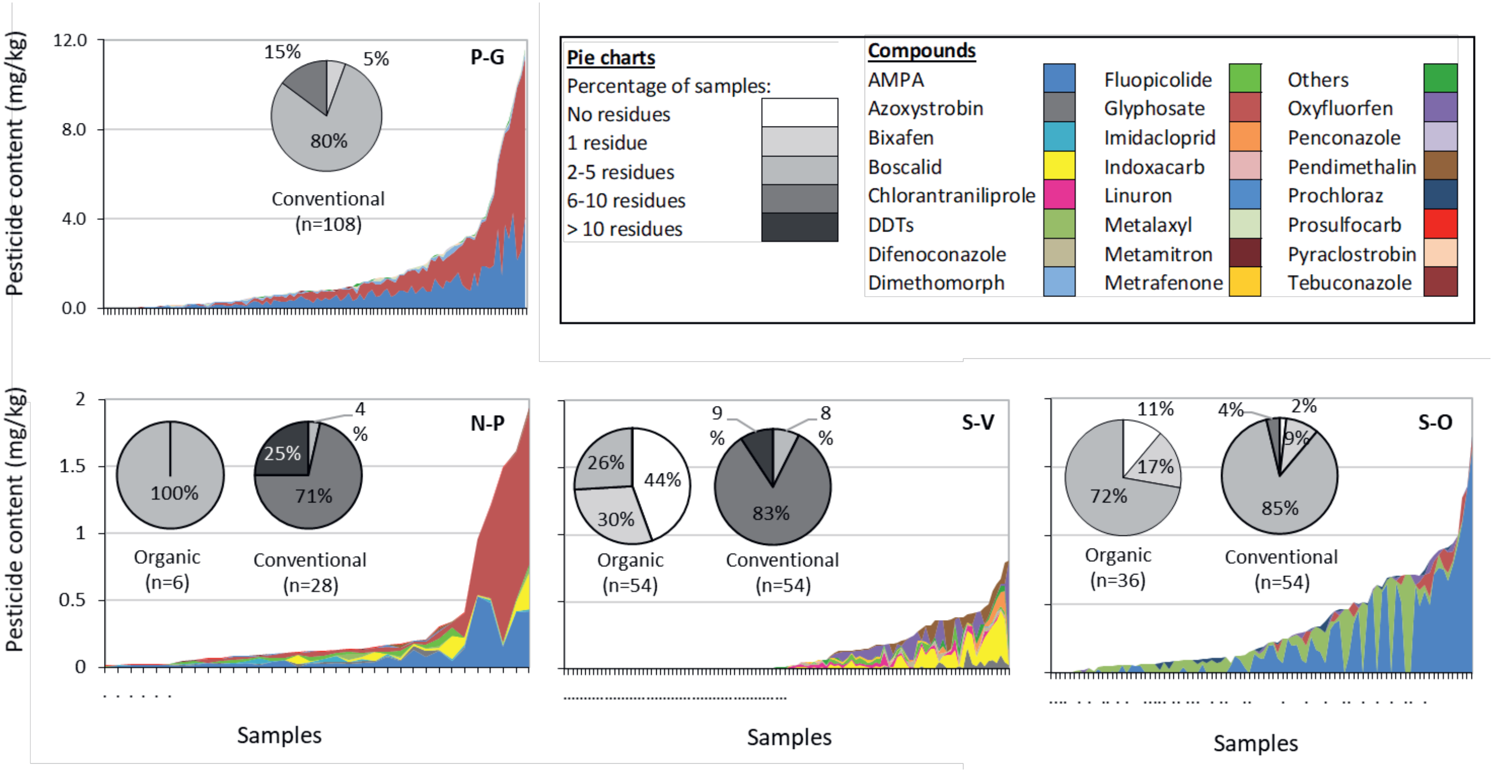

Figure 4.3 - Number of pesticide residues and total pesticide content found in the organic and conventionally managed soils from P-G, N-P, S-V, S-O. The number of residues in soils were aggregated per classes, being the distribution of each class is presented in the pie-charts. The total pesticide content is presented as a cumulative curve, being the topsoil samples from each CSS organized by increasing total pesticide content. The . below the x axis indicates soils under organic management, the remaining values are related to conventionally managed fields. Each colour under the curves represent a different pesticide residue.

The highest number of residues per sample were found in N-P-C. If only median values are considered, the number of residues found in soil decreased according to the following order: N-P-C> S-V-C> P-G-C> S-O-C (*Fig. 4.2*). In total, 15 residues were detected with a frequency above 50% in one or more of the CSS and 7 residues with a frequency between 20 and 50% in one or more of the CSS (*Table 4.3*). The group of 15 residues with a frequency >50% included 3 very persistent (VP) residues, 7 persistent (P) residues, 4 moderately persistent (MP) residues, and 1 non-persistent residue (NP). This group included 1 banned organochlorine pesticide. 8 out of the 15 more common residues were fungicides, 4 were herbicides, and 3 were insecticides. Of the 7 residues with a frequency of 20-50%, 4 were VP, 2 P and 1 MP; 4 were fungicides and 3 were insecticides (2 of them banned, DDT metabolites). From the residues with moderate-high detection frequencies (>20%, *Table 4.3*), only 46% were reported to be applied.

In P-G-C, the number of pesticide residues in soil ranged from 2 to 8, with a median of 4 residues per soil sample (*Fig. 4.2*). 26% of the applied compounds in the P-G site were detected as residues in soil. None of the banned pesticides tested were detected in the P-G-C samples (*Table 4.3*, *Table S4.3*). 4 compounds were detected with a frequency >50%: AMPA (83%) and glyphosate (78%) and the fungicides metalaxyl (51%) and dimethomorph (100%). 3 other compounds, all fungicides, were detected with a frequency between 20 and 50%: penconazole, tebuconazole and pyraclostrobin (*Fig.4.3, Table 4.3*).

In N-P-C, 3 to 16 residues were found with a median of 9 residues per soil sample. In the organically-managed fields in N-P-O, a median of 5 residues/sample was identified although no pesticides had been reportedly applied in the past 10 years (*Fig. 4.2*). 17% of the applied compounds were detected as residues in the soils. In N-P-C, 6 compounds were present with an overall frequency > 50% (3 fungicides, 2 herbicides, 1 obsolete insecticide) and 2 compounds were detected with a frequency between 20-50%: bixafen, a VP fungicide, and an obsolete insecticide (*Table 4.3*). In N-P-O, only 1 compound (AMPA, a VP herbicide metabolite) was identified with a frequency > 50%. The glyphosate metabolite AMPA was the most frequent residue found in both conventional and organic fields, with a frequency of 96 and 83%, respectively. The metabolites of the banned insecticide DDT were also identified in soils under both conventional and organic farming (*Table 4.3*). The fungicides boscalid, bixafen and fluopicolide as well as the herbicide glyphosate were detected with frequencies > 50% in N-P-C but were not present in N-P-O.

In S-V-C, the number of positively quantified residues ranged from 1 to 13, with a median of 8 compounds per soil sample. In S-V-O samples, a maximum of 4 residues was detected in a unique soil sample (*Fig. 4.2*). 47% of the applied compounds in this CSS were detected as residues in the soils. In S-V-C, 9 compounds (2 herbicides, 5 fungicides and 2 insecticides) were detected with a frequency > 50 % and 3 (2 F, 1 I) with a frequency between 20 and 50%. The 9 different residues consisted of 2 NP, 5 MP, 4P and 2 VP. The compounds occurring with the highest frequency were the insecticides chlorantraniliprole (100%) and imidacloprid (92%). The herbicide pendimethalin was detected with a frequency of 63%. In S-V-O, only the persistent insecticide Imidacloprid occurred with a frequency >20%.

S-O-C, the number of quantified residues ranged from 0 to 7, with a median of 2 residues per sample. In S-O-O samples, a maximum of 6 residues were detected (*Fig. 4.2*). 18% of the applied compounds were detected in soil. In S-O-C, the very persistent metabolites AMPA and DDE were the only compounds detected with a frequency above 50%. The herbicides glyphosate (P) and oxyfluorfen (P) and the fungicide prochloraz (VP) presented frequencies between 20 and 50%. Soils from S-O-O presented residues of glyphosate and AMPA along with high levels of DDT metabolites, with frequencies between 44 and 89% (*Table 4.3).*

			P-G (conv)				N-P (conv/org)				S-V (conv/org)				S-O (conv/org)			
	Compound	Persistence	% freq	Q1	Max	Median	% freq	Q1	Max	Median	% freq	Q1	Max	Median	% freq	Q1	Max	Median
>50% frequency	AMPA (M-H)	VP	83	0.260	4.294	0.505	96/ 83	0.027/ 0.012	0.528/ 0.015	0.038/ 0.014					87/ 17	0.102/ 0.069	1.626/ 0.593	0.261/ 0.070
	Azoxystrobin (F)	NP	4	0.014	0.022	0.019	86/ 0	0.002/ <LoQ	0.044/ <LoQ	0.005/ <LoQ	72/ 0	0.005/ <LoQ	0.153/ <LoQ	0.009/ <LoQ				
	Boscalid (F)	VP					61/ 67	0.008/0.001	0.270/0.002	0.015/0.001	85/ 0	0.011/ <LoQ	0.330/ <LoQ	0.055/ <LoQ				
	Chlorantranilprole (I)	P									100/ 7	0.010 / 0.001	0.101/ 0.001	0.017/ 0.001				
	DDE pp (I)	VP	0	<LoQ	<LoQ	<LoQ	68/ 83	0.002/0.002	0.030/0.004	0.003/0.002					78/ 89	0.016/ 0.045	0.161/ 0.570	0.031/ 0.080
	Difenoconazole (F)	P									65/17	0.006/0.001	0.062/ 0.001	0.019/0.001				
	Dimethomorph (F)	MP	100	0.029	0.301	0.056					24/ 0	0.001/<LoQ	0.011/ <LoQ	0.003/<LoQ				
	Fluopicolide (F)	P					79/ 0	0.012/<LoQ	0.061/ <LoQ	0.017/ <LoQ	48/ 0	0.009/<LoQ	0.096/ <LoQ	0.024/ <LoQ				
	Glyphosate (H)	P	78	0.179	7.843	0.452	93/ 0	0.019/ <LoQ	1.306/ <LoQ	0.030/ <LoQ					22/ 6	0.070/0.076	0.180/ 0.105	0.090/ 0.090
	Imidacloprid (I)	P									93/30	0.002/0.001	0.163/ 0.002	0.004/ 0.001				
	Metrafenone (F)	P									56/ 0	0.006/ <LoQ	0.021/ <LoQ	0.009/ <LoQ				
	Metalaxyl (F)	MP	51	0.017	0.173	0.034					0 / 0	<LoQ / <LoQ	<LoQ / <LoQ	<LoQ/ <LoQ	0 / 0	<LoQ/ <LoQ	<LoQ/ <LoQ	<LoQ / <LoQ
	Oxyfluorfen (H)	MP									70/ 0	0.009/ <LoQ	0.605/ <LoQ	0.051/ <LoQ	37/ 0	0.016 / <LoQ	0.085/ <LoQ	0.023/ <LoQ
	Pendimethalin (H)	P					43/ 0	0.002/ <LoQ	0.024/ <LoQ	0.004/ <LoQ	63/ 0	0.007/ <LoQ	0.234/ <LoQ	0.032/ <LoQ				
	Pyraclostrobin (F)	MP	32	0.018	0.058	0.029					56/ 0	0.002/ <LoQ	0.034/ <LoQ	0.003/ <LoQ				
20-50% frequency	Bixafen (F)	VP					71/ 83	0.008/ 0.001	0.050/ 0.003	0.011/ 0.001								
	DDD pp (I)	VP	0	<LoQ	<LoQ	<LoQ	32/ 17	0.001/0.002	0.005/0.002	0.002/0.002					13/ 44	0.011/ 0.014	0.032/ 0.071	0.017/ 0.017
	DDT pp (I)	VP	0	<LoQ	<LoQ	<LoQ	14/ 0	0.011/ <LoQ	0.022/<LoQ	0.012/ <LoQ					19/ 46	0.013/ 0.014	0.026/ 0.089	0.016/ 0.021
	Indoxacarb (I)	P									33/ 0	0.001/ <LoQ	0.022/ <LoQ	0.001/ <LoQ				
	Penconazole (F)	P	17	0.012	0.049	0.021												
	Prochloraz (F)	VP													33/ 17	0.012/ 0.028	0.054/ 0.083	0.013/ 0.033
	Tebuconazole (F)	MP	16	0.010	0.096	0.011	32/ 17	0.001/0.002	0.013/0.002	0.002/0.002								

legend:

known to be applied but not detected	known to be applied and detected	known to be applied but not tested	obsolete pesticide and not detected	known to be not applied but detected	not applied and not tested

Table 4.3: Pesticide residues detected with a frequency between 20 and 50% and > 50% in at least 1 of the Case Study Sites, CSS (H=herbicide, F=fungicide, I = insecticide, M=metabolite; VP = very persistent , P=persistent, MP = moderated persistent, NP=non persistent). The cells are colored according to whether the compounds were known to be applied (conventional fields), tested and detected (conventional and organic samples). LoQ – Limit of quantification. Q1 – The first quartile concentration, i.e. 25% of the values above LOQ. Southeast-Spain (S-V), orange production in Eastern Spain (S-O), grape production in Northern Portugal (P-G), and potato production in Northern Netherlands (N-P), conv=conventional, org=organic.

4

The highest pesticide content was found in P-G-C, with a total residue content of nearly 12 mg/kg, a value approximately 6 times higher than the maximum content in N-P-C and S-O-C fields, and 12 times higher than in S-V-C (with a maximum content of 2, 1.7 and 0.8 mg/kg, respectively; *Fig. 4.3, 4.4*). The residue content under organic farming in N-P and S-V did not exceed 0.2 mg/kg, i.e. 10% of the maximum content in the respective conventional fields. In S-O-O, the maximum residue content was 0.6 mg/kg, which was about 30% of the maximum residue content of the conventional fields (*Fig. 4.4*). The residues that contributed the most to the total residue content under conventional farming systems were: (i) glyphosate and AMPA in P-G; (ii) glyphosate, AMPA and boscalid in N-P; (iii) boscalid and imidacloprid in S-V; and (iv) AMPA and DDT metabolites in S-O. In organically managed fields, AMPA and DDT metabolites had the highest contributions, especially for S-O; in the other organic farming systems, the total content was low.

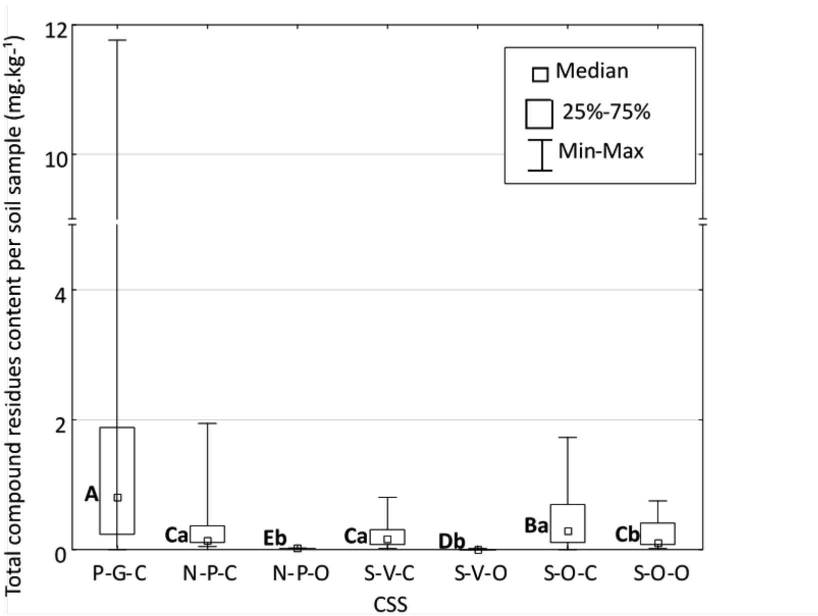

Figure 4.4 - Total pesticide residues content in soil samples. Significant differences among CSS with the same management system (Mann and Whitney U-Test, $p<0.05$): A>B>C; and between organic and conventional fields from the same CSS: a>b. Vegetable production in Southeast Spain (S-V), orange production in Eastern Spain (S-O), grape production in Northern Portugal (P-G), and potato production in Northern Netherlands (N-P), C=conventional, O=organic.

4.4 Discussion

4.4.1 Soil contamination status

The levels of total pesticide content in soil in 3 out of the 4 CSS (N-P, S-V and S-O) were in a range similar to those identified by Silva et al. (2019) for EU agricultural soils. Although most of the P-G samples were also within this range, some of them exceeded the maximum total content previously measured in EU soils, one of them by almost fourfold (12 versus 2.87 mg/kg). The very high levels of residues in these samples were almost exclusively a consequence of the high levels of glyphosate and AMPA, suggesting an intense use of glyphosate-based herbicides in some farms in this area. Unfortunately, P-G farmer's application records did not cover glyphosate amounts, which if available could corroborate this. Environmental factors such as climate, soil type or the organic matter content, known to affect the persistence of pesticides (Navarro et al., 2007; O'Loughlin et al., 2000), could also help explain our pesticide results. However, the effects of environmental parameters were never explored at a large scale (Vryzas, 2018). Our design does not allow such evaluations either because we focused on spatial coverage and selected the dominant crop per CSS to explore the impacts of organic and conventional management on soil quality. As we have only one crop per pedoclimatic region, we cannot differentiate the effects of crop management from the effects of climate or soil properties. We encourage further studies to elucidate the comparative effects of the environmental parameters on pesticides persistency.

Finally, and although we analyzed most of the compounds reported to be applied in these areas, as well as the most relevant banned pesticides (except in S-V), including a larger amount of residues into the analytical list would probably have revealed even more residues and higher pesticide levels in EU soils. This is however a common limitation of studies analyzing pesticide residues; due to the high number of pesticides approved per crop and the wide variety in physical-chemical properties of these compounds, it is nearly impossible to analyze all of the residues potentially present in soils. As a result, we only get an approximate, yet likely underestimated, picture of the real soil contamination status.

4.4.2 Possible effects of pesticide residue mixtures on soil health

Although most of the products used by our CSS farmers were non-persistent pesticides, only 5 out of the 22 most frequent residues found in soils (i.e. >20% in at least on CSS) are non- or moderately persistent (DT_{50} values below 100 days). Although this is partly justified by our soil sampling times – in P-G, S-V and S-O there was a minimum of a month between the last pesticide application and the soil sampling, and in N-P, at least a 6-month interval - this observation corroborates existing concerns on long-term impacts of pesticides. What do we know about the effects of accumulated pesticide residue mixtures on soil health? The current EC approach to approving pesticides for use on the European market considers soil health impacts based on single compound tests carried out on very few standard soil organisms (2 compost worm species: *Eisenia fetida*, *E. andrei*; 2 springtail species: *Folsomia candida, F. fimetaria*; 1 mite species: *Hypoaspis aculeifer*) and N transformation organisms (Ockleford et al., 2017). Since this approach does not reflect the real effects on soil biota, the EFSA Scientific Committee (McEntaggart et al., 2019) suggested the introduction of risk assessments related to residue mixtures that would test for the additive (default) or synergistic effects of compounds. Kosubová et al. (2020) already published risk assessments for soils based on the additive approach. However, data on toxicity (no-effect concentrations, lethal and other effect concentrations) are mainly available only for the EFSA test organisms (PPDB, 2021). Because soil biota consists of more than 1 million species, which provide different ecosystem functions such as nutrient and carbon cycling, water retention or pest suppression, it would be logical to expect that pesticide risk assessments should cover these functions. However, the effects of pesticide mixtures on these functions are rarely tested and scarce data are available. If the effects of pesticide mixtures are not known, several questions arise such as 'What concentrations of residues and what number of different residues can be considered a benchmark for soil health?' and 'When is pest suppressiveness significantly reduced?'. Some of these questions are highlighted by our findings:

i) Glyphosate along with its main metabolite AMPA and herbicides were dominantly present in the soils from P-G, N-P and S-O. Depending on the concentration and availability, glyphosate can kill all soil organisms that rely on the Shikimate pathway 1 for amino acid synthesis. Non-target organisms such as beneficial soil bacteria can also be killed. Unfortunately, soil-borne pathogens such as Fusarium fungi do not rely on the Shikimate pathway 1 and therefore, survive (Van Bruggen et al., 2018). This may therefore cause a decrease in the pest suppressiveness of glyphosate treated soils and ultimately lead to higher fungicide applications and more accumulated residues in soil. Although the combined effects of glyphosate, AMPA, and fungicide residues in soils on nutrient cycling has not been studied yet, we expect that the phosphorus cycle in the soil will be strongly affected by synergetic effects because mycorrhiza, the fungi essential to the P availability in soils, is killed by glyphosate and fungicides. This combined effect should be a central part of all the discussions surrounding plant growth and phosphorus availability.

ii) Soil samples from the S-V CSS presented relatively fewer pesticide residues than the other CSS. Plastic mulch was extensively used in this area and therefore, fewer pesticides were used (Beriot et al., 2020). Glyphosate was not used in the S-V CSS, with pendimethalin being used instead as the main herbicide. Together with imidacloprid and boscalid, these were the most dominant residues found in S-V. The synergetic effects of the main residues present in S-V, in combination with the microplastics present in these soils as a result of years of plastic mulch applications have not been studied sufficiently (Qi et al., 2020).

iii) DDT metabolites were still present in many soils, especially in S-O where they contributed significantly to the residue mixtures, even on organic farms. In S-V, we did not analyze the residues of banned pesticides, we focused only on approved ones. We assume that this fact could partly explain the lower number of residues found in S-V. Again, several questions arise such as 'What is the combined effect of the DDTs inhibiting Gaba Synthesis and AMPA?' 'Are the soil insects strongly affected by the dual effects: direct effects via Gaba inhibition and indirect effects due to changes in the gut microbiome?' 'Is AMPA killing the beneficial bacteria in the gut microbiome?'.

These questions are posed to illustrate the complexity of the topic and the difficulties facing realistic risk assessment approaches. Researchers need to define the requirements for innovative tests, taking into consideration the fact that soils in Europe are contaminated after 70 years of pesticide applications. Furthermore, tests should examine the effects of residue mixtures on soil functions. Policymakers should consider researchers to establish benchmarks related to the content and the number of pesticide residues to protect soil health. Since soil health covers the capacity of soils to support ecosystem services such as clean air and water, genetic resources or pollination (Costanza et al., 2017; Maes et al., 2014), all these may be jeopardized if soil diversity is at risk with the presence of pesticide cocktails.

4.4.3 Organic agriculture

Comparing conventional and organic management systems, we identified 30% fewer pesticide residues in the organic systems. The residues common to both systems presented 70-90% lower concentrations in organic soils than in conventional soils. The typical half-life of residues detected in organic fields ranged from 100 days to more than a year. Although synthetic pesticides are not applied under organic farming (Reganold and Wachter, 2016) soils under organic farming may contain pesticide residues (Witczak and Abdel-Gawad, 2012). The European Commission requires a conversion time of two years of organic management before certification for annual crops (EC, 2008a), which means that the content of very persistent compounds in soil (DT_{50}> 1 year) at the time an organic crop is finally harvested will be 1/4 of the content that the crop would have had at the start of the organic conversion. This estimation shows that the conversion time allows for a reduction of pesticide residues in soil but not their complete disappearance. The levels of the most persistent compounds are not affected in time, as corroborated by the still relatively high levels of DDTs measured in organic fields, especially in S-O-O. Because DDT has been banned in many European countries since the 1970s (including those selected for this analysis) and in all EU countries since 2009 (EC, 2009b), the concentrations measured were probably from historical applications. For other less persistent residues, the contamination could be the result of applications carried out before the farm converted to organic farming or, for instance, via spray drift and deposition after a neighboring conventional field was sprayed.

To guarantee minimal levels of pesticide residues in soils, conversion to organic farming requires adapted transition periods depending on the residue mixtures initially present in the soils. Studies on the uptake of the different pesticide residues by plants are urgently required to define threshold values for soils. Planning financial support for farmers transitioning to organic farming should consider this fact. Different environmental policies should also be established to stimulate farmers who seek to grow food and feed with less impact on the environment. The possibility of soil remediation should be made a priority in places where it is feasible. Moreover, the establishment of rich above-ground plant systems may mitigate the effect of historical and current pesticides in soils.

4.4.4 Food safety

Although the focus of this study has been on soil health, researchers know that pesticide residues in soils can enter the food chain and therefore can affect food quality and human health (Bevan et al., 2017; Brevik et al., 2020). Contrary to EU soils, EU food products are exhaustively monitored every year for pesticide residues, in line with Regulation No 396/2005 concerning maximum residue levels (MRLs) of pesticides in or on food and feed of plant and animal origin (EC, 2005). According to the latest EFSA monitoring report (EFSA, 2020), 48% of the 91,015 EU-tested food products contained pesticide residues. Organically produced food seems to result in a lower burden of pesticides than conventionally produced food: 13.8 versus 46% of samples contained pesticide residues, and 1.4 versus 4.8% of samples had measurements exceeding current MRLs, respectively. However, if the total pesticide content in food products is not considered, individual MRL exceedance percentages might be misleading and not be a realistic reflection of the risk posed by contaminated food products. The dietary risks of pesticides in foods may be greater since 29% of the food samples tested had multiple residues, with a maximum of 29 different residues per sample (EFSA, 2020). Vegetables and fruits (the crops in three of our four CSS, and commonly assumed to be the healthiest food products) are among the food items most likely to be contaminated by cocktails of residues (EFSA, 2020). Although EU-harmonised MRLs are available for 495 pesticide residues and 381 food products, MRLs exist only for a few metabolites and do not exist for total pesticide content (EU Pesticide database, 2021). Furthermore, there are no specific MRLs for organic products (EU, 2018). MRLs should be quickly established for pesticide residue mixtures in food and should relate to total MRLs for the sum of all residues as well as to the total number of residues. These MRLs should be significantly lower for organically produced foods as compared to conventionally produced foods.

Only a couple of the pesticide residues found in our CSS soils were present in more than 5% of the EU food samples (azoxystrobin and boscalid). Glyphosate, prosulfocarb, boscalid, metalaxyl, and tebuconazole exceeded their respective

MRLs occasionally (EFSA, 2020). DDTs were also found in a few food products, including organic samples, and most likely originated from the soil (EFSA, 2020). Although some parallelism can be drawn between our observations in EU soils and EFSA and FAO pesticide data on food products, a direct conversion between matrices, or between chemical data and health impacts, cannot be done. On one hand, pesticide application might not reach the harvested product (in the case of early-season pesticide applications as well as in the case of herbicides that are often only applied to the base of tree trunks or vines in orchards). In these situations, soil contamination is far more likely than food contamination. For vegetables and root crops grown in soil or on the soil surface, food contamination might still be possible. On the other hand, food contamination might occur not in the field but during the handling, packaging, storage or processing of food products, including organic food products.

4.4.5 Implementation of the Farm to Fork Strategy

The Farm to Fork Strategy (EC, 2020d) sets an EC target to reduce the use and the risk of chemical pesticides by 50% by 2030, and the reduction of the more hazardous pesticides by 50% also by 2030. For the first time, a quantified pesticide reduction target at the EU level has been set. Moreover, this same Farm to Fork Strategy encourages organic farming intending to have at least 25% of EU agricultural land under organic farming management by 2030. As shown by this study, although the accumulated residue content in organic soils was 70-90% lower than in conventionally managed soils, some soils still contain between 2 and 5 residues, even after more than 10 years of organic farming. Our results raise two main questions related to the Farm to Fork strategy that should be addressed in the short term:

i) Which pesticide mixtures pose the highest risk to soil health and which pesticides should preferably be subject to use restrictions or even banned? To answer these questions, a new approach to risk assessment should be implemented by EFSA and EC procedures in due time, considering pesticide cocktails occurring on the major agricultural systems and crops.

ii) Benchmarks for residue cocktails are required for soils from certified organic farms. In effect, only management requirements are regulated through the European level Regulation (EC) No 834/20072 and Regulation (EC) No 889/20083. Persistent synthetic pesticide residues in soils are not taken into account since they are not applied in organic farming. However, > 80% of the soils in Europe (Silva et al., 2019), contain residues. Even assuming that all these originate from conventionally managed farms, part of these soils are likely to be converted to organic soils during the coming years, and therefore there should be clear regulations to guarantee that certified organic products are not affected by environmental contamination. Benchmarks for residues in soils are urgently required.

4.5 Conclusions

- Mixtures of pesticide residues were present in all case study sites under conventional farming, both in samples taken at the start of the crops season, and samples taken post-harvest.
- In organic soils, the residue levels were 70-90% lower than in conventional fields, however, most of the organic soils contained residue mixtures as well.
- The overall effect of the cocktails on soil health is unknown. Innovative tests are urgently required to test the effects of detected pesticide cocktails on soil health in a holistic way, before approving new pesticides for the EC market.
- Benchmarks must be defined for pesticide residue cocktails in all agricultural systems to protect soil health, soil biodiversity and food quality.
- The time required for transitioning to (certified) organic farming should also depend on the pesticide residues mixtures in the soil at the starting point of the transition.

See supplementary materials on pages 236-246.

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Chapter 5

Environmental and human health at risk: scenarios to achieve the Farm To Fork 50% pesticide reduction goals

Abstract: *The recently released Farm to Fork Strategy of the European Union sets, for the first time, pesticide reduction goals at the EU level: a 50% reduction in overall use and risk of chemical pesticides and a 50% use reduction of more hazardous pesticides. However, there is little guidance provided as to how to achieve these targets. In this study, we compiled the characteristics of all 230 EU-approved, synthetic, open-field use active substances (AS) used as herbicides, fungicides and insecticides, and explored the potential of seven Farm to Fork-inspired pesticide use reduction scenarios to achieve the 50% reduction goals. The pesticide reduction scenarios were based on recommended AS application rates, pesticide type, soil persistence, presence on the candidate for substitution list, and hazard to humans and ecosystems. All 230 AS have been found to cause negative effects on humans or ecosystems depending on exposure levels. The results of the scenarios indicate that only severe pesticide use restrictions, such as allowing only low-hazard substances, will result in the targeted 50% use and risk reductions. Over half of the 230 AS considered are top use or top hazard substances, however, the reduction actions depend on the still to be defined EC priority areas and action plans, also for other recent and related strategies. Broader scenario implications (on productivity, biodiversity or economy) and the response of farmers to the pesticide use restrictions should be explored in those plans to define effective actions. Our results emphasize the need for a re-evaluation of the approved AS and of their representative uses, and the call for open access to AS, crop and region-specific use data to refine scenarios and assess effective reductions.*

Based on :

Silva V, Yang X, Fleskens L, Ritsema CJ, Geissen V. Environmental and human health at risk – scenarios to achieve the Farm To Fork 50% pesticide reduction goals, accepted for publication in Environment International.

5.1 Introduction

Pesticides are used in agriculture to reduce crop losses due to pests, weeds and pathogens (Damalas, 2009; Sharma et al., 2019). Farming systems have been facing increasing pressure to produce more food as a result of the rapidly growing population and higher caloric diets observed over the last few decades (Nellemann et al., 2009). Currently, global pesticide use exceeds 4 million tonnes per year and Europe alone is responsible for using almost 400,000 tonnes (FAOSTAT, 2021). The long-term and intensive use of pesticides raises major health and environmental concerns since several pesticide active substances (AS) or their metabolites are persistent (Masiá et al., 2013; Silva et al., 2019), bio-accumulative (Goutner et al., 2012; Wang et al., 2011), or toxic to humans and non-target-species (Colin et al., 2019; Damalas and Koutroubas, 2016; Kim et al., 2017; Ullah et al., 2018). The awareness of undesired side effects of pesticide use has triggered biotechnological developments (Grillo et al., 2021; McConnell et al., 2016) and multiple efforts to minimize pesticide use and its negative impacts (EC, 2009c; Lee et al., 2019). The recently published EC Farm to Fork Strategy (EC, 2020c), part of the European Green Deal, sets the first pesticide reduction targets at the EU level: a 50% reduction in overall use and risks from chemical pesticides by 2030, which includes a 50% reduction in the use of more hazardous pesticides by 2030. The first target will be measured based on quantities of AS on the market and their hazard properties (using the Harmonised Risk Indicator 1 methodology), the second target is based on more hazardous pesticide sales. The 2015-2017 period will be used as the baseline for both targets (EC, 2021d). Despite the clear targets, the Farm to Fork Strategy provides little guidance on how to achieve these goals, and the types/classes of pesticides and specific AS of first priority are not indicated. Closely related strategies, such as the Chemicals Strategy for Sustainability (EC, 2020e), the Zero Pollution Action Plan (EC, 2020h), or the new EU Soil Strategy (EC, 2021a), do not specify any pesticide priorities or actions to achieve these reductions.

Significant pesticide use reductions at the farm level are usually the result of the adoption of a new farming strategy with lower and more regulated pesticide use (Lamichhane et al., 2016), while pesticide risk reductions are generally the result of restrictions on the use of hazardous pesticides [e.g., neonicotinoids banned after proven to be a risk to honeybees (EC, 2018a)]. Integrated pest management (IPM) and organic farming, with reduced and no synthetic pesticide input, respectively, are felt to be adequate strategies to follow towards achieving sustainable food production (Eyhorn et al., 2019). IPM has been compulsory in the EU since 2014 (EC, 2009a). Organic production is highly encouraged and expected to represent at least 25% of the EU's agricultural land by 2030 (EC, 2020c). Nevertheless, even IPM and organically managed areas can be affected by pesticides, due to current and past use of pesticides, or due to off-site contamination (Fagan et al., 2020; Geissen et al., 2021; Riedo et al., 2021). Environmental and bio-monitoring data on pesticide residues are essential to quantify exposure and assess the risks of pesticides [risk = hazard * exposure (Damalas and Eleftherohorinos, 2011)], yet such data are scarce or fragmented (ECA, 2020), especially for some areas and matrices, certain AS, and low/no pesticide input farming systems.

Addressing risk reductions also requires addressing pesticide use and toxicity data fragilities. FAOSTAT and EUROSTAT, the reference databases for pesticide statistics, provide use and sales data on groups of AS only (EC, 2017b). The groups of FAOSTAT are more detailed than those of EUROSTAT (the former includes classes of pesticides, e.g., insecticides – pyrethroids; the latter only major pesticides groups, e.g., insecticides and acaricides), but individual AS data are required for verification of the efficacy of specific measures, and the achievement of the reduction targets. Other pesticide use data sources also have limitations: i) the world pesticide use review (Sharma et al., 2019) does not indicate the applied amount per AS either; ii) the PEST-CHEMGRIDS dataset (Maggi et al., 2019) has use estimates for only some of the AS allowed in the EU; and iii) there is data availability/accessibility issues and heterogeneity in the use data collected among the Member States (Galimberti et al., 2020). The existing monitoring data for soils (Sabzevari and Hofman, 2022; Silva et al., 2019), water (Casado et al., 2019) and air (Marlier et al., 2020) indicate that mixtures of pesticide residues are the rule rather than the exception, yet (eco)toxicity data on complex mixtures are rarely available, especially for observed concentrations in the environment, realistic mixture ratios, and other standard toxicity endpoints (Martin et al., 2021).

While designing ways to address the Farm to Fork pesticide reduction targets, an important aspect must be considered: pesticide use varies across regions and crop types (Damalas, 2015; Sharma et al., 2019). Given the already mentioned pesticide use data limitations, which are expected to be exacerbated by additional spatial and crop specification requests, AS representative uses can be a reasonable pesticide use proxy to explore the impacts of Farm to Fork driven measures for different farms, and to assess the feasibility of the pesticide use and risk targets in the first place, using scenario analyses. These representative uses are good agricultural practices for the use of AS and include the recommended number of applications per year and the recommended application rate per treatment, per crop and EU region. Furthermore, given the above-mentioned exposure data limitations, we used a second proxy (hazard), for exploring the pesticides risk aspect of the Farm to Fork Strategy. As pesticide risk is normally calculated as the product of hazard and exposure (Damalas and Eleftherohorinos, 2011), and since without hazard there is no risk, hazard was considered a suitable proxy for risk predictions. The European Food Safety Authority (EFSA) uses exposure and risk proxies in AS risk characterization - predicted environmental concentrations (PEC) and toxicity exposure ratios (TER) or hazard quotients (HQ), respectively.

In line with the above-described challenges, this study has two main objectives: i) establish a pesticide use and hazard baseline via a compilation of the representative uses and (eco) toxicity data of all 230 approved, synthetic AS used in open fields as herbicides, fungicides, and insecticides (91, 87, 50 AS, respectively, plus 2 multi-action substances); and ii) quantify total pesticide use and hazard reductions of different pesticide scenarios compared to a Business As Usual scenario (derived from the use and hazard baseline). The pesticide scenarios were designed as potentially applicable policy measures. As such, the respective use and risk reductions are estimated based on the current situation (Business As Usual scenario), and not on the 2015-2017 period.

5.2 Methodology

5.2.1 The pesticides in the EU market – selection and characterization

On February 5, 2019 (starting date of this study), there were 484 approved AS under the EC Regulation 1107/2009 concerning the Placing of Plant Protection Products on the EU market (EC, 2009c; EC, 2019a). From these, we selected the 365 fungicides (FU), herbicides (HB) and insecticides (IN) – the groups with the highest sales (EUROSTAT, 2019), and therefore of the highest relevance for pesticide reduction approaches. These 365 AS included 91 HB, 87 FU, 50 IN, and 2 multi-action AS (FU+HB, FU+HB+IN). The other 119 AS on the market were acaricides, attractants, bactericides, elicitors, molluscicides, nematicides, plant activators, plant growth regulators, repellents, rodenticides, or they did not fall into a specific category. The EU dossiers of these 365 FU/HB/IN AS were gathered and two types of data were retrieved from them: predicted environmental concentrations in soil (PECs) and soil degradation data. This step was required to i) establish a pesticide baseline in soils, a matrix where pesticide distribution data is particularly fragmented (manuscript in preparation), and ii) select the AS used in open-fields, which therefore may pose a risk to ecosystems and humans (including non-pesticide operators). PECs and soil degradation data were found for 249 FU/HB/IN AS. The remaining 116 FU/HB/IN AS were approved only for greenhouse or indoor uses, were not expected to be released to the surrounding environments (e.g., solid passive retrievable dispenser), were microbial substances, had no soil degradation data (data gap identified), or were not expected to present degradation (i.e., copper compounds). Of these 249 FU/HB/IN AS, 230 were synthetic substances and 19 were natural or inorganic substances (*Table S5.1*). These 230 synthetic FU/HB/IN AS constitute the primary group of interest for this study and were used to characterize the Business As Usual scenario.

General information, environmental fate data, and (eco)toxicological data for these 230 AS were extracted from the Pesticide Properties DataBase – PPDB (PPDB, 2021). The representative uses of these AS were extracted from their EU dossiers (i.e., EFSA conclusion reports on the peer review of the pesticide risk assessment, and draft or renewal assessment reports). In the case of multiple EU dossiers for the same AS we considered the information present in the latest dossier. PPDB was selected as the main data source due to its practicality and the existence of qualitative classes for (eco)toxicity data consistent with EU or EFSA guidance documents, EU regulatory values, or common use literature-based classification systems. PPDB is a reputable database, regularly updated, and with a vast number of primary data sources. Most of the data retrieved were A4-5 data, i.e., verified data used for regulatory purposes, from EC/EFSA publications. The other retrieved data was verified or unverified data from other sources. We considered all PPDB available data to reduce data gaps, accepting some data quality heterogeneity introduced by PPDB into our overview.

PPDB retrieved data covered pesticide type, chemical group, mode of action, volatility (from vapor pressure at 20^{o}C), leachability (GUS index), solubility (in water at 20°C), persistence (based on DT_{50} values on soil and water-sediment), bioaccumulation potential (from octanol-water partition coefficients at pH 7, 20°C), metabolites (number, relevance and formation fraction), and (eco)toxicological information. Such ecotoxicological information covered twenty ecotoxicological endpoints (on acute and chronic effects on mammals, birds, fish, aquatic invertebrates, aquatic plants, algae, sediment-dwelling organisms, honeybees, earthworms, other macro- and meso fauna, and soil micro-organisms), and eleven specific human health issues (carcinogen, mutagen, endocrine disruptor, reproduction/development effects, acetylcholinesterase inhibitor, neurotoxicant, respiratory tract irritant, skin irritant, skin sensitizer, eye irritant, and phototoxicant). These are standard toxicity endpoints and are in line with the endpoints considered in EC and EFSA assessments (EC, 2015d) (see PPDB and EFSA endpoints correspondence in *Table S5.2*). Note that PPDB provides a single value per AS-eco-toxicological endpoint combination, which is often the 'worst-case' data. Exceptions exist when the worst-case value appears wildly out of character with the majority of studies published.

5.2.2 The pesticide scenarios

Nine pesticide scenarios were defined in this study (*Fig. 5.1; Table S5.3*): a reference, Business As Usual scenario and seven pesticide reduction scenarios inspired by the Farm to Fork Strategy pesticide reduction goals (EC, 2020c). The scenarios were defined based on practical AS cut-off criteria (pesticide type, soil persistence, presence on the candidate for substitution EC list, and hazard to humans and/or ecosystems), being linked to current policy discussions, ongoing EC efforts, technological developments, or trends in pesticides on the EU market. Scenario descriptions are provided below and their representativity and implications are further explored in the discussion. The scenarios differ on the type and number of AS allowed; the application rates of individual AS remain the same across scenarios to guarantee efficient pest control.

1. Business As Usual - BAU: a scenario with no pesticide use restrictions. BAU covers the 230 selected AS (FU/HB/IN) and assumes all EU farms have current recommended pesticide input. BAU is assumed to be the initial condition for the following reduction scenarios.

2. No Herbicides - NH: a scenario where herbicides are not allowed. NH covers the 139 FU/IN or multi-action AS and assumes all EU farms will use non-chemical alternatives to control weeds.
3. Fast Degradable Pesticides only - FDP: a scenario where only the 106 FU/IN/HB with half-life times (DT_{50}) in soil less than 100 days are allowed. FDP assumes all EU farms will only use fast degradable pesticides.
4. Total Pesticides Ban - TPB: a scenario where all the 230 synthetic AS are no longer allowed. TPB assumes all EU farms will be converted to organic production. In hazard reduction assessments, PBT covers the 60 FU/IN/HB that are still likely to be found in the environment after pesticide use stops (i.e., AS with 90% degradation rate, DT_{90}>365 days), and posing possible risks to humans and ecosystems.
5. Candidates For Substitution Excluded - CFSE: a scenario where the 49 AS identified by the EC as candidates for substitution are no longer allowed. CFSE covers the other 181 FU/IN/HB not included in the candidates for substitution list. CFSE links the two Farm to Fork pesticide reduction goals, i.e., reduction of overall pesticides and the more hazardous pesticides.
6. Low Hazard Pesticides only – LHP: a scenario where the AS with cumulative hazard scores ≥ 15 for humans or cumulative hazard scores ≥ 31 for ecosystems are not allowed. Cumulative hazard scores were estimated based on the severity of effects on standard (eco)toxicity endpoints (see methods for details). The 15 and 31 thresholds were retrieved from the BAU cumulative hazard score histograms. These values are histogram cut-off values that appear after distribution peaks and that are linked to a ~25% reduction of AS on the market (this percentage was assumed to be reasonable for farmers, and potentially relevant for Farm to Fork goals). LHP covers 136 AS with low hazard scores and assumes all EU farms will only use these lower hazard pesticides.
7. Safe Human Health only - SHH: a scenario where only the 49 AS known to not cause appreciable human health problems are allowed. These AS are known to be non-carcinogenic and non-mutagenic, and most likely not (i.e., known not to be + no data available) an endocrine disrupter, neurotoxin or the causing agent of adverse reproduction/development effects. SHH assumes the whole EU will only use SHH pesticides.
8. Low Ecosystem Toxicity only - LET: a scenario where only the 57 AS with low or moderate toxicity to the ecosystem are allowed. These AS are known to have low or moderate toxicity for mammals (acute), birds, fish, aquatic invertebrates,

aquatic plants, algae, honeybees, earthworms (acute), and no significant adverse effects on soil micro-organisms. LET assumes all EU farmers only have access to LET pesticides.

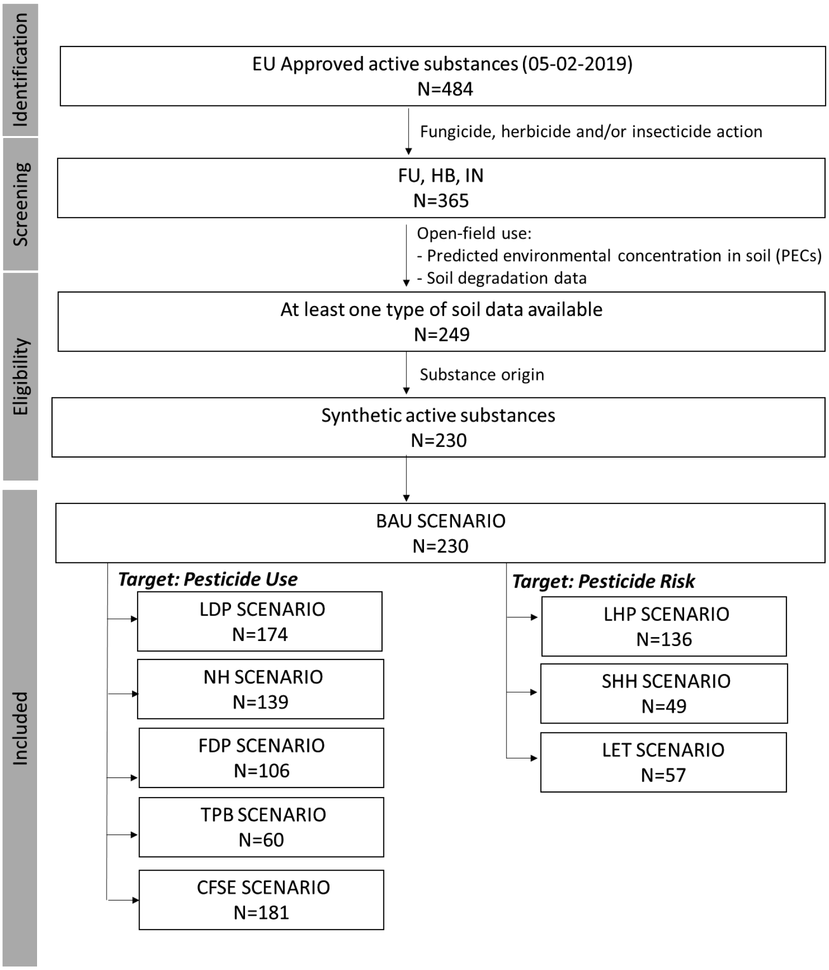

Figure 5.1 – Diagram used in the selection of the pesticides considered in this study, including the different pesticide reduction scenarios. BAU = Business As Usual, LDP = Low Dose Pesticides only, NH = No Herbicides, FDP = Fast Degradable Pesticides only, TPB = Total Pesticides Ban, CFSE = Candidates For Substitution Excluded, LHP = Low Hazard Pesticides only, SHH = Safe Human Health pesticides only, LET = Low Ecosystem Toxicity pesticides only. For the list of active substances excluded per criterion, see *Table S5.1*. For the list of substances allowed per pesticide scenario, see *Table S5.3*. N = number of active substances.

5.2.3. Pesticide-crop profiles

As mentioned above, each AS on the EU market has been approved by the EC for specific representative uses. When the representative uses of all substances approved per pesticide scenario are compiled and re-organized by crop type, a list of allowed AS per crop arises (a pesticide-crop profile). To explore a reasonable yet relevant number of pesticide-crop profiles, the specific crops from the representative uses were aggregated into eight crop classes: cereals, dry pulses-vegetables-flowers, grapes, (temporary) grassland, maize, non-permanent industrial crops, permanent crops, and root crops. The attribution of the specific crops of the AS representative uses into our crop classes followed the LUCAS 2018 classification (E4 LUCAS ESTAT, 2018) ; *Table S5.4*). Maize and grapes were not merged into broader classes due to their particularly high frequency in representative use records. Pesticide-crop profiles take into account the different AS and their application rates across the three EU regulatory zones (EC, 2009c): Northern Europe (NEU), Central Europe (CEU), and Southern Europe (SEU; *Table S5.5*).

5.2.4. Pesticide use and risk

In this study, recommended pesticide application rates and pesticide hazards are used as pesticide use and pesticide risk proxies, respectively. This is because pesticide statistics, access to application records, and post-approval monitoring data are limited. The full explanation of the need for a proxy, on the selected proxies and the relationships between the terms is already provided in the introduction of the paper. To stress that to assess pesticide use in future studies, detailed crop data (d'Andrimont et al., 2021) and information on area treated and application likelihood per area is required; and to assess risks, information on distribution and availability of pesticides across environmental and biological matrices.

Therefore, in this study, the impacts of the Farm to Fork overall pesticide use are inferred from total AS recommended application rates. These total AS application rates were calculated using a conservative approach based on AS current representative uses; it is assumed that all the AS allowed per crop class-EU region-scenario are applied at the recommended application scheme leading to their maximum annual application rate. Annual application rates were calculated as the product of the (highest) number of recommended applications per year and the (maximum) recommended application rate per treatment in the respective representative use. When an AS had the same annual application rate for different representative uses, we selected the representative use leading to the highest predicted concentration in soil (highest PECs 0; values extracted or calculated from the AS EU dossiers), to account for the worst-case exposure scenario. The overall reductions in total AS application rate (*Fig. 5.7*) are the average of the reductions across crop class-EU region-scenarios.

Hazard reduction predictions involved a slightly more complex approach, with the attribution of hazard scores to the PPDB categorical/qualitative classes. The hazard scores were attributed to these qualitative classes as follows: a) human endpoints: known to have no effect=0, no data available=1, possible effect (status not identified)=2, known effect=3; b) other terrestrial and aquatic non-target species' endpoints: low toxicity=0, no data available=1, moderate toxicity=2, high toxicity=3; c) soil micro-organisms' endpoints: no significant adverse effect=0, no data available=1, EC/NOEC value or chronic effect=3. The score of 0 was attributed to 'low toxicity' because while aiming for a similar score system for human and ecosystem endpoints, the 'low toxicity' class seemed the closest to 'no effect', or to a possibly acceptable effect. Remember that to be market approved by the European Commission, an AS must not have any harmful effects on animal or human health nor any unacceptable effects on plants or the environment (EC, 2009c). A slightly higher score was attributed to the 'no data available' class to account for possible toxicity situations hidden by data confidentiality. The main reasons why (eco)toxicity data might be missing in the PPDB relates to the fact that data may have not been made available for the public domain, or because the toxic mechanism of action of the pesticide suggests that testing on specific organisms groups is not relevant. This assumption is challenged by the indirect effects of pesticides, see the case of glyphosate acting on the shikimate pathway present in most bacteria in the human intestinal tract (van Bruggen et al., 2021).

According to the system above, a 0-3 hazard score was attributed to each AS - endpoint combination. The scores of the human and ecosystem endpoints for each AS were then summed up to obtain cumulative hazard scores for each AS. These cumulative scores allowed for overall hazard comparisons between AS. In the calculation of the cumulative hazard scores, the same weight was attributed to the different (eco)toxicological endpoints; adding a second layer to the scoring system based on our interpretation of the endpoint severity could lead to a biased LHP scenario. Hazard reductions were calculated based on the difference in the number of AS per qualitative class-endpoint-scenario compared to respective BAU figures. Overall, hazard reductions are the average of the reductions in high or moderate ecotoxicity endpoints or the reductions in known or possible human effects. As in use predictions, it was assumed that all AS allowed in each scenario (or covered in the case of TPB) were applied.

5.3. Results

5.3.1. Pesticide use and hazard baseline

The 230 EU-approved, synthetic, and open-field use fungicides/herbicides/insecticides present a great variability in physicochemical properties, environmental persistence and (eco) toxicological profiles. Herbicides (HB) and fungicides (FU) dominate the EU pesticide market, representing 40% and 38% of the selected AS, respectively. The 230 selected AS cover 99 chemical groups and 64 modes of action. The chemical groups most represented (in terms of numbers of substances per group) are the sulfonylureas, carbamates, triazoles and pyrethroids, and the most frequent modes of action are inhibition of plant amino acid synthesis, inhibition of ergosterol/sterol biosynthesis and inhibition of succinate dehydrogenase (*Table S5.6*). In general, the selected AS present low volatility, low solubility in water, and low leachability (90%, 57%, 55% of AS, respectively). Around half of these 230 AS are expected to be moderately persistent to very persistent in soil (51-55%, lab-field data) or water-sediment medium (47%). Approximately half of the 230 AS present high bio-concentration potential (51%), a characteristic especially common in moderately persistent and persistent compounds. The 230 selected AS have 414 known metabolites, 243 of which have maximum formation fractions above 10% and biological relevance (i.e., target activity comparable to the parent substance, comparable or higher risk to organisms than the parent substance or severe toxicological properties (EC, 2009c); *Fig. S5.1*). Finally, 49 out of the 230 selected AS are in the EC's candidates for substitution list. Almost all of those AS (45 out of the 49) i) meet two of the PBT criteria - Persistent, Bio-accumulative or Toxic substance (n=33, 67%); ii) have a low ADI - Acceptable Daily Intake, low ARfD - Acute Reference Dose, or low AOEL - Acceptable Operator Exposure Level (n=9, 18%); or iii) are toxic for reproduction category 1A or 1B [n=3, 6%; see (EC, 2015c) for further details on these categories]. The remaining 4 AS meet two or three cut-off conditions.

Nearly half (49%) of the 230 AS are specific to one of our crop classes while the other half can be applied to two, three, four, or all the eight classes (31, 16, 3 and 1%, respectively). The highest number of AS is expected to be used in cereals (51-88 AS approved/region), however, the highest total AS application rate is expected in dry pulses-vegetables-flowers, grapes, and root crops (*Table 5.1*). These are the crops where the soil sterilant metam, the AS with the highest application rates among the 230 HB/FU/IN, is allowed. Total AS application rate differs substantially across EU regions, being, in general, the highest in SEU. AS application rates are highly variable, with a couple of AS being allowed at extremely high levels (*Fig. 5.2*). Metam and dazomet have maximum application rates of 1,020 and 500 kg/ha/year, respectively, i.e., rates 2-3 orders of magnitude higher than most of the other pesticides on the market. Paraffin oils, tolclofos-methyl, dodemorph, folpet, captan and fosetyl have high application rates (>10-100 kg/ha/year), 47 compounds have moderate application rates (1 -10 kg/ha/year), and the remaining 174 AS have low application rates (< 1 kg/ha/year).

Most of the 230 AS are expected to present low or moderate toxicity for the different ecotoxicological endpoints, except for mammals, if exposed short-term via the diet (*Table 5.2*). However, there are data gaps in all 20 ecotoxicological endpoints; these "no data available" situations range from 4 to 224 AS, depending on the endpoint. The largest data gaps occur for long-term endpoints and soil macro-organisms, arthropods, and sediment-dwelling organisms (*Table 5.2*). Acute and long-term endpoints often result in different levels of toxicity that are organism- and pesticide-dependent. Mammals, birds and earthworms, for instance, appear to be highly resistant to acute pesticide exposures, with ≥90% of selected AS showing low or moderate toxicity to them. However, when long-term endpoints are considered, only birds remain highly resistant, with 79% of AS showing low or moderate toxicity. Mammals appear highly vulnerable to pesticides, with at least 50% of AS showing high long-term toxicity. Earthworm resistance becomes highly questionable, with long-term toxicity data missing for 46% of the AS.

The AS with the highest ecosystem-cumulative hazard scores are chlorpyrifos, bifenthrin, beta-cyfluthrin, dimethoate, gamma-cyhalothrin, alpha-cypermethrin and esfenvalerate (*Fig. 5.3*), of which bifenthrin, dimethoate and esfenvalerate are candidates for substitution. There were no AS with a cumulative hazard score of 0. Chlorpyrifos, known to affect twelve of the twenty ecotoxicological endpoints considered, was banned at the end of 2019. Bifenthrin is known to affect eleven endpoints, beta-cyfluthrin, alpha-cypermethrin and esfenvalerate are known to affect nine of the endpoints, gamma-cyhalothrin affect eight and dimethoate seven endpoints. Most of the other AS are known to affect one or two ecotoxicological endpoints (36% and 15% of AS; *Fig. S5.2*).

Table 5.1 – Number of active substances (AS) allowed under the Business As Usual (BAU) scenario, maximum recommended annual application rate among allowed AS, and total AS application rate (i.e., sum of the maximum recommended annual application rate of all allowed AS) per crop-EU region combination. Annual application rates were calculated as the product of the (maximum) number of recommended treatments per year and the (maximum) recommended application rate per treatment in respective EC approved, AS representative use (retrieved from individual AS EU dossiers). The average of total AS application rate in NEU, CEU and SEU was used in the European characterization (the last column of the table). Maximum annual application rates among allowed AS are presented with zero or two decimal places (if above or below 100 kg/ha/year, respectively). Total AS application rates are presented with zero decimal places. NEU - Northern Europe, CEU - Central Europe, SEU - Southern Europe. DPVF = dry pulses, vegetables, flowers; NPIC = non-permanent industrial crops; Perm. = permanent; Max. = maximum; rec. = recommended.

Crop	Parameter	NEU	CEU	SEU	EUROPE
Cereals	Number of AS allowed	77	51	88	98
	Max. rec. application rate/AS (kg/ha/year)	4.00	2.16	4.00	4.00
	Total AS application rate (kg/ha/year)	31	18	31	*27*
DPVF	Number of AS allowed	49	30	68	72
	Max. rec. application rate/AS (kg/ha/year)	612	612	612	612
	Total AS application rate (kg/ha/year)	1,210	713	1,196	*1,039*
Grapes	Number of AS allowed	40	19	56	56
	Max. rec. application rate/AS (kg/ha/year)	15.00	1,020	1,020	1,020
	Total AS application rate (kg/ha/year)	54	1,046	1,088	*729*
Grassland	Number of AS allowed	8	7	8	11
	Max. rec. application rate/AS (kg/ha/year)	1.44	1.80	1.44	1.80
	Total AS application rate (kg/ha/year)	4	6	4	*5*
Maize	Number of AS allowed	21	18	23	24
	Max. rec. application rate/AS (kg/ha/year)	2.16	2.16	2.16	2.16
	Total AS application rate (kg/ha/year)	8	7	9	*8*
NPIC	Number of AS allowed	28	18	32	39
	Max. rec. application rate/AS (kg/ha/year)	3.00	2.40	2.40	3.00
	Total AS application rate (kg/ha/year)	18	11	19	*16*
Perm. crops	Number of AS allowed	29	9	39	40
	Max. rec. application rate/AS (kg/ha/year)	12.50	16.38	94.80	94.80
	Total AS application rate (kg/ha/year)	60	45	157	*87*
Root crops	Number of AS allowed	58	30	64	67
	Max. rec. application rate/AS (kg/ha/year)	153	153	153	153
	Total AS application rate (kg/ha/year)	198	178	280	*219*

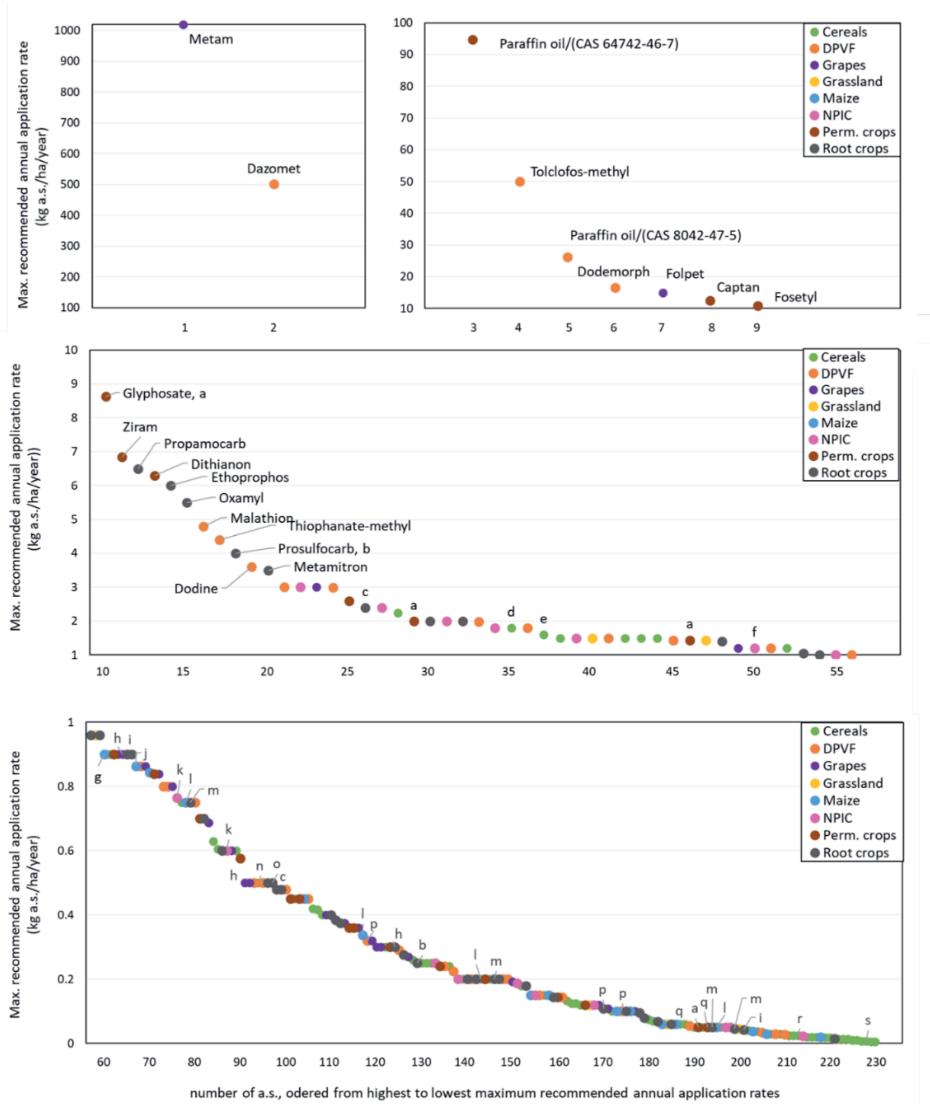

Figure 5.2 – Maximum recommend annual application rate of the 230 selected AS, according to their EU representative uses. The dot colour indicates the crop for which the maximum recommended annual application rate per AS is expected. Given the high variability of maximum annual application rates across AS, data is presented in four panels according to input ranges: >100 kg/ha/year, 10-100 kg/ha/year, 1-10 kg/ha/year, <1 kg/ha/year. For readability purposes, only the name of the 20 top use AS were added to the graph. When the maximum annual application rate of an AS was common to more than one crop, a lower-case letter was added. Letters correspond to (the first crop mentioned is the one presented in the figure) - a: Perm. crops/grapes, b: root crops/cereals, c: root crops/DPVF, d: cereals/DPVF/grassland, e: cereals/DPVF/root crops, f: NPIC/maize, g:maize/DPVF, h: grapes/DPVF, i: root crops/grapes, j: maize/root crops/NPIC, k: NPIC/DPVF, l: maize/cereals, m: root crops/NPIC, n: DPVF/cereals, o: root crops/Perm. crops, p: DPVF/NPIC/root crops, q: DPVF/Perm. crops/grapes, r: cereals/NPIC/DPVF, s: cereals/grassland. max = maximum, DPVF = dry pulses, vegetables, flowers, NPIC = non-permanent industrial crops, Perm. = permanent.

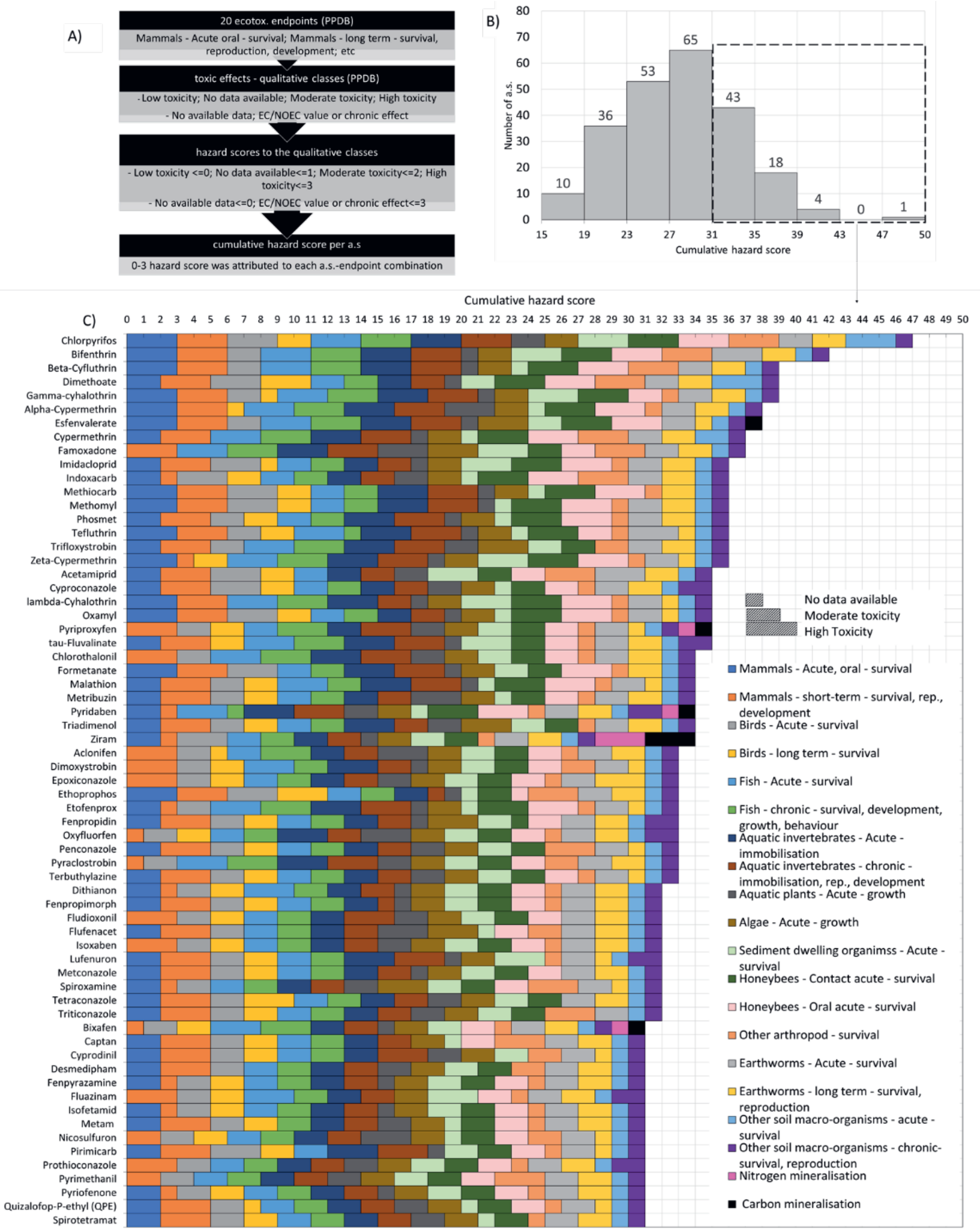

Figure 5.3 – Cumulative hazard scores of the selected 230 AS for ecosystems. A) cumulative hazard scores per AS: 0-3 hazard scores were attributed to the severity of effect, and the scores in the different endpoints were summed up to obtain the cumulative score per AS. B) Histograms for the ecosystem-cumulative hazard scores of the 230 selected AS [Number of bins was defined as (√230/2) and the width of bins as ((max-min cumulative hazard score)/number of bins)]. C) Hazard profile of the 66 AS with ecosystem-cumulative hazard scores ≥31 were considered highly hazardous AS, and therefore excluded in the LHP scenario. For complete AS hazard profiles see *Supplementary Fig. 5.2*.

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Table 5.2 – Ecotoxicological profile of selected active substances (AS, n=230) according to the PPDB: Pesticide Properties DataBase (PPDB, 2021). The numbers in the table indicate the number of AS known to have low, unknown, moderate or high toxicity to a respective organism-endpoint. PPDB toxicity thresholds are defined according to EU guidelines or EU regulatory values. The detailed timescale was provided whenever this information was available. LC – lethal concentration; EC – effect concentration; NOEC – highest no observed effect concentration. Grey highlighted cells show the most represented toxicity class per ecotoxicological endpoint. Blue cells indicate the average number of AS considered per hazard score (for the 18 ecosystem endpoints or the 2 microbial endpoints considered).

Hazard score	**0**	**1**	**2**	**3**
Organisms – Time scale, exposure route – Endpoint	**Low toxicity**	**No data available**	**Moderate toxicity**	**High toxicity**
1- Mammals – acute, oral – LD_{50}, survival	108 (47%)	8 (3%)	99 (43%)	15 (7%)
2- Mammals – short-term, dietary – NOEL, survival, reproduction or development	0 (0%)	98 (43%)	16 (7%)	116 (50%)
3- Birds – acute – LD_{50}, survival	73 (32%)	9 (4%)	134 (58%)	14 (6%)
4- Birds – short-term, dietary – LC_{50}/LD_{50}	83 (36%)	45 (20%)	99 (43%)	3 (1%)
5- Fish – acute 96 hour – LC_{50}, survival	17 (7%)	4 (2%)	175 (76%)	34 (15%)
6- Fish – chronic 21 day – NOEC, survival, development, growth or behaviour	31 (13%)	36 (16%)	136 (59%)	27 (12%)
7- Aquatic invertebrates – acute 48 hour – EC_{50}, immobilisation	17 (7%)	7 (3%)	165 (72%)	41 (18%)
8- Aquatic invertebrates – chronic 21 day – NOEC, immobilisation, reproduction or development	30 (13%)	31 (13%)	128 (56%)	41 (18%)
9- Aquatic plants – acute 7 day – EC_{50}, growth	19 (8%)	89 (39%)	94 (41%)	28 (12%)
10- Algae – acute 72 hour – EC_{50}, growth	47 (20%)	8 (3%)	154 (67%)	21 (9%)
11- Sediment dwelling organisms – Acute 96hour – LC_{50}, survival	10 (4%)	123 (53%)	82 (36%)	15 (7%)
12- Honeybees – acute 48 hour – LC_{50}, survival (contact)	55 (24%)	10 (4%)	142 (62%)	23 (10%)
13- Honeybees – acute 48 hour – LC_{50}, survival (oral)	81 (35%)	18 (8%)	110 (48%)	21 (9%)
14- Earthworms – acute 14 day – LC_{50}, survival	9 (4%)	9 (4%)	207 (90%)	5 (2%)
15- Earthworms – long-term 56 day – NOEC, survival or reproduction	13 (6%)	106 (46%)	109 (47%)	2 (1%)
16- Soil macro-organisms other than earthworms** – acute – LC_{50}, survival	0 (0%)	224 (97%)	3 (1%)	3 (1%)
17- Soil macro-organisms other than earthworms** – chronic – NOEC, survival or reproduction	7 (3%)	209 (91%)	14 (6%)	0 (0%)
18- Other arthropods* – not available – LC_{50}, survival	49 (21%)	144 (63%)	10 (4%)	27 (12%)
Average number of a.s. per hazard score	36 (16%)	65 (28%)	104 (45%)	24 (11%)
	No significant adverse effect	**No data available#**	**EC/NOEC value or chronic effect**	
19- Soil micro-organisms – long-term 100 days – Nitrogen mineralisation	194 (84%)	34 (15%)	2■ (1%)	
20- Soil micro-organisms – long-term 100 days – Carbon mineralisation	192 (83%)	36 (16%)	2□ (1%)	
Average number of a.s. per hazard score	193 (84%)	35 (15%)	2 (1%)	

The 230 selected pesticides are also associated with several human health issues, the most common being eye, skin and respiratory tract irritations (37%, 25% and 22% of AS, respectively), skin allergies (21%), and reproductive/development toxicity (24%; *Table 5.3*). Similar to ecotoxicological data, human health endpoints also present data gaps. The biggest gaps are in phototoxicity, skin sensitivity, endocrine disruption and the mutagenicity character of AS (82%, 56%, 54% and 47% of the AS, respectively). The AS with the highest human-cumulative hazard scores are fenoxycarb, pendimethalin, ziram, chlorothalonil and gamma-cyhalothrin, of which only pendimethalin and ziram are candidates for substitution (*Fig. 5.4*). Chlorothalonil is known to affect six of the eleven human endpoints considered, gamma-cyhalothrin and pendimethalin are known to affect five of the endpoints, and ziram and fenoxycarb four. Most of the AS are known to affect one, two, or three human endpoints (29%, 23%, and 16% of AS, respectively; *Fig. S5.3*). The only AS that proved to not affect any of the eleven human endpoints is fluoxastrobin.

Table 5.3 – Human health problems associated with the use of the 230 selected active substances according to the PPDB (2021). The numbers in the table indicate the number of active substances known to cause the problem, known to not cause the problem, with status not identified or no data available. Grey highlighted cells show the most represented class per endpoint. Blue cells indicate the average number of AS considered per hazard score.

Hazard scores	**0**	**1**	**2**	**3**
Effect? / **Endpoint**	**No (known to not cause a problem)**	**Unknown (No data available)**	**Possibly (status not identified)**	**Yes (known to cause a problem)**
1- Carcinogen	126 (55%)	11 (5%)	81 (35%)	12 (5%)
2- Mutagen	106 (46%)	108 (47%)	13 (6%)	3 (1%)
3- Endocrine disruptor	55 (24%)	125 (54%)	42 (18%)	8 (4%)
4- Reproduction/development effects	47 (20%)	20 (9%)	107 (47%)	56 (24%)
5- Acetyl cholinesterase inhibitor	194 (85%)	19 (8%)	7 (3%)	10 (4%)
6- Neurotoxicant	147 (64%)	37 (16%)	30 (13%)	16 (7%)
7- Respiratory tract irritant	76 (33%)	86 (38%)	17 (7%)	51 (22%)
8- Skin irritant	133 (58%)	10 (4%)	29 (13%)	58 (25%)
9- Skin sensitiser	32 (14%)	128 (56%)	21 (9%)	49 (21%)
10- Eye irritant	110 (48%)	10 (4%)	25 (11%)	85 (37%)
11- Phototoxicant	36 (16%)	189 (82%)	4 (2%)	1 (<1%)
Average number of a.s. per score	97 (42%)	68 (29%)	34 (15%)	32 (14%)

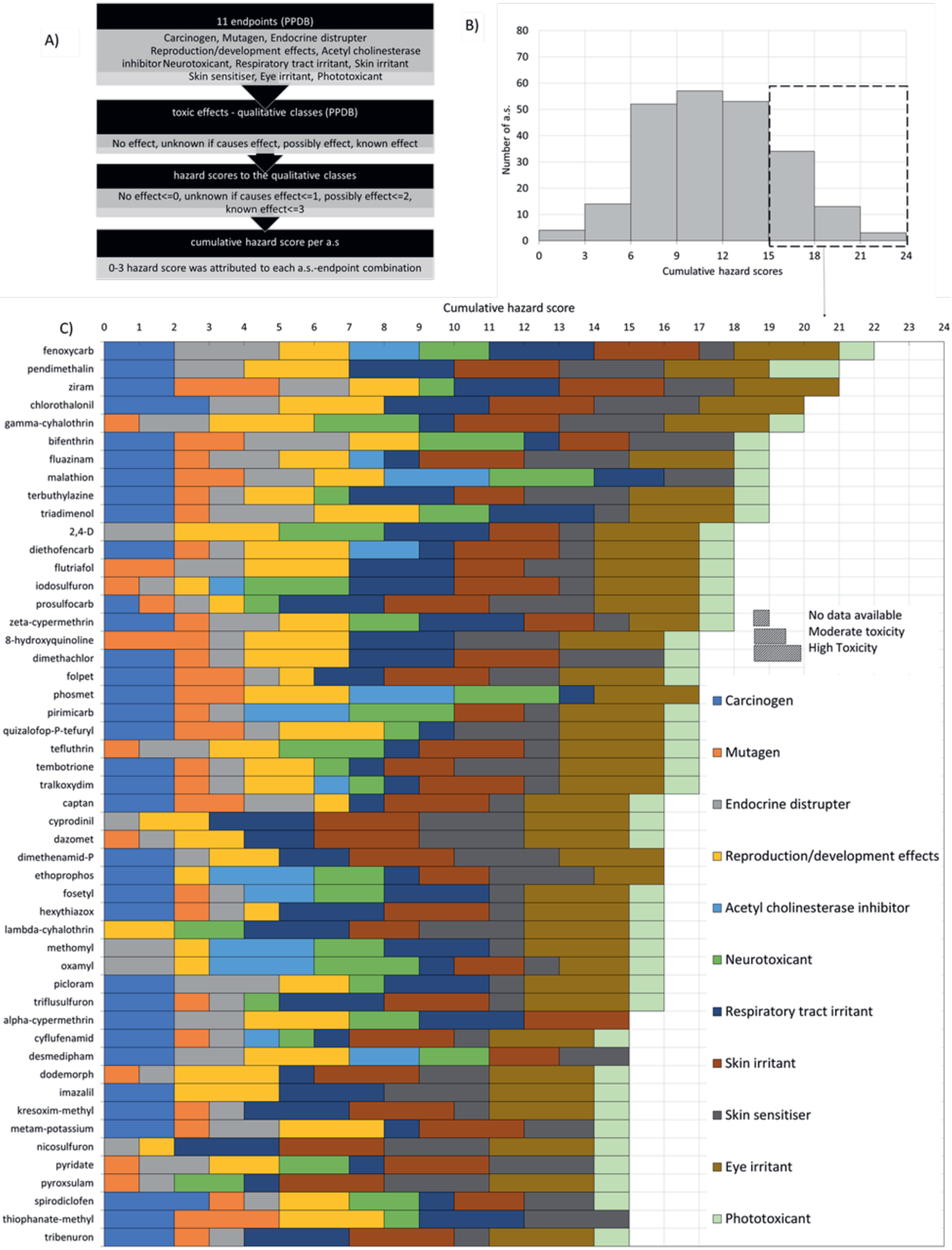

Figure 5.4 – Cumulative hazard scores of the selected 230 AS to humans. A) cumulative hazard scores per AS: 0-3 hazard scores were attributed to the severity of effect, and the scores in the different endpoints were summed up to obtain the cumulative score per AS. B) Histograms for the human-cumulative hazard scores of the 230 AS. [Number of bins was defined as (√230/2) and the width of bins as ((max-min cumulative hazard score)/number of bins)]. C) Hazard profile of the 50 AS with ecosystem-cumulative hazard scores ≥15, excluded in the LHP scenario. For complete AS hazard profiles see *Supplementary Fig. 5.3*.

The AS with the highest application rates are often not the most hazardous for the ecosystem or humans (*Fig. 5.5*). Only seven AS are among the top use AS (i.e., the 56 AS with maximum annual application rates >1 kg/ha/ha), top hazard for ecosystems (i.e., the 66 AS with cumulative hazard scores ≥ 31, *Fig. 5.3*) and top hazard for humans (i.e., the 50 AS with cumulative hazard scores ≥ 15; *Fig. 5.4*): captan, chlorothalonil, ethoprophos, fluazinam, malathion, oxamyl, and ziram. Thirty-four AS are in two of these three top positions - i) in top use and top hazard for the ecosystem: aclonifen, dithianon, fenpropidin, fenpropimorph, fenpyrazamine, isofetamid, metamitron, metribuzin, oxyfluorfen and pyrimethanil; ii) in top use and top hazard for humans: 8-hydroxyquinoline, dazomet, dimethachlor, dodemorph, folpet, fosetyl, metam, pendimethalin, prosulfocarb, thiophanate-methyl; and iii) in top hazard for ecosystem and top hazard for humans: alpha-cypermethrin, bifenthrin, cyprodinil, desmedipham, gamma-cyhalothrin, lambda-cyhalothrin, methomyl, nicosulfuron, phosmet, pirimicarb, tefluthrin, terbuthylazine, triadimenol and zeta-cypermethrin. Over half of the selected AS (124 out of the 230 AS) are in one of these top use or top hazard positions.

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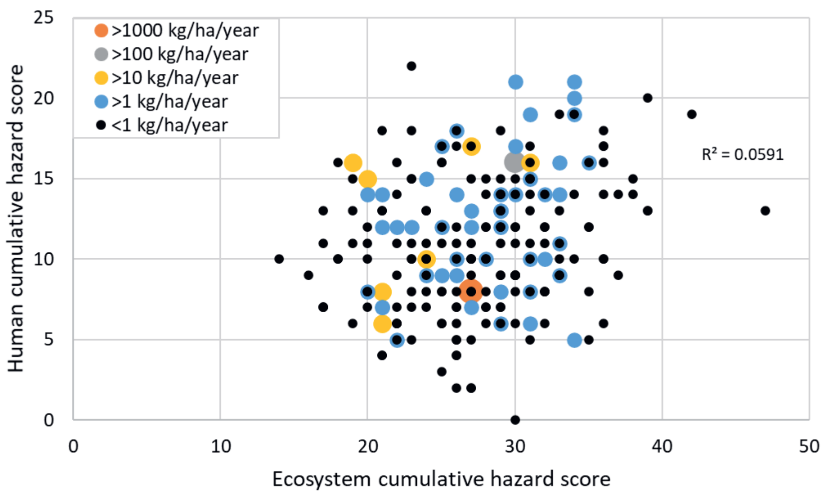

Figure 5.5 – Scatter plot of human and ecosystem cumulative hazard scores of the 230 selected AS. Different colours were attributed to different classes of maximum recommended annual application rates and increasing symbol sizes were attributed to higher input levels, to allow the visualization of AS with the same human-ecosystem scores but different input classes.

5.3.2. Pesticide reduction scenarios

Our pesticide reduction scenarios represent a decrease from 21 to 100% in the number of AS allowed on the EU market (from the least to the most restrictive scenario: CFSE> NH>LHP>FDP>LET>SHH>TPB; *Fig. 5.6*, *Tables S5.7-S5.12*). The number of AS allowed per crop type vary greatly across pesticide reduction scenarios but, similar to BAU, the highest number of AS is expected for cereals and SEU. The reductions in the number of AS allowed per crop-region-scenario are not necessarily translated into similar reductions of application rates (*Table S5.13*). NH, SHH and LET presented similar reductions in the number of AS and the total AS application rate (reductions in the number of AS were ± 7% reductions in the total AS application rate), but the FDP 54% reduction in the number of AS leads to only a 28% reduction in the total AS application rate. Overall, the reduction scenarios result in a 28% to 100% lower total AS application rate than in BAU (from lowest to highest reduction: FDP>CFSE>NH>LHP>LET> SHH>TPB; *Fig. 5.6*). Four out of the seven pesticide reduction scenarios lead to an overall input reduction of ≥50%. Except for LHP, the highest total AS application rate is expected for dry pulses-vegetables-flowers, grapes or permanent crops, and in SEU. In LHP, root crops and CEU have some of the highest AS uses.

All pesticide reduction scenarios led to reductions in the number of AS with high or moderate toxicity to non-target organisms; the percentage of the reduction was endpoint and scenario dependent (*Tables S5.14-S5.20*). NH performed worse than the other scenarios with 0% hazard reductions for nine endpoints (mammals – acute, birds – acute and short-term, sediment-dwelling organisms, honeybees – contact and oral acute, earthworms – acute and chronic, and other soil macro-invertebrates - acute). Overall, ecosystem hazard reductions ranged from 27 to 80% (from lowest to highest reduction: NH>CFSE>FDP>LHP>TPB>SHH=LET; *Fig. 5.6*). Five out of the seven pesticide reduction scenarios lead to a hazard reduction of ≥50% (FDP, LHP, TPB, SHH, and LET).

Similar to ecosystem results, the number of AS known to cause or possibly causing effects in humans was reduced for almost all endpoints after pesticide scenario restrictions; the exceptions were: i) mutagen in NH and FDP, ii) acetylcholinesterase inhibitor in NH, and iv) phototoxicant in NH, TPB, CFSE and LHP (*Tables S5.21-S5.27*). These 0% hazard reduction situations were observed at the four endpoints with less AS in BAU. For instance, as only 1 out of the 230 selected AS is known to be phototoxic, and this AS is a persistent fungicide, both NH and TPB (where fungicides/insecticides and very persistent AS are allowed, respectively) present no hazard reductions (*Table S28*). Overall, human hazard reductions ranged from 27 to 88% (from lowest to highest reduction: CFSE>NH> FDP>LHP>TPB>LET>SHH; *Fig. 5.6*). Five out of the seven pesticide reduction scenarios lead to a hazard reduction of ≥50% (same scenarios as in the ecosystem).

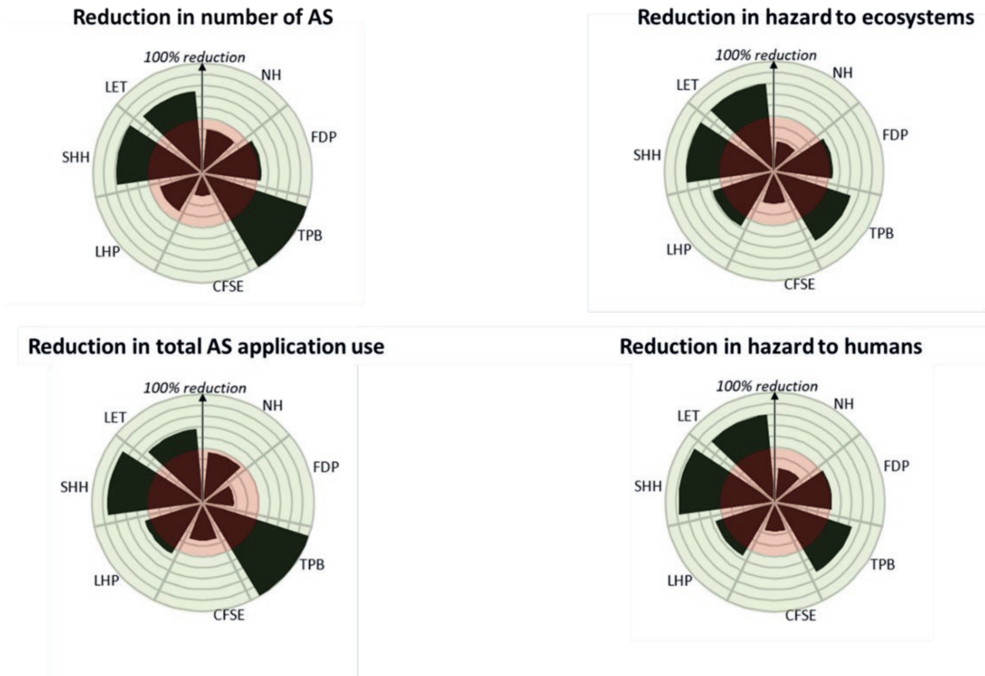

Figure 5.6 – Reductions in the number of active substances (AS) allowed, total AS application rate, and on the overall hazard to ecosystem and humans in the different scenarios in relation to Business As Usual figures. Overall use reductions are the average values of all crop-EU region reductions in respective scenario. Overall hazard reductions are the average values of all ecotoxicological or human endpoint reductions in the respective scenario. NH = No Herbicides, FDP = Fast Degradable Pesticides only, TPB = Total Pesticides Ban, CFSE = Candidates For Substitution Excluded, LHP = Low Hazard Pesticides only, SHH = Safe Human Health, LET = Low Ecosystem Toxicity. For crop-EU regions use reductions see Supplementary Table 13. For (eco)toxicological endpoints hazard reductions see Supplementary Table 5.28. Reductions below the 50% target are marked in red, and those above 50% in green.

5.4 Discussion

5.4.1. Pesticide use and hazard baseline

Use baseline

BAU, the reference scenario to assess pesticide use and hazard reductions, assumes that all AS allowed per crop-EU region are applied at their maximum recommended annual application rates. We recognize that it is unlikely that all AS allowed per crop-EU region are applied to each field, also because regulations, the pesticide market and agricultural practices may differ widely among regions (Damalas, 2015; Sharma et al., 2019). Interviews with, and application records of, EU conventional farmers indicate a smaller number of AS and lower pesticide input than predicted here (Chiaia-Hernandez et al., 2017; Geissen et al., 2021). Geissen et al. (2021) reported a maximum of 22, 18 and 44 AS applied per field/year, and a total pesticide input up to 86, 38 and 49 kg/ha/year, in Spanish vegetable fields, Portuguese vineyards and Dutch potato fields, respectively. For these crop-regions, BAU considers 68, 56 and 58 AS, and a total pesticide input of 1196, 1088 and 198 kg/ha/year. If the soil sterilant metam and the soil fumigant dazomet, with very high recommended application rates, are not considered in our predictions (both substances were not reported to be applied by farmers), estimates becomes 98, 179 and 92% of applied amounts. The interviews (Geissen et al., 2021) revealed that the number of recommended applications and the recommended application rates are sometimes exceeded in the field when pest pressure is severe, and that some AS are applied in crops not listed in the EU dossiers. Chaia-Hernandez et al. (2017) reported a maximum of 20, 20 and 10 AS applied per field/year, and a total pesticide input up to 33, 17, and 15 kg/ha/year in Swiss orchards, vineyards, and vegetables, respectively. For these crops, BAU-CEU considers 9, 19 and 30 AS, and 45, 1046 and 178 kg/ha/year. Chaia-Hernandez et al. (2017) provide the list of pesticides used across the monitored sites and respective applications. That list does not include metam or dazomet (which explain most of the difference between real applications and in our estimates) and corroborates that AS recommended rates are sometimes exceeded by farmers. No more studies were found with real (not estimated) pesticide application data in Europe.

FAOSTAT (2020) reports a maximum pesticide use oscillating between 8.79 and 13.76 kg/ha/year for EU croplands (this is for the years between 1990-2018).

FAOSTAT data suggest that AS with high recommended application rates are not being applied in most EU fields, but individual AS use data would be necessary to corroborate this hypothesis. One could think that the pesticide use reduction targets would be easily achieved by restricting the use of only a few AS with high application rates, however, these are often low-persistence compounds and of intermediate hazard to humans and the ecosystem (Fig. 5.5), so such measures would be misleading and would not guarantee the coupled 50% risk reduction target. Phase-out AS should be selected via an integrated use and risk approach. Finally, the fact that both Geissen et al. (2021) and Chaia-Hernandez et al. (2017) reported higher pesticide use than FAOSTAT raises concerns on the quality of reference pesticide statistics data. Facilitated access, clarification and improvement of pesticide use data, and to pesticide application information, is urgently needed to quantify exposure to pesticides. Exposure, and the mitigation of pesticide risks, is highly dependent of the behaviour of the pesticide applicator, and his/her knowledge of the different aspects of pesticide use (Damalas, 2015). Exposure data, together with health and toxicity data, can be used to predict the impact of pesticides on environment, plant, animal and human health (Silva et al., 2021).

Hazard baseline

According to recent EC data (EC, 2020a), 61% of the 2018 approved AS are intermediate hazard AS, 37% low hazard AS, and the other 2% high hazard AS. How this overall hazard classification per AS is determined is unfortunately not completely clear, neither are the hazard thresholds. Our review revealed a different picture, with all 230 selected AS having the potential to cause adverse effects on human or non-target organisms. Over half of the selected AS (124 out of the 230 AS) are in one of these top use or top hazard positions. As many pesticides are missing data for multiple endpoints, and as the hazard model assigns a "1" for missing data, it may be biased towards underestimating the health effects. We conducted a sensitivity analysis, assigning a "2" for missing data, which corroborate top hazard AS (see SM for details).

Our review exposed major gaps in the hazard knowledge of many of the AS on the market, raising serious concerns about the protection level of current pesticide policies. Our ecosystem and human-effects review was performed based on PPDB data; different percentages of adverse effects, and non (public) available data, are expected if other data sources are considered (EU Pesticides Database/EU dossier reports, EFSA OpenFoodTox database, US-EPA ECOTOX database, PubChem database, eChemPortal), or if more or other effects (Corsini et al., 2008) and non-target organisms are considered (Gunstone et al., 2021; Ockleford et al., 2017). The same applies if metabolites or pesticide adjuvants are also considered. Remember that the 230 selected AS have 414 known soil metabolites, which sometimes are more persistent and more toxic than their parent compounds (Karas et al., 2018; Vasileiadis et al., 2018). Some adjuvants (i.e., additives added to pesticide formulations to enhance the function or application of the AS) can also be toxic to non-target species, consider POEA and organosilicon surfactants used in some glyphosate-based herbicides or some neonicotinoid insecticides, respectively (Mesnage and Antoniou, 2018).

An especially concerning aspect of this review relates to the fact that we could not find any mixture toxicity data in PPDB, and that EC does not account for the combined effects of different AS in the authorization process of such AS. This would be particularly relevant for AS known to be applied together (tank-mixing) or commonly found in environmental mixtures. Access to the Member States report evaluations on pesticides formulations, which sometimes have more than one AS, could also provide valuable information on risk of mixtures. One could think that the EFSA framework for combined exposure to multiple chemicals (EFSA Scientific Committee et al., 2019) could be used to characterize the risks of such mixtures, however, the framework approach requires co-occurrence, concentration and toxicity data of pesticides which, as exposed above, might not be available for all AS in the mixture, even less so for whole mixtures. Furthermore, the framework does not consider different mixture compositions over time, which are very likely to occur under field conditions with sequential applications of pesticides, and different degradation rates of pesticide residues. More research and legislative efforts should focus on the combined effects of pesticides (including with recently or long term banned but still detected pesticide residues) on human and ecosystem health.

Finally, it is important to mention that existent (eco)toxicological information originates mostly from acute toxicity tests, or relates to long-term effects from short exposures; however, chronic exposure of pesticides is more likely to be a concern (Damalas and Eleftherohorinos, 2011). Most of the chronic studies focus on farmer workers (Muñoz-Quezada et al., 2016; Ohlander et al., 2020), and broader, general population assessments are needed. Pesticides-chronic diseases associations should also be further investigated (Mostafalou and Abdollahi, 2013). Moreover, although it is known that repeated exposure to low doses of pesticides can change non-target population structure and function (Liess et al., 2013), the capacity of the ecosystems to withstand pesticide effects is still poorly explored (Kosnik et al., 2022).

5.4.2. Pesticide reduction scenarios

Seven pesticide reduction scenarios were explored in this study to provide the EC with options for change: NH, FDP, TPB, CFSE, LHP, SHH and LET. Their representativity and implications are explored below. It is important to stress that the estimated reductions are not about absolute data but about the relative expected reductions of the scenarios. We considered maximum recommended rates of individual AS in BAU and the different pesticide reduction scenarios, but if we would have used a different (lower) application rate per AS, the differences between BAU and the scenarios would show the same pattern. Furthermore, although recognized that pesticide hazard is not directly translated into risk (risk assumes exposure and organisms susceptible to the exposed substances), the available exposure data was considered to be too limited to explore this transition properly. Our approach still allows the identification of priority AS for risk assessments and risk reduction strategies, which was ultimately the objective of this study.

NH and TPB are linked to existing farming strategies, IPM and organic farming, respectively. The NH scenario is particularly relevant for farms with (or planning to convert to) herbicide-free production. In these farms, weeds are often controlled by tillage applications, although precision farming techniques such as robotic weed control have gained more popularity over the years (Wu et al., 2020). Several EU farms are expected to present a BAU-NH intermediate situation, using chemical and mechanical weed control methods. Indeed, at least for orchards and vineyards, it is common to apply herbicides only within-rows of trees and plough soil every other year, in alternate inter-rows (Ferreira et al., 2018b; Mailly et al., 2017). The NH scenario is one of the easy scenarios to be implemented at both EC and farm levels. This scenario is close to the 50% use reduction goal and relevant due to the health concerns raised over the last few years concerning glyphosate-based herbicides (EFSA, 2015c; IARC, 2015b; Myers et al., 2016b), but leads to rather low hazard reductions as the highly toxic AS on the market seem to be mostly insecticides and fungicides. At the same time, if the use of herbicides is replaced by ploughing, and such action is not coupled with preventive, cultural and agronomic practices (PAN, 2017), NH may aggravate soil erosion. The TPB scenario is particularly relevant for areas recently converted or in the state of converting to organic farming. The EU has one of the biggest shares of organic agricultural land globally, with 12.8 million hectares – 65% of which is fully converted to organic and 19% is in conversion (Willer and Lernoud, 2019). These 12.8 million hectares correspond to 8% of the EU's agricultural land, a value that, as mentioned before, is expected to increase to at least 25% by 2030 (EC, 2020c). TPB meets use and hazard reduction goals, yet all EU farmland area would have to be converted to organic, which seems unlikely in the near future unless organic farmers receive financial support to compensate for the lower yields and in the first instance, higher production costs (Kılıç et al., 2020). The PBT results also highlight the possibility of legacy effects of recently banned compounds. The problem with past applications of persistent pesticides on soil health and transitioning to (certified) organic farming has already been addressed in Geissen et al. (2021). Furthermore, and although not accounted for in the Farm to Fork Strategy, and therefore not addressed in this study, the risks of the pesticides allowed in organic farming (e.g., copper) need further attention as well.

CFSE that excludes the AS in the EC list of the candidates for substitution subject to comparative assessments and gradual substitution, represents a predictive scenario for planned EC efforts. The CFSE results stress the need for additional action from the EC to meet the Farm to Fork goals; even if all candidates of substitution are removed from the market before 2030 and not replaced by other AS, their sole removal will result in use and hazard reductions far below the 50%. The right selection of AS to be removed is essential. The FDP scenario considers pesticide persistence in the soil as the only criterion to cut-off pesticides from the market. Soil half-life times are available for all the selected AS, making this scenario in principle easy to implement by the EC. Less persistent pesticides result in shorter exposure to pesticides, but not necessarily in lower use or toxicity (Sabatier et al., 2014). Although more than half of the 230 initial AS were excluded in the FDP scenario, its performance rates only borderline for hazard reduction and poorly for use reduction.

The remaining hazard-based scenarios LHP, SHH and LET, are the leading ones for use and hazard reductions >50%, indicating hazard as the best criterion for pesticide restrictions. LHP is a promising scenario as it has larger differences between the reductions in the number of AS and the reductions in hazard compared to SHH and LET. However, the SHH and LET scenarios outperform all the others on protecting human and ecosystem health and are most likely the ones attracting the most attention from the general public for possible implementation. LHP, SHH and LET, aiming for medium and high human and ecosystem protection, are the scenarios with higher impact and benefit for humans and ecosystems and of higher interest for regulatory entities as these scenarios are based on (eco)toxicological observations across the endpoints considered in EFSA documents and EC decision making. These scenarios could be refined further by considering a different weight to the different endpoints (namely carcinogenic, mutagenic, and toxic for reproduction), and indirect exposure and risks of (mixtures of) pesticides.

5.4.3. Limitations

On top of the PPDB data quality heterogeneity presented in section 2.1., we identify three main limitations of our approach. The first limitation concerns the equal weight of all crops on pesticide use estimates. According to the latest EU data (EUROSTAT, 2020), over 60% of EU arable land is used for cereal production, 30% for permanent grassland, and the remaining 10% for permanent crops, including grapes. Since cereals have lower pesticide inputs than permanent crops [this based on our estimates and the unique yet old report on pesticide use in Europe per crop type (Muthmann, 2007)], cereal dominance of the agricultural landscape affects the total application (mass) of pesticides. We chose, however, to give similar importance to cereals, permanent and other types of crops, because i) pesticide restrictions or reductions are expected to have a greater health/risk impact on specialty crops, with the most intensely applied pesticides; ii) there is an increasing demand for organic vegetables, fruits and wine (EC, 2019b), which indicate great public awareness and interest in pesticide risks and regulations of these crops with lower area representation; and iii) the Farm to Fork Strategy does not specify priority substances or crops, excluding or attributing a lower representation of some crops could compromise the utility of the generated data. Some details exist on more hazardous pesticides [group 3 of the Harmonised Risk Indicator 1, (EC, 2021d)], but due to the multiple uses of several AS, direct links between AS and crops are not easy. Second, our scenarios assume that crop-area relationships remain constant across EU regions and over time. Although some agricultural land conversions are expected to occur up until 2030, there is great uncertainty at the moment on the degree, location, and flow of the changes (EEA, 2017) to integrate this dimension into the scenarios. Third, it was also assumed that pesticides will continue to be used at today's recommended rates and that no new substances would enter the market. Although recognized that if a preferred chemical is outlawed, a farmer may increase the use of allowed substitutes, the lack of an action plan on pesticide and related Green Deal challenges makes other types of pesticide use predictions too speculative. As the introduction of new substances on the EU market has decreased over the last few years, the Farm to Fork Strategy legally binding reduction targets are most likely resulting in a more pronounced reduction.

5.5 Conclusions

Despite the increasing concerns and evidence of the negative effects of pesticides on human health and the environment, this study is the first overview of properties, hazard profiles, and recommended application rates (as a proxy for use) of the 230 EU-approved, synthetic AS used as herbicides, fungicides and insecticides on open fields. Our compilation revealed i) a high diversity of allowed inputs of pesticides across crops and EU regions; ii) that all 230 AS are potentially harmful to humans and ecosystems; and iii) that there are incomplete hazard profiles for several AS. All these issues require more and better attention in the future, which should also be extended to metabolites, adjuvants and mixtures. The potential of seven pesticide reduction scenarios to achieve the Farm to Fork Strategy 50% pesticide reduction goals was also explored. According to our results, the 50% use and risk reduction will only be met if the pool of AS on the EU market is significantly reduced, or the uses of AS are strongly restricted. Hazard-based scenarios (LHP, SHH and LET) performed better on the coupled use and risk reduction targets than more practical scenarios (NH, FDP) or those related to ongoing activities and trends (TPB, CFSE). The broader implications of the scenarios on productivity, biodiversity or economy should be further explored. Particular attention is also required for the 124 AS with higher human/ecosystem-cumulative hazard scores, since it is evident that the development of transition pathways away from reliance on pesticides must be driven by an integrative, global health perspective. Our results highlight the need for an EC action plan, covering one or a combination of pesticide reduction scenarios, to achieve and maintain the Farm to Fork Strategy reduction goals.

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See supplementary materials on pages 247-298.

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Chapter 6

Synthesis

Pesticides have become the foundation of modern agriculture. The intensive and widespread use of pesticides has sparked serious concerns about the impact that current agricultural practices have on human health and the environment. A rigorous pesticide regulatory system, such as the European system, gives rise to a “safe use” perception, but the system has many shortcomings and insufficient validation. Holistic risk approaches, as well as close monitoring for pesticide residues and vigilant adherence to protocols, are needed to avoid the adverse effects of these compounds and encourage sustainable agricultural production. This PhD thesis focuses on two obvious yet greatly unknown aspects: i) the distribution (presence and levels) of pesticide residues in EU agricultural soils, and ii) the needed market restrictions on pesticide use in order to meet the Farm to Fork 50% pesticide reduction goals. To address this, we measured multiple pesticide residues in LUCAS 2015 topsoil samples from across Europe (*Chapter 2* and *3*), compared conventional and organic farming systems in four different areas (*Chapter 4*), and developed scenarios to reduce pesticide impacts (*Chapter 5*). In the current chapter, we synthesize and discuss our main findings, explore implications, address thesis shortcomings and provide recommendations for future work.

6.1 Major findings

The main findings for each chapter are summarized in *Figure 6.1* and discussed in the respective chapters. Overall findings are listed below, supported by *Table 6.1*, and discussed in light of actual literature.

i. Pesticide residues are present in most EU agricultural soils, and the presence of multiple pesticide residues in soil is apparently the rule rather than the exception. 99% of the conventional samples tested in *chapter 4*, 71% of the organic samples tested in *chapter 4*, and 83% of the EU-LUCAS survey soils (of unknown farm management) tested in *chapter 2/3* contained at least one pesticide residue. 95% of the conventional samples, 48% of organic, and 58% of unknown farm management samples contained mixtures of pesticides. The maximum number of pesticide residues detected per sample was 16 for conventional, 6 for organic, and 13 for unknown farm management.

ii. The total pesticide content in soil was highly affected by the use of glyphosate-based herbicides. Glyphosate and/or AMPA were present in 86/29/45% of conventional/organic/EU-LUCAS soil samples. In 85% of the samples with glyphosate and/or AMPA, these compounds represented 51-100% of the total pesticide content. The highest glyphosate concentration in soil was 7.84 mg/kg, the highest AMPA content was 4.29 mg/kg, and the highest total pesticide content was 11.6 mg/kg. Glyphosate and AMPA levels in soil varied significantly across EU countries, and the total pesticide content among EU countries and crop systems.

iii. Eighteen out of the 65 compounds found in EU agricultural soils were not approved for use on the EU market at the time of sampling. Overall, 31% of the tested soil samples contained at least one non-approved compound; a maximum of 7 non-approved compounds were present per sample. The residues of the long-forbidden DDT were the most frequently detected, including in the soils from organic farms. In general, levels of p,p'-DDE were the highest of all non-approved compounds measured, with a maximum concentration of 0.57 mg/kg (Spain-orange production fields).

iv. Pesticides may persist in soil longer than expected, at least compared to their reference persistence classes. This is supported by i) the presence of non-persistent (NP) and moderately persistent (MP) compounds in "before growing season" samples, ii) the presence of NP compounds in "after growing season" samples; and iii) the presence of non-organic approved NP, MP and persistent (P) compounds in fields converted to organic farming at least five years before soil sampling.

v. Approved/recommended pesticide uses do not always reflect real pesticide applications, which together with a possible longer persistence, may lead to an underestimation of pesticides risks. This is further supported by: i) interviews with farmers who revealed that the number of recommended applications and the recommended application rates are sometimes exceeded in the field, when pest pressure is severe; ii) the presence of NP or MP compounds in soils from crops not covered in the EU recommended uses; and iii) the fact that some of our soil measurements had higher than predicted environmental concentrations of pesticides (PECs).

vi. Most of the pesticides on the EU market are potentially harmful to humans and/or ecosystems. A compilation of PPDB data revealed that all of the 230 approved, synthetic, open-field use active substances used as herbicides, fungicides and insecticides are hazardous to at least 1 of the 20 ecotoxicological endpoints or the 11 human health issues considered in EFSA assessments. This is despite the fact that none of these 230 active substances have a complete hazard profile (i.e. hazard information not available for one or multiple endpoints). Of the 94 active substances that are of high hazard for ecosystem or humans, 23 of them were found in the EU soils (*Table 6.1*).

vii. Severe pesticide use restrictions are required to meet the Farm to Fork 50% pesticide use and risk reduction goals, and hazard seems to be a good criterion for pesticide restrictions. Three out of the four least restrictive scenarios in terms of number of active substances on the market ("Candidates For Substitution Excluded", "No Herbicides", and the "Fast Degradable Pesticides only") led to rather low use and/or risk reductions. The fifth, "Low Hazard Pesticides only", met the coupled use and risk reduction targets. The most restrictive scenarios: "Safe Human Health", "Low Ecosystem Toxicity only" and "Total Pesticide Ban" met the coupled targets as well.

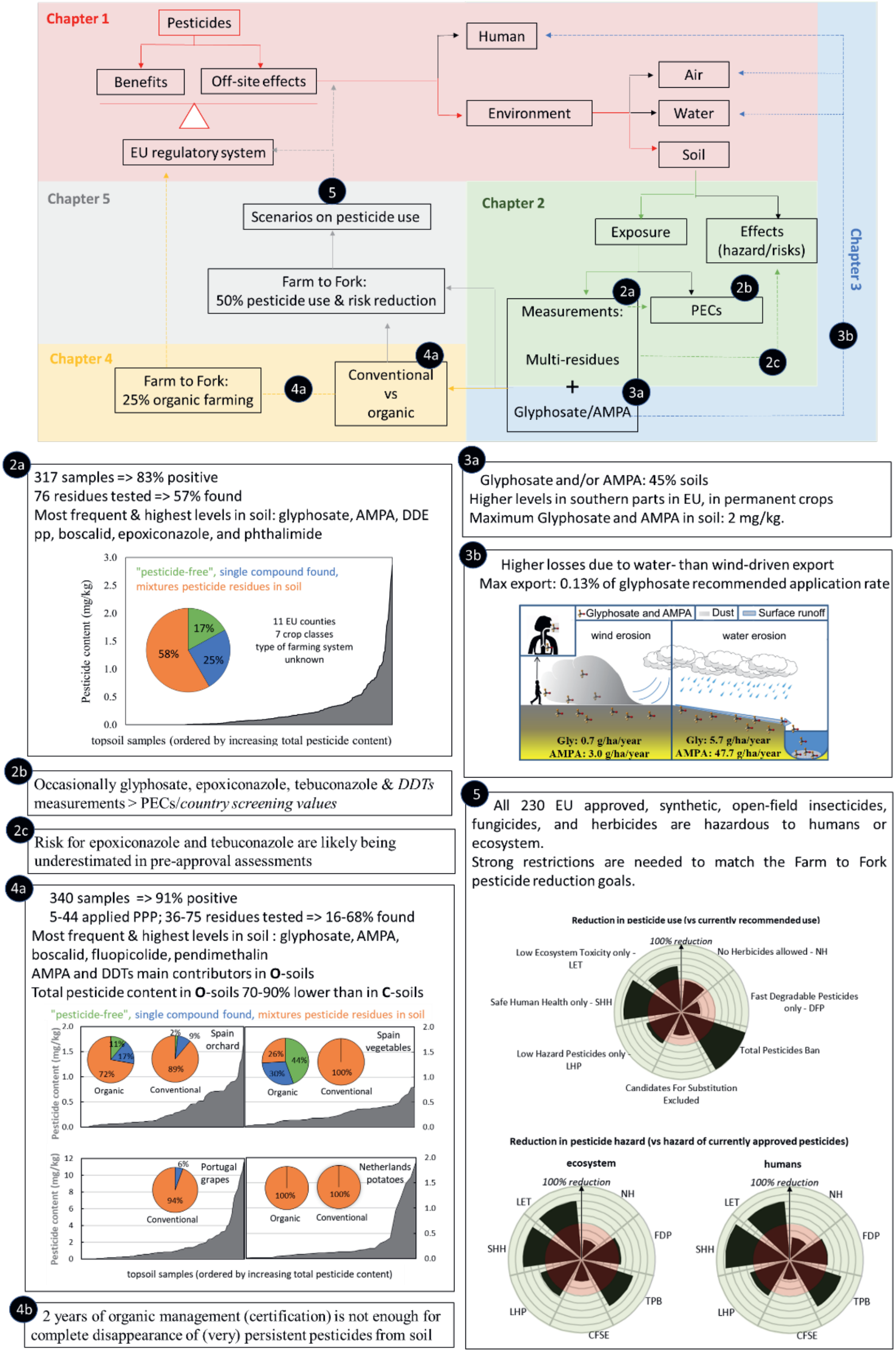

Figure 6.1 – Outline of the PhD thesis with the main findings per chapter.

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Table 6.1 – Overview of the pesticide residues found in EU soils. Compounds are listed per class of soil persistence and marked in red when not approved at sampling time, in blue when approved at sampling time but not-approved now, and green in case of approved substances. Case study results/chapter results are organized according to sampling time: before, during and after growing season. Overall frequency refers to the number of positive samples in relation to the number of samples that were tested (if > 30% they are highlighted in red). The last column reveals the hazard of substances; the list of found residues was crossed with the list of the 94 active substances with the highest cumulative hazard scores – see details on scores in Chapter 5. S-V and S-O = vegetable and orange production in Spain, respectively; P-G = grape production in Portugal; N-P = potato production in the Netherlands. I = insecticide, F = fungicide, H = herbicide, m=metabolite, - = not tested.

		BEFORE GROWING SEASON	DURING GROWING SEASON	AFTER GROWING SEASON				
		Chapter 4	Chapter 2, 3	Chapter 4				Chapter 5
		N-P, n=34 (28 conv./6 org)	EU, n=317 (unknown farm	P-G, n=108 (108 conv.)	S-V, N=108 (54 conv./54 org)	S-O, N=90 (54 conv./36 org)		TOP HAZARD?
	Compound	Freq.	Freq.	Freq.	Freq.	Freq.	Overall Freq.	
Non-persistent	3-Hydroxycarbofuran (Im)	-	3%	0%	-	-	2%	
	Chloridazon (H)	36/0%	-	-	-	-	29%	
	Chlorpyrifos (I)	-	1%	0%	6/0%	7/0%	2%	E
	Cymoxanil (F)	0/0%	2%	-	0/0%	-	1%	
	Cypermethrin (I)	-	-	-	22/0%	-	11%	E
	Fenpropimorph (F)	6/0%	2%	-	-	-	3%	E
	Folpet (F)	-	7%	4%	-	0/0%	5%	H
	Glyphosate (H)	93/0%	21%	78%	-	22/6%	35%	
	Isoproturon (H)	-	1%	-	-	0/0%	1%	
	Kresoxim-methyl (F)	-	-	-	7/0%	-	4%	H
	Metamitron (H)	46/0%	5%	-	-	-	8%	
	Metolachlor (H)	18/0%	-	-	-	-	15%	
	Metribuzin (H)	11/0%	-	-	0/0%	-	9%	E
	Phthalimide (Fm)	-	19%	-	-	0/0%	14%	
	Propamocarb (F)	0/0%	-	-	2/0%	-	1%	
	Prosulfocarb (H)	100/100%	-	-	-	-	100%	H
	Prothioconazole (F)	7/0%	7%	-	-	-	3%	E
	Terbuthylazine (H)	-	3%	0%	-	-	2%	E, H
Moderately persistent	Atrazine (H)	-	<1%	0%	-	0/0%	<1%	
	Azoxystrobin (F)	86/0%	7%	4%	72/0%	-	16%	
	Cyflufenamid (F)	-	-	-	4/0%	-	2%	H
	Cyfluthrin (I)	-	-	-	2/0%	-	1%	
	Cyhalothrin (I)	-	-	-	0/2%	-	1%	
	Cyprodinil (F)	-	2%	0%	-	0/0%	1%	E, H
	Deltamethrin (I)	-	-	-	4/2%	-	3%	
	Difenoconazole (F)	-	3%	-	65/17%	-	13%	
	Dimethomorph (F)	-	4%	100%	24/0%	-	25%	
	Endosulfan alpha (I)	-	1%	0%	-	0/0%	<1%	
	Ethion (I)	-	0%	-	-	4/0%	<1%	
	Linuron (H)	61/0%	7%	-	4/0%	0/0%	7%	
	Metalaxyl (F)	-	1%	51%	0/0%	0/0%	9%	
	Myclobutanil (F)	-	2%	0%	-	-	1%	
	Oxyfluorfen (H)	-	-	-	70/0%	37/0%	29%	E
	Penconazole (F)	-	1%	17%	-	-	5%	E
	Pirimicarb (I)	-	-	-	2/0%	-	1%	E, H
	Prochloraz (F)	-	2%	-	-	33/17%	7%	
	Propiconazole (F)	-	3%	0%	-	-	2%	
	Propyzamide (H)	-	-	-	6/0%	-	3%	
	Pyraclostrobin (F)	-	1%	31%	56/0%	-	12%	E
	Pyrimethanil (F)	-	-	4%	-	-	4%	E
	Quinoxyfen (F)	-	2%	0%	-	-	<1%	
	Tebuconazole (F)	32/17%	12%	16%	-	-	14%	
	Triadimenol (F)	-	<1%	-	-	-	<1%	E, H
Persistent	Boscalid (F)	61/67%	27%	-	85/0%	0/0%	28%	
	Bixafen (F)	71/83%	-	-	-	-	74%	E
	Chlorantraniliprole (I)	-	-	-	100/7%	-	54%	
	Cyproconazole (F)	-	2%	-	-	-	2%	E
	Epoxiconazole (F)	-	24%	-	-	-	24%	E
	Fluopicolide (F)	79/0%	-	-	48/0%	-	34%	
	Heptachlor (I)	-	<1%	0%	-	-	<1%	
	Imidacloprid (I)	-	7%	-	93/30%	-	21%	E
	Indoxacarb (I)	-	-	-	33/0%	-	17%	E
	Metrafenone (F)	-	-	-	56/0%	-	28%	
	Pendimethalin (H)	43/0%	-	-	63/0%	-	32%	H
	Procymidone (F)	-	<1%	0%	-	-	<1%	
Very persistent	AMPA (Hm)	96/83%	42%	83%	-	87/17%	56%	
	Chlordane (I)	-	<1%	0%	-	-	<1%	
	DDD op (Im)	0/0%	7%	0%	-	0/3%	4%	
	DDD pp (Im)	32/17%	3%	0%	-	13/44%	8%	
	DDE op (Im)	0/0%	<1%	0%	-	0/0%	<1%	
	DDE pp (Im)	68/83%	23%	0%	-	78/89%	31%	
	DDT op (I)	0/0%	<1%	0%	-	0/8%	1%	
	DDT pp (I)	14/0%	7%	0%	-	19/56%	10%	
	Dieldrin (I)	-	5%	11%	-	-	6%	
	Hexachlorobenzene (F)	-	<1%	0%	-	-	<1%	

Pesticide residues in soil

In total, 657 soil samples were tested in this thesis and 574 of them contained at least one pesticide residue above the respective limit of quantification. From the 657 tested samples, 244 samples originated from conventionally managed fields, 96 from organically managed fields, and 317 from unknown farm management. Considering the fact that organic farming represented only 6.2% of the EU agricultural area in 2015[5], the worst-case criteria used on the LUCAS 2015 sample selection, and the high percentage of pesticide positive soils, most of our samples of unknown farm management are likely to be from conventional management. In total, 159 pesticide residues were tested in this thesis and 65 were found at least once (*Table 6.1*). The compounds with the overall highest frequency of detection were prosulfocarb (100% up to 0.006 mg/kg), bixafen (74% up to 0.050 mg/kg), AMPA (56% up to 4.3 mg/kg), chlorantraniliprole (54%, up to 0.10 mg/kg), glyphosate (35% up to 7.8 mg/kg), fluopicolide (34% up to 0.096 mg/kg), pendimethalin; (32% up to 0.23 mg/kg) and DDE pp (31%, up to 0.57 mg/kg). Except for p,p'-DDE, all of these compounds are (metabolites of) pesticides approved for use in the EU.

Prosulfocarb is a non-persistent herbicide used to control grass and broad-leaved weeds in a wide range of crops[6]. It was found in all (conventional and organic) soil samples from the Netherlands' potato farms (N-P) collected during the pre-growing season. Its presence is not surprising, at least for conventional soils, since it is a pre-emergence herbicide reported to be applied by our farmers. Below, you will find a reflection on the occurrence of synthetic pesticides found in soils from organically managed fields and how well soil data matched application records. Prosulfocarb's low levels in soil suggest an early application of this pesticide; the measured values fit between PECs 50 and PECs 100 values [these predicted concentrations in soil 50 and 100 days after application were calculated using the maximum application rate reported by our farmers and using standard PEC parameters for this compound (EFSA, 2007)], and/or some off-site transport. Detailed application records (which are often not available) would allow for some inferences on the off-site transport contribution. There is only one other study analyzing this compound in soil. This was a Swiss study where the prosulfocarb frequency of detection was 0%, likely due

[5] https://ec.europa.eu/eurostat/documents/2995521/7709498/5-25102016-BP-EN.pdf/cee89f9e-023b-4470-ba23-61a9893d34c8

[6] http://sitem.herts.ac.uk/aeru/ppdb/en/Reports/557.htm

to a later soil sampling time (Chiaia-Hernandez et al., 2017). The limit of quantification in the study was slightly lower than ours. Note that this compound has moderate/unknown (data not available) toxicity to soil organisms but is associated with several human health effects such as respiratory tract irritation, skin irritation, skin sensitization and eye irritation[2]. Prosulfocarb is absorbed by leaves and roots and inhibits lipid synthesis.

Bixafen is a persistent fungicide used on cereals to control stem and leaf diseases[7]. It was found in N-P samples from both conventional and organic farms. This is most likely a legacy effect of past potato and cereal crop rotations. Bixafen content was always below its PECs 100 value (EFSA, 2012). There was only one other "soil-study" found for this compound, where exposure, effects, and long-term risk to earthworms in cereal fields was investigated (Ernst et al., 2021). The authors of this German study found pre-application levels in the same order of magnitude as ours, and post-application levels (the applied amounts were similar to those reported by N-P farmers) up to 0.29 mg/kg at 0-5 cm deep, 0.15 mg/kg at 5-10 cm deep, and 0.054 mg/kg 10-20 cm deep. The authors found some acute effects but no long-term risk for earthworms at these levels. Bixafen is a succinate dehydrogenase (an enzyme involved in cell respiration) inhibitor, with moderate/unknown (data not available) toxicity to soil organisms but highly toxic to fish and associated with reproduction / development effects in humans[3].

Chlorantraniliprole is a persistent insecticide used to control a broad spectrum of pests on diverse crops[8]. It has been found in the soils from Spanish-vegetable (S-V) farms, almost exclusively in conventional ones, at levels lower than its PECs 100. There has been some research done on this compound, but only a few studies report soil levels (i.e., from normal, not spiked samples). This compound was found in only 1 out of the 100 agricultural soil samples from Jordan, at a concentration of 0.12 mg/kg (Kailani et al., 2019). In South Korea, it was detected at lower frequencies and levels, i.e., 5% of the 40 tested rice paddy soils and at a concentration of 0.008–0.038 mg/kg (Jo et al., 2021). In a method development study, three Malaysian paddy soils tested positive for this compound, with concentrations of 0.004–0.021 mg/kg (Zaidon et al., 2019). Finally, in Nepal, this compound had a frequency of 31%, and a maximum concentration of 0.014 mg/kg

[7] http://sitem.herts.ac.uk/aeru/ppdb/en/Reports/1250.htm
[8] http://sitem.herts.ac.uk/aeru/ppdb/en/Reports/1138.htm

in vegetable farm soils (Bhandari et al., 2020). Chlorantraniliprole disrupts Ca^{2+} homeostasis (this ion plays a central role in the nervous system). It has low/unknown toxicity (data not available) for soil organisms but is highly toxic to aquatic invertebrates. It is not associated with any human health issues [4].

Fluopicolide is a persistent fungicide used to control a range of Oomycete diseases in diverse crops[9]. It was found in most of the N-P and S-V soil samples but only in conventional fields. Our sampling times suggest a legacy source for N-P, and recent application in S-V. However, concentrations suggest that there was an early application to potatoes fields – our median and maximum concentrations in soil were similar in both areas and close to PECs 0 concentrations (EFSA, 2009). Again, only one soil study was found for this compound. Pazikowska-Sapota et al. (2020), who screened for pesticide residues in the Puck commune and the Puck Bay part of the Baltic Sea, found fluopicolide in soil at a maximum level of 0.15 mg/kg. This compound was found at similar levels in sediments from drainage ditches surrounding the investigated agricultural parcels, corroborating the fact that soil can be a source of pesticide residues. Fluopicolide delocalises are spectrin-like proteins. It has moderate/unknown (data not available) toxicity to soil and aquatic organisms, and is not associated with any human health issues[5].

Pendimethalin is a persistent herbicide used to control most annual grasses and common weeds in cereals, fruits and vegetables[10]. This compound was found in N-P conventional soils at rather low levels, corroborating its expected background concentrations (EFSA, 2016) and in S-V conventional soils at higher levels, in line with those expected from a recent application before sampling. Among the eight common compounds listed above, pendimethalin has been examined in more soil studies, on different crops and in different countries (Chiaia-Hernandez et al., 2017; El-Saeid et al., 2013; Goncalves and Alpendurada, 2005; Hvězdová et al., 2018; Karasali et al., 2016; Karasali et al., 2017; Kosubová et al., 2020; Marković et al., 2009; Noh et al., 2012; Park et al., 2013; Park and Lee, 2011). Pendimethalin was found in soils in 9 out of the 11 studies above, at frequencies up to 48% (Chiaia-Hernandez et al., 2017), mean concentrations of up to 0.37 mg/kg, and maximum concentrations of up to 6.9 mg/kg (Goncalves and Alpendurada, 2005). This

[9] http://sitem.herts.ac.uk/aeru/ppdb/en/Reports/337.htm
[10] http://sitem.herts.ac.uk/aeru/ppdb/en/Reports/511.htm

corroborates a widespread use and widespread soil contamination by this compound. Goncalves and Alpendurada (2005) did not provide an explanation for the extremely high level reported during one of their sampling periods in an intensive horticulture area in North Portugal. Pendimethalin is absorbed by roots and leaves and inhibits mitosis and cell division. It has moderate/unknown (data not available) toxicity to soil organisms but is highly toxic to fish. It is also associated with multiple human health effects: reproduction/development effects, respiratory tract irritation, skin irritation, skin sensitization and eye irritation[6].

Glyphosate is the world's most widely used herbicide. It is a broad-spectrum herbicide used on a wide range of crops and assumed to be non-persistent[11]. AMPA (short for aminomethylphosphonic acid) is glyphosate's main metabolite and very persistent in soil[12]. Glyphosate and AMPA were tested in almost all of our EU soil samples and found in around half of them. In Spain, vegetable farmers have been using pendimethalin instead of glyphosate-based herbicides so glyphosate and AMPA were not tested in these soils (note that analyzing these compounds requires a specific analytical method). The highest levels of these compounds occurred in Portuguese vineyard soils: 7.8 mg/kg for glyphosate and 4.3 mg/kg for AMPA. Maximum predicted values in soil (PECinitial + plateau concentration) for permanent crops was 4.60 mg/kg for glyphosate and 6.18 mg/kg for AMPA (EFSA, 2015b). Application rates were only made available for the N-P case study site, with the reported applied levels measuring lower than expected (0.071 kg/ha/year vs maximum recommended application of 4.32 kg/ha/year). Despite all the attention and controversy surrounding glyphosate-based herbicides, only a few studies have analyzed these compounds in agricultural soils. Karanasios et al. (2018) tested them in soils of olive farms in Greece. The authors detected glyphosate in 13% of the conventional samples at concentrations up to 0.35 mg/kg, and AMPA in 63% of the conventional samples at concentrations up to 0.65 mg/kg. We got very similar figures for Greek samples from permanent crops. Primost et al. (2017) tested these two compounds in Argentinian soils originating from cereal and oilseed fields. These authors found glyphosate and AMPA in all samples, with maximum concentrations of 8.1 mg/kg and 38.9 mg/kg, respectively. Maximum reported application rates were about 9 kg/ha/year, suggesting that accumulation in soil may

[11] http://sitem.herts.ac.uk/aeru/ppdb/en/Reports/373.htm

[12] http://sitem.herts.ac.uk/aeru/ppdb/en/Reports/842.htm

be happening ("pseudo-persistent" contaminants). Finally, Materu et al. (2021), tested soils from sugarcane, teak and rice plantations in Tanzania. These authors found glyphosate in 29% of soils, AMPA in 18%, at maximum concentrations of 0.55 mg/kg and 0.49 mg/kg, respectively. Glyphosate inhibits EPSP synthase, a key enzyme in the shikimic acid pathway, which is involved in the synthesis of the aromatic amino acids. Glyphosate and AMPA have similar hazard profiles, with low-moderate/unknown toxicity to terrestrial and aquatic organisms and humans[7,8].

DDE is a metabolite of the obsolete DDT insecticide. DTT, a very persistent organochlorine insecticide, was widely used in agriculture until the 1960s. Its use was partly banned in Europe in 1978, and totally banned in 1983[13]. p,p'-DDE was ubiquitous in our tested soils, excepted for those from P-G, where its limit of quantification was rather high (0.010 mg/kg). DDE pp was the DDT metabolite with the highest levels. We measured a maximum p,p'-DDE and ∑DDTs concentration of 0.31 mg/kg, in Danish soils. Our DDTs measurements occasionally exceeded maximum limits of the respective countries. Soil contamination by DDTs has been widely studied in Europe (*Table S2.14*), with a maximum reported content of 5.83 mg/kg in topsoils from Romania (Ene et al., 2012). DDT's high toxicity was observed for bees and pollinators, aquatic invertebrates, sediment dwelling organisms, and humans[14]. DDE is equally as toxic[15].

<u>Pesticides known or expected to be applied compared to residues found in soil</u>

In chapter 2, with the LUCAS 2015 survey samples, the selection of analytes was done based on the active substances often applied to the crops (Muthmann, 2007) and on findings of previous studies concerning the distribution of pesticide residues in EU soils. We analyzed 76 compounds, of which 57% were found. In chapter 4, the selection of pesticides to be analyzed in the soil analysis was based on interviews with local farmers and pesticide retailers. Long banned pesticides were added to assess the full picture in organic soils. Here, we tested 36-75 compounds across the case study areas, and found 16-68% of them. Therefore, according to the classification laid out by Chiaia-Hernandez et al. (2017), we got a medium-high percentage of false negatives, i.e., compounds likely to have been/reported as applied but not detected in soil. This is somehow expected when the applied

[13] https://ec.europa.eu/commission/presscorner/detail/en/MEMO_03_219
[14] http://sitem.herts.ac.uk/aeru/ppdb/en/Reports/204.htm
[15] http://sitem.herts.ac.uk/aeru/ppdb/en/Reports/754.htm

amounts of a pesticide are low, when there is degradation before sampling time, or when there is off-site transport of pesticides. Addressing these points would require detailed application data, the analysis of metabolites of currently and recently applied active substances, and a comprehensive environmental sampling strategy.

When comparing the list of pesticides found in soil and those reported as applied, we also noticed some false positives: detected but not applied. The majority of these related to long-banned and very persistent pesticide residues, but there were exceptions. Chiaia-Hernandez et al. (2017) also observed this. The difference was that in our case, the long-banned compounds were mostly DDTs, and in their case, triazine herbicides (DDTs were not analyzed). False-positive cases are most likely the result of incomplete application information, off-site contamination, and a higher than expected persistence in soil of some compounds. The higher persistence is most likely the result of limited bioaccessibility or bioavailability for microbial degradation (Chiaia-Hernandez et al., 2017). Nevertheless, scientists should take a closer look into DT_{50} values and persistence thresholds. Indeed, some compounds present large DT_{50} ranges, with values relating to different persistence classes. In this thesis, mean values of DT_{50} as found in the PPDB database were considered for practical reasons (i.e., the large number of pesticides analyzed, and of soil locations and soil properties covered). Preference was given to field values but when not available, typical values were used. Typical values are calculated considering all data available in literature and are often a mean of field and laboratory studies. A PPDB feature or an EC platform (a simple data spreadsheet would probably suffice) covering the different DT_{50} values of different pesticide residues would facilitate multi-compound evaluations. This would allow quick and tailored DT_{50} selection, persistence data interpretation, and identification of data gaps (per soil type, climate, or overall field studies).

<u>Pesticides in organically managed fields</u>

Humann-Guilleminot et al. (2019), Riedo et al. (2021) and Karanasios et al. (2018) are the only other published studies on currently used pesticides in soils from organically managed fields. The first two studies were conducted in Switzerland, the third in Greece. The first study covered five neonicotinoid insecticides and 82 fields (27 organic, 26 reduced pesticide input, 29 conventional fields); the second study 46 pesticide residues and 100 fields (40 organic, 60 conventional), and the third study glyphosate and AMPA and 91 fields (13 organic, 22 where no glyphosate was used, 56 conventional). All these authors found pesticide residues in soils from organic fields and suggested a twofold general explanation for such findings, which is applicable to the observations in this thesis as well: off-site contamination sources (runoff water, pesticide drift from adjacent fields, wind erosion from other fields) and legacy effects of past conventional management (with the possibility of some compounds persisting far longer than expected). See below for more details on the findings of these studies.

Humann-Guilleminot et al. (2019) found imidacloprid, clothianidin, thiacloprid, and acetamiprid in soils from fields converted to organic farming at least 10 years before samples were collected for testing. Imidacloprid was the most frequent in organic fields. This compound presented a similar frequency in soils from conventional fields but at levels nearly 40-fold higher. We tested S-V soils for imidacloprid and clothianidin and found imidacloprid in soils from both conventional and organic fields, but at lower frequencies and levels than those reported in Switzerland. Since the Swiss soils were sampled during the early growing season in the first study and soils from our study after the growing season, and this persistent compound, our lower frequencies and levels can be attributed to a lower use and/or lower application rates of this insecticide in our case study site. Unfortunately, application data was not provided in the Humann-Guilleminot study. Humann-Guilleminot et al. (2019) also suggested an additional, specific source of contamination: dust from sowing insecticide-coated seeds, which authors corroborated by analyzing seeds. We are not aware of the use of insecticide-coated seeds in any of our case study sites, and it is not very plausible considering the crops grown in the sampling fields.

The lower number and levels of pesticides found in organic soils during our study were in agreement with findings by Riedo et al. (2021). These authors found mixtures of pesticide residues in all tested fields, with soils from organic fields presenting half of the residues and a median total pesticide content 85% lower than soils from conventional fields. Their study included fields with 5 to >20 years of organic management. They observed that linuron, napropamide, chloridazon, atrazine, carbendazim were the compounds that remained in soil the longest. These findings go against predictions based on half-life times and application rates suggesting that only boscalid, epoxiconazole, fluopicolid, flusilazole, and an S-metolachlor could be detectable after ten years of organic management. We tested four of the five long-lasting compounds (linuron, chloridazon, atrazine, and carbendazim) and two of the compounds that researchers expected to find in this previous study (boscalid and fluopicolid) and found only boscalid in organic soils, and only in N-P. Such differences are probably the result of the higher limits of quantification for these compounds in our study, or again, different uses and application rates of compounds between study areas (past pesticide application records were not available for our study areas).

Karanasios et al. (2018) almost never found glyphosate in soils from organic farms nor in conventional farms where glyphosate was not used for weed control. Glyphosate was found in a single sample at 0.27 mg/kg. AMPA was more common in these soils and presented higher levels. We saw similar results in our study for S-O and N-P soils. Karanasios et al. (2018) observed that two sites had rather high AMPA levels (0.30 and 0.44 mg/kg). The authors later discovered that their sampling points were in proximity to an area where application equipment was washed after use in nearby fields. In our case, AMPA reached even higher values in S-O organic soils at 0.59 mg/kg. This is likely because of the proximity and the lack of a fence between some conventional and organic orchards.

6.2 Implications

Implications for soil monitoring programs

Soil health, recently defined as the ability of the soil to sustain the productivity, biodiversity, and environmental services of terrestrial ecosystems (ITPS, 2020), is evaluated based on chemical, physical and biological indicators (Raghavendra et al., 2020). Despite the importance of healthy soils, including towards the achievement of several United Nations Sustainable Development Goals (Bouma, 2021), there have been no specific EU laws protecting or monitoring pesticide residues in EU soils. Frelih-Larsen and Bowyer (2022) gave an overview of policies addressing soil and Morvan et al. (2008) wrote an overview of the parameters monitored in EU soils. Due to the lack of regulation and monitoring programs, pesticide-soil data are scarce and fragmented from a spatial, temporal and compound perspective.

EU Member States are requested to do post-approval pesticide monitoring, yet most of the pesticide measurements taken for soil happen only in special cases and in limited capacity [e.g., in case of a spill, or in buffer areas of water bodies (Carlon, 2007)]. Access to these measurement results is extremely difficult to acquire as proved by a recent SPRINT consortium exercise covering ten EU countries[16]. Such post-approval data is not available to the general population or scientists working on the topic, and raw data is often not shared due to confidentiality issues. Although chemical data is becoming more consistently available via IPCHEM[17], almost no data concerning pesticides in soil can be found there. A basic search in this platform [CHEMICAL (pesticide), MEDIA (soil)] directs the user to metadata files of six projects/programs, only one of which has data on pesticides in soil (ESB-UBA: Environmental Specimen Bank of Germany). This is expected to change soon after a special pesticide module is added to the EC LUCAS 2018 topsoil survey (Land Use/Cover Area frame Survey). The continuation of the module along with its frequency and expansion to include more samples and pesticides is not yet certain. The vast majority of existing pesticide-soil data originate from individual studies. Sabzevari and Hofman (2022) reviewed soil data from currently/recently used pesticides, reporting 33 European studies with numerical data available, covering a total 306 compounds (200 active substances, 106 metabolites). Forty percent of the pesticides were only tested in a single study. The different scopes, limits of quantification, and methods of the studies hamper aggregation of results and direct comparisons of mixtures as well as total pesticide levels in soil.

The interpretation of monitoring data requires more attention as well. Currently, there are no Environmental Quality Standards (EQS) for soil. Most EU countries have soil screening values but the high variation in the types of soil screening values from different countries [e.g., background levels, target and intervention values, maximum acceptable concentrations, cut off values, etc.; (Carlon, 2007)], making large scale evaluations very difficult. Most of the soil screening values for pesticides cover long-banned pesticides (especially DDT and atrazine) with only a few countries including “other pesticides”. Occasionally, our measurements exceeded the maximum acceptable concentrations of individual and sum of “other

[16] https://sprint-h2020.eu/index.php/project-documents/registered-users/confidential-deliverables/256-sprint-d2-2/file

[17] https://ipchem.jrc.ec.europa.eu/#discovery

pesticides", and our pesticide content curves suggest that it may also happen in non-tested locations. The real meaning and/or suitability of these limits in agricultural areas with intensive pesticide use have not yet been fully explored. There are several pressing questions that need to be answered:

i) Are maximum admissible concentrations remediation triggers or indicators of urgency for specific pesticide use restrictions and a transition to more sustainable practices?
ii) Which pesticides, if any, should be exempt from these individual/total limits and why?
iii) Should soil remediation action be triggered by levels and risk assessments only in soil or should the risks connected to ecosystems count too?

When remediation is justified [also in line with the EC soil health mission and the EC Zero pollution action plan objectives – ensuring 75% of soils are healthy by 2030 and 100% by 2050 (EC, 2020h)], bioremediation seems to be one of the best options. A combination of biostimulation and bioaugmentation treatments have proved to greatly accelerate pesticide degradation rates (Cycoń et al., 2017; Pimmata et al., 2013; Sun et al., 2018). The former involves stimulating the activity of soil microorganisms by adding organic and/or inorganic additives, and the latter requires the addition of new, specific microorganisms to soil based on their catalytic capabilities. Physical remediation, via addition of biochar or surfactants, are also commonly used but can reduce the desired effects of the pesticides (Tang et al., 2013). See Marican and Durán-Lara (2017) and Sun et al. (2018) for a review of biological, physical and chemical remediation options for soils with pesticides and the efficiencies of treatments.

<u>Implications for environmental risk assessment</u>

The presence, type, amount and bioavailability of pesticide residues in soil may trigger a cascade of effects which can ultimately compromise normal soil ecosystem services (Ockleford et al., 2017; Rodríguez-Eugenio et al., 2018). Pesticides can be transported off-site by wind- and water-driven erosion (*chapter 3*), potentially affecting aquatic systems, as well as animal and human health (ITPS, 2017; Ockleford et al., 2017; Sánchez-Bayo et al., 2016; Science Communication Unit, 2013). In the previous thesis chapters, using simple hazard- and risk-based assessments, we attempt to link soil and human health. For hazard, we looked at the properties of pesticides available on the EU market (*Chapter 5*) and for risk, we looked at the pesticide levels found in soils and their known toxic endpoints (*Chapter 2* mostly). Most of the studies examining soil contamination by pesticide residues either performed no assessments or very similar assessments (Bhandari et al., 2021; Gunstone et al., 2021; Vašíčková et al., 2019). A few researchers performed ecotoxicological tests to attribute biological meaning to (some of) the environmental findings (Ernst et al., 2021; Kemmitt et al., 2015; Morgado et al., 2018).

Environmental risk assessments are evolving in complexity in order to answer increasing demands for realism (EFSA Scientific Committee et al., 2019; Sewell et al., 2021), yet there is still room for improvement. Some of the main criticisms relate to the limited number and representativeness of the tested species, but mostly on the poor integration of mixtures (Ockleford et al., 2017), which we corroborate to be the rule in soils. Several authors have proposed solutions for this (Bopp et al., 2019; Meek et al., 2011; Rotter et al., 2019) and new tools are emerging [e.g., the MITAS model on mixture risk of a real pesticide spray series; (Sybertz et al., 2020)]. There have also been several EU funded consortia working to improve the assessment and management of combined exposures to multiple chemicals (Bopp et al., 2018). We identified 8 common residues in EU agricultural soils, signalling a need for testing terrestrial mixtures of compounds. As the mixtures of compounds in the soil depend on the crops planted over the course of the year and the persistence of the pesticides used on them, these 8 residues may not be tested altogether, but rather across a set of mixtures. These mixtures should contain one or more of these highly frequent compounds along with other less frequent but potentially even more relevant compounds. The eight most frequent compounds found in soil were also often the ones with the highest levels in soil. Although this makes them particularly interesting for pesticide use and soil contamination reduction strategies and indicators, these compounds are not necessarily the most hazardous and higher levels do not necessarily translate into higher risks (see the rather low risk reductions for the No Herbicide scenario in *Chapter 5*). To address coupled use and risk targets such as the ones in the Farm to Fork Strategy, it is necessary to carry out deep evaluations of the characteristics and range of concentrations of the different compounds detected, not only in the soil but across all environmental and biological matrices. The same applies for pollution or health targets, such as the ones from Soil Mission, or to set an overall priority list of contaminants of major and/or emerging concern.

Implications for pesticide approval procedures

The high frequency of reports, along with the diversity and severity of negative effects of some pesticides, challenge the adequacy of approval procedures for pesticides on the market. The EU has a strict pesticide regulatory system but securing EU competitiveness while safeguarding environmental and human health is clearly a difficult task, with different aspects of the system requiring clarifications and improvement. A few of these relate directly to soils while others are more general and arise from the recent Farm to Fork Strategy pesticide reduction targets.

Soil-related aspects that need improvement are linked to both pre-approval (representative uses/PECs, persistence, risk assessment, unknown hazards) and post-approval phases (poor monitoring and lack of quality/health indicators). Pesticide approval procedures account for ecotoxicological effects in standard toxicity tests, and for the risks potentially arising from the pesticide representative/recommended uses. Representative Recommended uses instruct users on when, how often, and how much pesticide to apply for effective pest control while keeping risk to non-target species and the environment at acceptable levels (EC, 2009c). These recommended uses initiate a cascade of indices towards risk characterization: they are considered in the calculation of predicted environmental concentrations (PEC), used in the calculation of toxicity exposure ratios (TER), which are then compared with EC trigger values defined in the Uniform Principles establishing whether the risk is low (acceptable) or high (unacceptable) (EU, 2011; Ockleford et al., 2017). Our interviews with farmers revealed that the maximum recommended application rates are sometimes exceeded in the field, which can explain why some of our pesticide measurements in soil exceeded predicted levels. The overuse of pesticides should be further explored along with the adequacy of the DT_{50} values used in PECs calculations and off-site sources of contamination. Our results and those of other authors show that certain compounds are more persistent in soil than first assumed earlier in the degradation studies conducted within the frame of pre-registration. More field data, accounting for different soil and climate conditions, could be requested by the EC, and this data could then be used in the re-evaluation / renewal of approval. PECs are calculated with the assumption that the pesticide applications were the only source of pesticides in soil. However, wash-off from the canopy, deposition from spray drift, or off-site contamination can also play a role in the concentrations of pesticides found in soil as well as in the composition of pesticide mixtures. The frequency and complexity of the pesticide residue cocktails found in tested soils stress the lack of knowledge with regard to the potential hazards and risk impacts that these cocktails pose for ecosystem health. A less flexible EC position concerning incomplete application dossiers could prevent this, e.g., not approving substances with data gaps. Furthermore, the possibility of adding new approval requirements should be explored, namely for tank and environmentally relevant mixtures.

The EC performs regular re-evaluations of individually approved substances and sets partial or total restrictions on their use when unacceptable risks are found, or major concerns associated to their use arise. However, considering the ambitious EU Farm to Fork pesticide reduction goals for 2030, we need to consider major pesticide restrictions for groups of pesticides and/or pesticide uses. Having only the “best” products on market, i.e., pest-specific pesticides, with no or low toxicity to non-target species, can lead to significant risk reductions. Precision farming (and more sustainable practices with less pesticide reliance) could help with the coupled pesticide use reduction goal. The scenarios analyzed in *chapter 5* suggest that a shift in the precautionary basis, from risk to hazard, could have a major impact on pesticide reduction targets. An EC action plan, covering one or a combination of pesticide reduction scenarios, accompanied by specific implementation and monitoring measures, is needed to achieve and maintain the reduction goals.

Implications for sustainable plant protection

Current food production seems to be caught in a “vicious circle”: increasing pesticide use to increase yields, leading to worsening environmental degradation, and escalating health costs (Oliver et al., 2018). Re-evaluation of agronomic practices, technological development and transfer, and implementation of strategies to overcome “lock-ins” of undesired status are not only necessary for safer production but also more sustainable production (Oliver et al., 2018; Tilman et al., 2011). This becomes particularly urgent when we consider the Earth’s finite resources, its vulnerability to multiple threats and trade-offs. For example, some agricultural areas are close to achieving maximum yields and climate change is affecting pest incidence as well as growing season times and agricultural yields. We also need to consider the environmental and social aspects of sustainability

(Godfray et al., 2010; Wu and Sardo, 2010). In order to feed everyone, re-evaluation and changes must go beyond production and also cover how food is processed, stored, distributed and accessed and include food consumption patterns and food waste (Godfray et al., 2010; Oliver et al., 2018; Tscharntke et al., 2012).

Organic farming is often perceived to be the most sustainable production strategy and it is expected to represent at least 25% of the EU agricultural area by 2030 (EC, 2021c). One of the main organic agriculture goals relates to the reduction of all forms of pollution resulting from agricultural practices (Gomiero et al., 2011). Although our results confirm less soil contamination by pesticide residues in organic soils (simpler mixtures and lower pesticide contents were observed in soils from organic farms than in soils from conventional farms), they challenge the length of the period of conversion. The European Commission requires an appropriate conversion period for organic management before certification is given. This conversion period is usually set at two or three years for annual and perennial crops, respectively (EU, 2022). Interestingly, we discovered multiple pesticide residues in soils converted to organic farming more than 10 years before soil sampling. Although the presence of some long-banned and very persistent DDT residues could be expected [they had been reported in organic fields before, (Malusá et al., 2020; Witczak and Abdel-Gawad, 2012)], the frequent detection of some moderately persistent or persistent compounds in organic soils made us question the reduction targets of organic farming (complete or substantial degradation of the synthetic pesticides used while conventionally farmed). Soil-pesticide screening values for currently used pesticides seems to be relevant for organic farming as well. Contamination by organic-approved pesticides [see list here: (PAN UK, 2022)], which at the moment is not monitored, should be counted too as well as organic-approved fertilizers and plastics debris due to the use of plastic mulching (Wu and Sardo, 2010). See more on the implications and trade-offs of these practices in Gomiero et al. (2011), FAO (2021), Wanner (2021), Qi et al. (2018), Steinmetz et al. (2016), or Beriot et al. (2020).

Most of the indicators used to compare organic and conventional farming perform better or much better in organic farming, except for productivity (Gomiero et al., 2011; Knapp and van der Heijden, 2018; Seufert et al., 2012), which can be economically balanced or surpassed by lower input costs, higher market prices of organic food and premiums (Nemes, 2009; Pimentel et al., 2005). However, several researchers believe that rigid organic farming principles are not necessarily compatible with the needs of farmers nor sustainable agriculture, stressing the need of more flexible, site/custom-tailored managements (Deguine et al., 2021; Gibson et al., 2007; Gomiero et al., 2011; Wu and Sardo, 2010). The combination of methods from different practices is expected to be advantageous in most cases. A more holistic approach would be in line with the new IPM paradigm (Dara, 2019) and the addition of eco-schemes in the new CAP - common agricultural policy (EC, 2021e). Fourteen eco-schemes have pesticide reduction as their main target. The schemes supporting agroecological practices and natural pest prevention methods are the ones getting more expert support (BirdLife Europe et al., 2021). As conventional/IPM production represents the vast majority of agricultural production in Europe, it is imperative to promote agroecological and organic principles to farmers and put control programs in place to check their implementation. This is factored into IPM already, but although compulsory in the EU since 2014 (EC, 2009a), several farmers prefer tradition over innovation and technology which often means that pesticides are used because they have always been used and not as a last resort to secure high yields. A compromise between intensive production and the negative effects of pesticides is acceptable by all food system actors, in principle, yet the degree of the compromise and strategies to overcome obstacles in terms of revenue and food availability has been poorly explored. This must be an EC priority as well because such assessment may reveal that the EU Green Deal pollution goals are not realistic, and/or that a severe change in current production paradigms is indeed needed.

The implications of the Farm to Fork 50% pesticide reduction goals on productivity and economy were explored by Bremmer et al. (2021). These authors used a reversed 50% goal reasoning as a scenario foundation (in ours, we used potentially applicable policy cut-off criteria) and observed yield losses of up to 30% for perennial tree crops, a 0-7% price decline in food commodities, and a negative impact of around 6 billion euros on the value of production (Hollender et al., 2017). It is not clear if these were EC-envisioned compromises between intensive and sustainable productions. The EC action plan should also account for parallel plans for other Green Deal parameters and their implications - e.g., a reduction in fertilizer use could lead to production declines of up to 15% (Hollender et al., 2017). Several more responsibilities seem to be attributed to the EC, a consequence of complexity and urgency surrounding sustainable production. Legal mandates and setting clear responsibilities for the different food system actors, together with guidance and support for the work, can streamline the process while safeguarding the success of the action plan (Hassold et al., 2021).

6.3 Thesis shortcomings

The main limitations of the work described in this thesis were presented and explored in respective chapters. However, there are a few common topics as well as some shortcomings of the PhD approach. These relate mostly to the lack of pesticide background information on the tested samples, the use of targeted analyte lists, the nature of the field work (focused on soil contamination assessment and not fate or (eco)toxicological assessment), and the scenario foundations (based on the use of use and risk proxies and practical cut-off criteria).

i. While targeting large-scale soil contamination assessment, we accepted the fact that we had no pesticide history information on more than half of the tested samples, i.e., those originating from the LUCAS2015 survey. Using these samples also brought uncertainties about farm management types and sampling times which further limited data interpretations. In the remaining samples, those we collected in *Chapter 4*, we had no detailed application records although we did receive an indication of the pesticides used and the amounts applied. As a consequence, comparisons between measurements and time-precise predictions were not possible.

ii. Due to the high number of samples along with the high number and the wide variety in the nature and properties of pesticides applied now and in the past, we chose to analyze selected priority pesticide residues in soil. The list of analytes varied across chapters and study areas based on study scope and knowledge about the applied pesticides, but often included approved active substances, legacy pesticides, and metabolites of both groups. As a consequence, overall contamination figures should be examined carefully and make note that our results are most likely underestimating the full pesticide residue contamination levels in soils.

iii. Single sampling times in chapter 2/3 and in chapter 4 allowed for the aimed snapshot of soil contamination by pesticides but hampered the evaluation of pesticide use or pesticide degradation dynamics, which are important for management and risk evaluations. Off-site transport of pesticides was estimated from potential water- and wind-erosion rates, but not validated in field, experimental, or modelling setups [similar to what was done for some compounds in (Bento et al., 2019; Figueiredo et al., 2021; Yang et al., 2015)]. Some of the pesticide residues found in soils have also been found in water and/or air by other researchers, but (inter)relations between compartments were assumed to be too speculative. This is because of the different times of collection and locations for the available information on water and soil. Parallel sampling of multiple matrices in monitoring programs could help those type of analyses and improve our understanding of the fate of pesticides. Similar limitations apply to soil-food contamination links. Studying residue uptake seems to be the most relevant approach to follow here, which is relevant to food safety discussions.

iv. We employed a preliminary, exploratory scenario approach because of the lack of guidance from the EC on how to achieve the 50% reduction targets. The acceptance and implementation likelihoods were not explored with farmers and regulators. A cost-benefit analyses of at least the most plausible scenarios could add to the discussion. Hazard-based scenarios seemed to be the most promising ones for achieving the Farm to Fork pesticide targets, yet a couple of points must be explored before presenting an action plan. First, hazard/risk information is primarily available from studies of acute toxicity effects or long-term effects from short exposure; however, chronic exposure is more likely to be a concern. This underestimation bias could vary by pesticide, e.g., chronic exposure may be more problematic for pesticides with long-half lives. Second, due to the high frequency of missing data, performing a sensitivity analysis would be important to guarantee that risk will not be underestimated in cumulative hazard indices.

6.4 Recommendations for future work

Pesticides, soil contamination and food production are complex and interlinked, holding implications for different actors at different scales, and which are linked to multiple and ambitious EC targets to achieve over the next few decades (EC, 2020c; EC, 2021b). As such, multiple areas for future work exist, some pitched already in this thesis. The main ones considering the scope of this PhD work are:

- Better soil monitoring programs for pesticide residues are urgently needed due to the limited data available.

There are about 2.8 million contaminated sites in the EU and only 25% of them have been identified and inventoried (Pérez and Eugenio, 2018a). Agricultural area represents 42% of the EU land area (EC, 2018c), making pesticide monitoring in soil a key piece in soil management strategies. Currently, most of the pesticide-soil data originate from individual scientific studies. Establishing a European pesticide residue soil monitoring program (a new pesticide-specific program or the extension of an already existing soil program for pesticides), better coordination of EU national post-approval monitoring programs, and more directed research would lead to a better understanding of the contamination status of EU soils. Such information is also relevant to define a pollution baseline, pesticide indicators for soil, pesticide post-approval control, and evaluation of performance/efficiency of pesticide reduction measures. Despite some recognized logistical limitations due to the relatively high costs of pesticide analyses, increased coverage of these programs, especially in terms of the compound analyses, would have a major positive impact on the quality of the assessment. Ideally, this would mean full scan measurement of all past and currently used pesticide active substances, but also metabolites and pesticide product additives (an often ignored part of the potential contamination puzzle of soils). The potential of full scan measurements is already being explored in other matrices . Furthermore, it is also important that EU Member States regularly update their programs and their screening values in light of scientific findings, the pesticides on the market, and EC regulatory targets. Sampling and analytical methods should be harmonized (those of LUCAS and NORMAM network[18]) and all monitoring data should be centralized and available in IPCHEM.

[18] https://www.normandata.eu/sites/default/files/files/WG7/Kick-offMeeting20April2021/NORMAN_WG%20CEC%20in%20Soil_PSM_tb210420.pdf

- Detailed pesticide use data are needed in order to understand chemical results, predict risk or design transitions.

Difficult and limited access to detailed pesticide use data was a recurrent topic across the different thesis chapters. Pesticide use data is highly valuable for different scientific and regulatory aspects, e.g., for the interpretation of pesticide findings in soil, validation of pesticide recommended uses vs. identification of overuse situations, more accurate risk predictions, more realistic pesticide use and risk scenarios, confirmation of pesticide specific actions, etc. Nevertheless, EU and national datasets present aggregated pesticide use or pesticide sales data due to confidentiality reasons (EC, 2017b) and farmers often refuse to share their field books for fear of repercussions. Interviews and questionnaires about pesticide use usually result in incomplete information. The necessity for alternatives for current EC confidentiality rules must be explored; transparency and open access to pesticide data from industry and regulators must be strongly encouraged (similar to what is already done with researchers and their findings). Furthermore, the trust and engagement of farmers should be improved for instance, via focus groups on key issues with scientists and policymakers. This is expected to not only facilitate exchanges but also to improve the effective transition towards more sustainable production (Baveye et al., 2016).

- Protectiveness and requirements for pesticide approval for the market must be re-evaluated, especially in relation to longer pesticide persistence, hazard gaps and the lack of data on environmental mixtures.

Most of the EU agricultural soil samples contained mixtures of pesticide residues. Some of these residues were present at higher levels than predicted in respective pre-approval/renewal dossiers, and some were found to be more persistent in soil than assumed earlier in the dossier's legislation studies. These findings raise concerns on the suitability of PECs values (not on the reasoning per se but on the underlying assumptions of pesticide use and half-life times), and on possible risk underestimations in PEC-based assessments. Moreover, little knowledge exists not only for the related potential hazard and risk impacts of those cocktails for soil, but also for ecosystems and human health in general. Hazard and risk gaps for approved compounds, acknowledged in individual pesticide dossiers, existing for different reasons, were revealed to be extremely common. Information on mixtures was non-existent in the dossiers. Considering the ambitious pesticide use and risk reduction goals for 2030, and the severity of some effects with no data available, one wonders about the justification and necessity of having so many active substances available on the EU market. The risk of environmentally relevant mixtures (again, ideally of active substances, metabolites and additives) should become a pesticide pre-approval requirement, at least in the renewal assessment reports, where monitoring data is expected to exist. Multi-species ecotoxicological tests would be preferred over inferences from pesticide measurements/predicted levels and standard ecotoxic endpoints, since the latter do not account for bioavailability or indirect effects of pesticides. Research should also cover simultaneous and repeated exposure pulses of pesticides in the test designs (Sybertz et al., 2020; Weisner et al., 2021).

- It is urgent to explore the contamination potential of organic farming practices and include soil contamination in organic transitions and the certification process.

Organic farming has the potential to reduce most of the negative impacts of agriculture, especially if done on a large scale. The EC highly encourages organic farming with another ambitious target for 2030: organic farming should represent at least 25% of the EU agricultural area. At the same time, there are some uncertainties and concerns about potential side effects from organic-approved pesticides, fertilizer and plastic mulch for terrestrial and connected ecosystems. Soil contamination by such pesticides and plastic debris should be monitored as well. The presence of some pesticides in soil from organic farm samples requires a clarification of pesticide reduction targets for soil from these farms such as the substantial or total degradation of the pesticides (not accounting for legacy pesticides here). The need for soil-pesticide benchmarks specific for different farming types should be explored. The time required for transitioning to (certified) organic farming should account for the pesticide residue mixtures in the soil at the starting point of the transition, and the predicted time evolution in terms of levels and risk.

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Supplementary material – Chapter 2

Table S2.1 – Distribution of topsoil samples by crop class and specific land cover type.

Crop	Number of samples
CEREALS	*112*
Common wheat	37
Maize	36
Barley	23
Rye	6
Triticale	5
Oats	3
Durum wheat	2
PERMANENT CROPS	*101*
Vineyards	57
Other fruit trees and berries	12
Olive groves	11
Apple fruit	9
Oranges	6
Pear fruit	3
Cherry fruit	2
Nuts trees	1
ROOT CROPS	*27*
Potatoes	18
Sugar beet	9
NON-PERMANENT INDUSTRIAL CROPS	*23*
Oilseed rape and turnip rape	17
Sunflower	4
Other fibre and oleaginous crops	2
DRY PULSES & FODDER CROPS	*21*
Temporary grassland	10
Dry pulses	3
Lucerne	2
Other leguminous and mixtures for fodder	2
Clovers	2
Floriculture and ornamental plants	1
Strawberries	1
VEGETABLES	*9*
Other fresh vegetables	9
OTHERS	*24*
Bare soils	24

Table S2.2 - Distribution of the number of samples by EU region, country, NUTS 2 region and crop class. perm. = permanent.

EU region	Country	NUTS 2	Cereals	Perm. crops	Root crops	Non-perm. industrial crops	Dry pulses, flowers and fodder crops	Vegetables	Others
North	United Kingdom	UKC2				1			
		UKE1	1						
		UKE3	1						
		UKE4			1				
		UKF1							1
		UKF3				1		1	
		UKG1	1					1	
		UKG2	1					1	1
		UKH1	2						
		UKJ1	1						
		UKK1	2				1		
		UKK2	1		1				
		UKM2	2			3			1
		UKM3							1
		UKM5	1						
		UKN0		1					1
	Denmark	DK02	5		1				
		DK03	5			1	1		
		DK04	9		1	2	3		
		DK05	2						
South	Italy	ITC1	2	3					
		ITC4	2	2		1			
		ITF1		1					
		ITF3		1					
		ITF5		1					
		ITG1		5					
		ITH1		1					
		ITH2		1					
		ITH4	1						
		ITH5	2		1	1	1		
		ITI1		2					1
		ITI4					1		
	Greece	EL43		1					
		EL51	2		1		1		
		EL52	2	6		1	1		
		EL53		1					
		EL61	1	1					
		EL63		1					
		EL64		3					1
		EL65		7					
	Spain	ES11	2				1		
		ES22	1						
		ES23		2	1				
		ES24	1	2					
		ES41	3						1
		ES42	1	4					
		ES43	1						
		ES61	1	1					
		ES62	1	1				2	4
	Portugal	PT16		17					

Table S2.2 (cont.) - Distribution of the number of samples by EU region, country, NUTS 2 region and crop class. perm. = permanent.

EU region	Country	NUTS 2	Cereals	Perm. crops	Root crops	Non-perm. industrial crops	Dry pulses, flowers and fodder crops	Vegetables	Others
East	Hungary	HU10	1	1					
		HU21	2						
		HU22	4			3			1
		HU23		1					
		HU32	7	1	1				
		HU33	6	1					1
	Poland	PL11		1					
		PL12	1		1				
		PL21		1					
		PL22	2						
		PL31	1	4	3				1
		PL33		1			1		
		PL41	2	1	1	1			
		PL51	3			1			
		PL52	1						
		PL61	1						
		PL63	1				1		
West	The Netherlands	NL11			4	1			
		NL12	1		2				
		NL13	1		3				
		NL21	1				1		2
		NL22					1		
		NL23	1		4		2	1	1
		NL34	2		1			1	
	France	FR22							1
		FR25					1		
		FR26		1					
		FR51				1			
		FR52	4	1					1
		FR53		1		2			
		FR61		2					
		FR71		1		1			2
		FR81		7					
		FR82		3			1		
	Germany	DE11	1	1					1
		DE12		1					
		DE13	1						
		DE26							1
		DE91	1						
		DE92	1						
		DE93				1			
		DE94				1	2		
		DEA3	2				1	1	
		DEA4	1						
		DEA5	1						
		DEB1		1					
		DEB2	1	1					
		DEB3	1	4				1	
		DEE0	2						
		DEF0	1						

Table S2.3- Characteristics of the pesticides analyzed in the 317 agricultural topsoil (0-15/20 cm) samples. Pesticide properties were obtained from the Pesticide Properties DataBase or from the PAN Pesticides Database (┼). When the time to reach 50% (DT_{50}) or 90% (DT_{90}) residue degradation under aerobic field conditions was not available, typical DT_{50} (*) or lab DT_{90} (**) values were reported. NA–not applicable to metabolites; Sw–solubility in water at 20ºC; Log P–octanol-water partition coefficient; Vp–vapor pressure at 25ºC; GUS–GUS leaching potential index; Koc–Soil Organic Carbon-Water Partitioning Coefficient. Interpretation of pesticide properties (i.e., *NP, MP, P, VP, L, M, H, T, NM, SM, MM, M, VM*) is provided at the bottom of the table.

Compound	Type	Chemical class	Mode of action	Status EC 1107/2009	DT_{50} ■ (days)	DT_{90} (days)	Sw ▲ (mg/l)	Log P ●	Vp ♦ (mPa)	GUS▼	Koc ♠ (ml/g)
Abamectin	Insecticide	Botanical	Interferes with glutamate-gated chloride channels	Approved	30 *MP*	-	1.21 *L*	-	-	-	5638 *NM*
Aldrin	Insecticide	Organochlorine	GABA-gated chloride channel antagonist.	Not approved	365 *VP*	-	0.027 *L*	6.5 *H*	8.6 *M*	-0.35 *L*	17500 *NM*
AMPA	Metabolite of glyphosate	Unclassified	NA	NA	419 *VP*	1000	1466561 *H*	-1.63 *L*	-	0.03 *L*	2002 *SM*
Atrazine	Herbicide	Triazine	Inhibits photosynthesis (photosystem II)	Not approved	29 *NP*	-	35 *L*	2.7 *M*	0.039 *L*	3.2 *H*	100 *MM*
Atrazine-deisopropyl	Metabolite of simazine and atrazine	Unclassified	NA	NA	-	-	980 *H*	1.15 *L*	-	-	130 *MM*
Atrazine-desethyl	Metabolite of atrazine	Triazine	NA	NA	45 *MP*	-	2700 *H*	1.51 *L*	12.44 *H*	4.37 *H*	110 *MM*
Azoxystrobin	Fungicide	Strobilurin	Respiration inhibitor	Approved	181 *P*	600	6.7 *L*	2.5 *L*	0.0000001 *L*	2.65 *T*	589 *SM*
Boscalid	Fungicide	Carboxamide	Succinate DeHydrogenase inhibitor	Approved	118 *P*	365	4.6 *L*	2.96 *M*	0.00072 *L*	2.66 *T*	772┼ *SM*
Carbaryl	Insecticide	Carbamate	Cholinesterase inhibitor	Not approved	16* *NP*	107	9.1 *L*	2.36 *L*	0.0416 *L*	2.02 *T*	300 *MM*
Carbofuran	Insecticide; metabolite of furathiocarb, carbosulfan and benfuracarb	Carbamate	Acetylcholinesterase inhibitor	Not approved	14 *NP*	-	322 *M*	1.8 *L*	0.08 *L*	2.28 *T*	25┼ *M*
Carbofuran, 3-hydroxy	Metabolite of carbofuran, carbosulfan and benfuracarb	Unclassified	NA	NA	<1* *NP*	1**	3207 *H*	1.45 *L*	0.0671 *L*	-0.53 *L*	682 *SM*
Carbofuran, -keto	Metabolite of carbofuran and benfuracarb	Unclassified	NA	NA	3 NP	16**	4464 *H*	-	2.02 *L*	0.71 *L*	48 M
Chlordane alpha	Insecticide	Organochlorine	GABA-gated chloride channel antagonist	Not approved	365* *VP*	-	0.1 *L*	2.78 *M*	1.3 *L*	-0.77 *L*	20000 *NM*
Chlordane gamma	Insecticide	Organochlorine	GABA-gated chloride channel antagonist	Not approved	365* *VP*	-	0.1 *L*	2.78 *M*	1.3 *L*	-0.77 *L*	20000 *NM*

Table S2.3 (cont.) - Characteristics of the pesticides analyzed in the 317 agricultural topsoil (0-15/20 cm) samples. Pesticide properties were obtained from the Pesticide Properties DataBase or from the PAN Pesticides Database (┼). When the time to reach 50% (DT_{50}) or 90% (DT_{90}) residue degradation under aerobic field conditions was not available, typical DT_{50} (*) or lab DT_{90} (**) values were reported. NA–not applicable to metabolites; Sw–solubility in water at 20ºC; Log P–octanol-water partition coefficient; Vp–vapor pressure at 25ºC; GUS–GUS leaching potential index; Koc–Soil Organic Carbon-Water Partitioning Coefficient. Interpretation of pesticide properties (i.e., *NP, MP, P, VP, L, M, H, T, NM, SM, MM, M, VM*) is provided at the bottom of the table.

Compound	Type	Chemical class	Mode of action	Status EC 1107/2009	DT_{50} ■ (days)	DT_{90} (days)	Sw ▲ (mg/l)	Log P ●	Vp ♦ (mPa)	GUS▼	Koc ♠ (ml/g)
Chlordecone	Insecticide; metabolite of mirex and kelevan	Organochlorine	GABA-gated chloride channel antagonist	Not approved	300 *P*	-	3 *L*	4.5 *H*	0.000035 *L*	1.6 *L*	2500 *SM*
Chlorfenvinphos	Insecticide	Organophosphate	Acetylcholinesterase inhibitor	Not approved	30 *MP*	-	145 *M*	3.8 *H*	0.53 *L*	1.83 *T*	680 *SM*
Chlorpyrifos	Insecticide	Organophosphate	Acetylcholinesterase inhibitor	Approved	28 *NP*	113	1.05 *L*	4.7 *H*	1.43 *L*	3.63 *H*	5509 *NM*
Chlorpyrifos-methyl	Insecticide	Organophosphate	Acetylcholinesterase inhibitor	Approved	1 *NP*	5	2.74 *L*	4 *H*	3 *L*	0.92 *L*	4645 *NM*
Cymoxanil	Fungicide	Cyanoacetamide oxime	Foliar with protective and curative activity	Approved	5 *NP*	5**	780 *H*	0.67 *L*	0.15 *L*	0.34 *L*	44┼ *M*
Cyproconazole	Fungicide	Triazole	Ergosterol-biosynthesis inhibitor	Approved	129 *P*	579	93 *M*	3.09 *H*	0.026 *L*	3.1 *H*	390┼ *MM*
Cyprodinil	Fungicide	Anilinopyrimidine	Inhibits protein synthesis	Approved	45 *MP*	120**	13 *L*	4 *H*	0.51 *L*	1.11 *L*	1470┼ *SM*
DDD op DDD pp	Insecticide; metabolite of DDT	Organochlorine	NA	NA	1000* *VP*	-	0.09 *L*	6.02 *H*	0.18 *L*	-2.59 *L*	150000 *NM*
DDE op DDE pp	Metabolite of DDT	Organochlorine	GABA-gated chloride channel antagonist	NA	5000 *VP*	-	0.12 *L*	6.51 *H*	-	-	50000 *NM*
DDT op DDT pp	Insecticide	Organochlorine	Sodium channel modulator	Not approved	6200* *VP*	-	0.006 *L*	6.91 *H*	0.025 *L*	-3.89 *L*	151000 *NM*
Diazinon	Insecticide	Organophosphate	Acetylcholinesterase inhibitor	Not approved	18 *NP*	61	60 *M*	3.69 *H*	11.97 *H*	1.14 *L*	609 *SM*
Dieldrin	Insecticide, metabolite of aldrin	Organochlorine	GABA-gated chloride channel antagonist	Not approved	1400* *VP*	-	0.14 *L*	3.7 *H*	0.024 *L*	-0.26 *L*	12000 *NM*
Difenoconazole	Fungicide	Triazole	Inhibits demethylation during ergosterol synthesis	Approved	85 *MP*	277	15 *L*	4.36 *H*	0.0000333	0.9 *L*	6120┼ *NM*

Table S2.3 (cont.) - Characteristics of the pesticides analyzed in the 317 agricultural topsoil (0-15/20 cm) samples. Pesticide properties were obtained from the Pesticide Properties DataBase or from the PAN Pesticides Database (┼). When the time to reach 50% (DT_{50}) or 90% (DT_{90}) residue degradation under aerobic field conditions was not available, typical DT_{50} (*) or lab DT_{90} (**) values were reported. NA–not applicable to metabolites; Sw–solubility in water at 20ºC; Log P–octanol-water partition coefficient; Vp–vapor pressure at 25ºC; GUS–GUS leaching potential index; Koc–Soil Organic Carbon-Water Partitioning Coefficient. Interpretation of pesticide properties (i.e., *NP, MP, P, VP, L, M, H, T, NM, SM, MM, M, VM*) is provided at the bottom of the table.

Compound	Type	Chemical class	Mode of action	Status EC 1107/2009	DT_{50} ■ (days)	DT_{90} (days)	Sw ▲ (mg/l)	Log P ●	Vp ♦ (mPa)	GUS▼	Koc ♠ (ml/g)
Dimethomorph	Fungicide	Morpholine	Cellulose synthesis inhibitor	Approved	44 *MP*	-	28.95 *L*	2.68 *L*	0.000985 *L*	2.56 *T*	1360┼ *SM*
Diuron	Herbicide	Phenylamide	Inhibits photosynthesis	Approved	89 *MP*	230**	35.6 *L*	2.87 *M*	0.00115 *L*	1.83 *T*	813 *SM*
Endosulfan alpha	Insecticide	Organochlorine	Non-competitive GABA antagonist	Not approved	86 *MP*	-	0.32 *L*	4.74 *H*	8.3 *M*	-0.1 *L*	11500 *NM*
Endosulfan beta	Insecticide	Organochlorine	Non-competitive GABA antagonist	Not approved	-	-	0.45 *L*	3.83 *H*	-	-	-
Endosulfan sulphate	Metabolite endosulfan, endosulfan alpha and endosulfan beta	Unclassified	NA	NA	-	-	0.48 *L*	3.66 *H*	-	-	5194 *NM*
Endrin	Insecticide	Organochlorine	Chloride channel-blocking agent	Not approved	4300* *VP*	-	0.24 *L*	3.2 *H*	0.0000002 *L*	0 *L*	10000 *NM*
Epoxiconazole	Fungicide	Triazole	Sterol biosynthesis inhibitor	Approved	120 *P*	-	7.1 *L*	3.3 *H*	0.01 *L*	2.28 *T*	1073┼ *SM*
Ethion	Insecticide, metabolite of chlormephos	Organophosphate	Acetylcholine esterase inhibitor	Not approved	90* *MP*	-	2 *L*	5.07 *H*	0.2 *L*	0 *L*	10000 *NM*
Fenpropimorph	Fungicide	Morpholine	Disrupts membrane function	Approved	26 *NP*	72**	4.32 *L*	4.5 *H*	3.9 *L*	0.46 *L*	2401┼ *SM*
Fluometuron	Herbicide	Phenylurea	Photosynthetic electron transport inhibitor (photosystem II)	Approved	64 *MP*	202**	111 *M*	2.28 *L*	0.125 *L*	3.92 *H*	80┼ *MM*
Fluroxypyr	Herbicide	Pyridine compound	Synthetic auxin	Approved	51 *MP*	44**	6500 *H*	0.04 *L*	0.0000038 *L*	2.42 *T*	66┼ *M*
Folpet	Fungicide	Phthalimide	Multi-site activity	Approved	3 *NP*	5**	0.8 *L*	3.02 *H*	0.021 *L*	1.02 *L*	304 *MM*
Glyphosate	Herbicide	Phosphonoglycine	Inhibits shikimic acid pathway	Approved	24 *NP*	170	10500 *H*	-3.2 *L*	0.0131 *L*	-0.25 *L*	1424 *SM*
Heptachlor	Insecticide	Organochlorine	Chloride channel-blocking agent	Not approved	250 *P*	-	0.0047 *L*	3.93 *H*	1.45 *L*	-2.31 *L*	24000 *NM*
Heptachlor epoxide	Metabolite of heptachlor	Unclassified	NA	NA	-	-	-	-	-	-	22485 *NM*

Table S2.3 (cont.) - Characteristics of the pesticides analyzed in the 317 agricultural topsoil (0-15/20 cm) samples. Pesticide properties were obtained from the Pesticide Properties DataBase or from the PAN Pesticides Database (┼). When the time to reach 50% (DT_{50}) or 90% (DT_{90}) residue degradation under aerobic field conditions was not available, typical DT_{50} (*) or lab DT_{90} (**) values were reported. NA–not applicable to metabolites; Sw–solubility in water at 20ºC; Log P–octanol-water partition coefficient; Vp–vapor pressure at 25ºC; GUS–GUS leaching potential index; Koc–Soil Organic Carbon-Water Partitioning Coefficient. Interpretation of pesticide properties (i.e., *NP, MP, P, VP, L, M, H, T, NM, SM, MM, M, VM*) is provided at the bottom of the table.

Compound	Type	Chemical class	Mode of action	Status EC 1107/2009	DT_{50} ■ (days)	DT_{90} (days)	Sw ▲ (mg/l)	Log P ●	Vp ♦ (mPa)	GUS▼	Koc ♠ (ml/g)
Hexachlorobenzene	Fungicide, metabolite of quintozene	Organochlorine	Fumigant action on fungal spores	Not approved	2000* *VP*	-	<1 *L*	3.93 *H*	1.45 *L*	-2.31 *L*	50000 *NM*
Hexachlorocyclohexane, alpha	Insecticide, metabolite of HCH gamma	Organochlorine	-	Not approved	175* *P*		2 *L*	3.82 *H*	5.99 *M*	1.62 *L*	1888 *SM*
Hexachlorocyclohexane, beta	Metabolite of HCH gamma	Unclassified	NA	NA	-	-	-	-	-	-	-
Hexachlorocyclohexane, gamma	Insecticide	Organochlorine	GABA-gated chloride channel antagonist	Not approved	148 *P*	523	8.52 *L*	3.50 *H*	4.4 *L*	3.95 *H*	1270 *SM*
Imazalil	Fungicide	Imidazole	Disrupts membrane function	Approved	6 *NP*	61	184 *M*	2.56 *L*	0.158 *L*	0.61 *L*	4753┼ *NM*
Imidacloprid	Insecticide	Neonicotinoid	Acetylcholine receptor agonist	Approved	174 *P*	717	610 *H*	0.57 *L*	0.0000004 *L*	3.74 *H*	262┼ *MM*
Isoproturon	Herbicide	Urea	Inhibits photosynthesis (photosystem II)	Approval expired 30.06.2016	23 *NP*	39	70.2 *M*	2.5 *L*	0.0055 *L*	2.07 *T*	122┼ *MM*
Linuron	Herbicide	Urea	Inhibits photosynthesis (photosystem II)	Approval expired 31.07.2017	48 *MP*	218	63.8 *M*	3 *M*	0.051 *L*	2.21 *T*	843 *SM*
Malathion	Insecticide	Organophosphate	Acetylcholinesterase inhibitor	Approved	1 *NP*	1**	148 *M*	2.75 *M*	3.1 *L*	-1.28 *L*	1800 *SM*
Metalaxyl	Fungicide	Phenylamide	Disrupts nucleic acid synthesis	Approved	39 *MP*	86**	8400 *H*	1.75 *L*	0.75 *L*	2.79 *T*	162 *MM*
Metamitron	Herbicide	Triazinone	Inhibits photosynthesis (photosystem II).	Approved	11 *NP*	37	1770 *H*	0.85 *L*	0.000744 *L*	2.64 *T*	78 *MM*
Myclobutanil	Fungicide	Triazole	Inhibits sterol biosynthesis	Approved	35 *MP*	365	132 *M*	2.89 *M*	0.198 *L*	3.3 *H*	518┼ *SM*
Parathion	Insecticide	Organophosphate	Cholinesterase inhibitor	Not approved	-	-	24 *L*	3.82 *H*	-	-	1610┼ *SM*
Parathion-methyl	Insecticide	Organophosphate	Cholinesterase inhibitor	Not approved	10 *NP*	-	55 *M*	3 *M*	0.2 *L*	1.46 *L*	240 *MM*
Penconazole	Fungicide	Triazole	Interfers with ergosterol biosynthesis	Approved	90 *MP*	-	73 *M*	3.72 *H*	0.366 *L*	1.36 *L*	2205┼ *SM*

Table S2.3 (cont.) - Characteristics of the pesticides analyzed in the 317 agricultural topsoil (0-15/20 cm) samples. Pesticide properties were obtained from the Pesticide Properties DataBase or from the PAN Pesticides Database (┼). When the time to reach 50% (DT_{50}) or 90% (DT_{90}) residue degradation under aerobic field conditions was not available, typical DT_{50} (*) or lab DT_{90} (**) values were reported. NA–not applicable to metabolites; Sw–solubility in water at 20ºC; Log P–octanol-water partition coefficient; Vp–vapor pressure at 25ºC; GUS–GUS leaching potential index; Koc–Soil Organic Carbon-Water Partitioning Coefficient. Interpretation of pesticide properties (i.e., *NP, MP, P, VP, L, M, H, T, NM, SM, MM, M, VM*) is provided at the bottom of the table.

Compound	Type	Chemical class	Mode of action	Status EC 1107/2009	DT_{50} ■ (days)	DT_{90} (days)	Sw ▲ (mg/l)	Log P ●	Vp ♦ (mPa)	GUS▼	Koc ♠ (ml/g)
Pentachlorobenzene	Metabolite of quintozene	Unclassified	NA	NA	275 *P*	-	0.83 *L*	5.17 *H*	-	0.3 *L*	7552 *NM*
Phthalimide	Metabolite of folpet[1]	Unclassified	NA	NA	2* *NP*	8**	360 *M*	1.15 *L*	0.00133 *L*	0.61 *L*	209 *MM*
Pinoxaden	Herbicide	Unclassified	Inhibits fatty acid synthesis	Approved	1 *NP*	2**	200 *M*	3.2 *H*	0.0002 *L*	-0.68 *L*	323┼ *MM*
Pirimiphos-methyl	Insecticide	Organophosphate	Acetylcholinesterase inhibitor	Approved	39 *MP*	-	11 *L*	3.9 *H*	0.002 *L*	1.03 *L*	1100 *SM*
Prochloraz	Fungicide	Imidazole	Disrupts membrane function	Approved	17 *NP*	1124	26.5 *L*	3.5 *H*	0.15 *L*	1.98 *T*	500 *SM*
Procymidone	Fungicide	Dicarboximide	Osmotic signal transduction	Not approved	208 *P*	349	2.46 *L*	3.3 *H*	0.023 *L*	4.12 *H*	378 *MM*
Propiconazole	Fungicide	Triazole	Interfers with ergosterol biosynthesis	Approved	35 *MP*	478	150 *M*	3.72 *H*	0.056 *L*	1.89 *T*	1086 *SM*
Prothioconazole	Fungicide	Triazolinthione	Sterol biosynthesis inhibitor	Approved	2 *NP*	6	300 *M*	3.82 *H*	0.0004 *L*	-0.18 *L*	1760┼ *SM*
Pyraclostrobin	Fungicide	Strobilurin	Respiration inhibitor (QoL fungicide)	Approved	32 *MP*	157	1.9 *L*	3.99 *H*	0.000026 *L*	0.06 *L*	9304 *NM*
Quinoxyfen	Fungicide	Quinoline	Signal transduction	Approved	97 *MP*	560	0.047 *L*	4.66 *H*	0.012 *L*	-0.93 *L*	22929┼ *NM*
Simazine	Herbicide	Triazine	Inhibits photosynthesis (photosystem II)	Not approved	90 *MP*	-	5 *L*	2.3 *L*	0.00081 *L*	2 *T*	130 *MM*
Tebuconazole	Fungicide	Triazole	Sterol biosynthesis inhibitor	Approved	47 *MP*	177	36 *L*	3.7 *H*	0.0013 *L*	2.85 *H*	1000┼ *SM*
Terbuthylazine	Herbicide	Triazine	Inhibits photosynthesis (photosystem II)	Approved	22 *NP*	74	6.6 *L*	3.4 *H*	0.12 *L*	3.07 *H*	219┼ *MM*
Terbuthylazine-desethyl	Metabolite of terbuthylazine	Unclassified	NA	NA	29 *NP*	95	327.1 *M*	2.3 *L*	0.35 *L*	3.65 *H*	-
Triadimenol	Fungicide	Triazole	Sterol biosynthesis inhibitor	Approved	65 *MP*	216	72 *M*	3.18 *H*	0.0005 *L*	3.34 *H*	750 *SM*
Trifloxystrobin	Fungicide	Strobilurin	Respiration inhibitor (QoL fungicide)	Approved	2 *NP*	21	0.61 *L*	4.5 *H*	0.0034 *L*	-0.3 *L*	2377┼ *SM*

■ Soil degradation: *NP*–Non-Persistent (DT_{50} <30 days), *MP*–Moderately Persistent (DT_{50}: 30–100 days), *P*–Persistent (DT_{50}: 100– 365 days), *VP*–Very Persistent (DT_{50} >365 days)
▲ Solubility in water: *L*–Low (Sw <50 mg l^{-1}), *M*–Moderate (Sw: 50–500 mg l^{-1}), *H*–High (Sw >500 mg l^{-1})
● Octanol-water Partition Coefficient: *L*–Low bioaccumulation (Log P <2.7), *M*–Moderate bioaccumulation (Log P: 2.7–3), *H*–High bioaccumulation (Log P >3.0)
♦ Vapour pressure: *L*–Low volatility (Vp <5.0 mPa), *M*–Moderately volatile (Vp: 5.0–10.0 mPa), *H*–Highly volatile (Vp >10.0 mPa)
▼ GUS Index: *L*–Low leachability (GUS <1.8), T–Transition state (GUS: 1.8–2.8), *H*–High leachability (GUS >2.8)
♠ Soil adsorption and mobility: *NM*–Non-Mobile (K_{oc} >4000 ml g^{-1}), *SM*–Slightly Mobile (K_{oc}: 500–4000 ml g^{-1}), *MM*–Moderately Mobile (K_{oc}: 75–500 ml g^{-1}), *M*–Mobile (K_{oc}: 15–75 ml g^{-1}), *VM*–Very Mobile (K_{oc} <15 ml g^{-1})
[1] Phthalimide may also originate from other sources than folpet.

Table S2.4 - Acquisition parameters for the compounds analyzed by LC-MS/MS-based methods. *internal standard. LOQ = limit of quantification.

Compound	Retention time (minutes)	Mass Parent 1	Mass Daughter 1	Cone voltage (V)	Collision energy (eV)	Mass Parent 2/3	Mass Daughter 2/3	Cone voltage (V)	Collision energy (eV)	LOQ (mg/kg)
Glyphosate and AMPA analysis										
Glyphosate-FMOC	4.20	390.2	168.1	20	12	390.2/ 390.2	150.2/ 124.2	20/ 20	24 / 28	0.05
AMPA-FMOC	5.00	332.2	110.2	20	6	332.2	136.1	20	14	0.05
1, 2–^{13}C ^{15}N Glyphosate-FMOC	4.20	393.2	171.1	20	12	-	-	-	-	
^{13}C ^{15}N AMPA-FMOC	5.00	334.2	112.2	20	6	-	-	-	-	
Multi-residue method										
Abamectin	9.32	890.5	305	24	22	890.5	567	24	22	0.01
Atrazine	5.77	216	174	30	20	216	96	30	20	0.01
Atrazine-deisopropyl	3.83	174	104	25	21	174	96	25	18	0.01
Atrazine-desethyl	4.48	188	104	25	22	188	146	25	17	0.01
Azoxystrobin	6.35	404	372	30	12	404	344	30	24	0.01
Boscalid	6.56	343	307	35	15	343	140	35	15	0.01
$^{13}C_3$-caffeine*	3.46	198	140	20	20	198	112	20	18	
Carbaryl	5.22	202	127	20	25	202	117	20	25	0.01
Carbofuran	5.04	222	123	18	20	222	165	18	12	0.01
Carbofuran, 3-hydroxy	3.87	255	163	35	15	255	220	35	11	0.01
Carbofuran, -keto	4.38	236	179	10	12	236	161	15	18	0.01
Chlorpyrifos	8.57	350	198	20	17	352	200	20	17	0.01
Chlorpyrifos-methyl	7.86	323.9	291.8	25	17	323.9	124.8	25	20	0.01
Cymoxanil	4.11	199	127.9	18	8	199	110.9	18	18	0.01
Cyproconazole	6.86	292.2	70.3	25	17	292.2	125.1	25	27	0.01
Cyprodinil	7.47	226	108	35	25	226	93	35	32	0.01
Diazinon	7.65	305	152.9	30	18	305	168.9	30	18	0.01
Difenoconazole	7.89	406	251	30	25	408	253	30	25	0.01
Dimethomorph	6.67	388	301	30	25	388	165	30	25	0.01
Diuron	5.85	235	72	30	15	233	72	30	15	0.01
Epoxiconazole	7.12	330.1	120.9	25	22	332.1	120.9	25	22	0.01
Ethion	8.50	385	199	20	12	385	143	20	25	0.01
Fenpropimorph	7.05	304	147	30	40	304	132	30	40	0.01
Fluometuron	4.85	233.2	72.2	34	18	233.2	46.4	34	18	0.01
Fluroxypyr	4.13	255	209	30	14	257	211	30	14	0.01
Imazalil	5.99	297	159	30	22	299	161	30	22	0.01
Imidacloprid	3.66	256	175	30	20	256	209	30	20	0.01
Isoproturon	5.82	207	72	30	20	207	165	30	20	0.01
Linuron	6.33	249	160	30	20	249	182	30	20	0.01
Malathion	6.68	331	98.8	20	25	331	126.8	20	10	0.01
Metalaxyl	5.92	280	220	30	15	280	192	30	17	0.01

Table S2.4 (cont.) - Acquisition parameters for the compounds analyzed by LC-MS/MS-based methods. *internal standard. LOQ = limit of quantification.

Compound	**Retention time (minutes)**	**Mass Parent 1**	**Mass Daughter 1**	**Cone voltage (V)**	**Collision energy (eV)**	**Mass Parent 2**	**Mass Daughter 2**	**Cone voltage (V)**	**Collision energy (eV)**	**LOQ (mg/kg)**
Multi-residue method										
Metamitron	3.91	203	175	30	20	203	104	30	20	0.01
Myclobutanil	6.73	289	70	32	17	291	70	32	17	0.01
Penconazole	7.44	284	159	30	26	286	161	30	26	0.01
Pinoxaden	7.80	401	317	35	20	401	57.1	35	20	0.01
Pirimiphos-methyl	7.83	306	164	30	25	306	108	30	25	0.01
Prochloraz	7.75	378	310	30	10	376	308	30	10	0.01
Propiconazole	7.61	342	158.8	30	25	344	161	30	25	0.01
Prothioconazole	7.57	344.1	326	12	10	344.1	125	12	28	0.01
Pyraclostrobin	7.7	388.3	193.9	30	12	388.3	162.9	30	25	0.01
Quinoxyfen	8.61	307.9	196.9	35	32	309.9	198.9	35	32	0.01
Simazine	5.07	202	132	30	20	202	124	30	20	0.01
Tebuconazole	6.48	308	124.7	30	30		310	126.7	30	0.01
Terbuthylazine	6.58	230	174	25	15	232	176	25	15	0.01
Terbuthylazine-desethyl	5.22	202	146	25	15	202	104	25	25	0.01
Triadimenol	6.88	296	70	15	10	298	70	15	10	0.01
Trifloxystrobin	8.02	409.2	186	20	17	409.2	206.1	20	15	0.01

Table S2.5- Acquisition parameters for the compounds analyzed by GC-HRMS. * internal standard. LOQ = limit of quantification.

Compound	Retention time (minutes)	Exact mass Quantifier	Exact mass Qualifier	LOQ (mg/kg)
Aldrin	10.39	262.85642	292.92669	0.005
Chlordane alpha	11.72	374.82247	376.81952	0.005
Chlordane gamma	11.96	374.82247	376.81952	0.005
Chlordecone	14.71	269.81257	284.84076	0.005
Chlorfenvinphos	12.08	266.93753	268.93458	0.005
DDD op	12.51	237.00463	235.00758	0.005
DDD pp	13.27	237.00463	235.00758	0.005
DDE op	11.59	245.99976	247.99681	0.005
DDE pp	12.21	245.99976	247.99681	0.005
DDT op	12.95	237.00463	235.00758	0.005
DDT pp	13.75	237.00463	235.00758	0.005
Dieldrin	12.65	276.87206	262.85641	0.005
Endosulfan alpha	12.18	194.93436	169.96846	0.005
Endosulfan beta	13.41	169.96846	194.93436	0.005
Endosulfan sulfate	14.91	271.80975	236.84076	0.005
Endrin	13.10	242.95295	260.85937	0.005
Folpet	12.32	259.93343	130.02874	0.005
Hexachlorobenzene	7.95	283.80962	285.80667	0.005
Hexachlorocyclohexane, alpha	8.32	180.93731	182.93436	0.005
Hexachlorocyclohexane, beta	9.14	180.93731	182.93436	0.005
Hexachlorocyclohexane, gamma	8.94	180.93731	182.93436	0.005
Heptachlor	9.84	271.80962	100.00742	0.005
Heptachlor epoxide	11.52	354.84071	350.84661	0.005
Parathion	12.03	291.03248	96.95076	0.005
Parathion-methyl	11.13	263.00118	124.98206	0.005
PCB198*	15.32	429.76002	427.76297	-
Pentachlorobenzene	6.41	247.85154	212.88263	0.005
Phthalimide	6.84	147.03147	103.04165	0.005
Procymidone	13.03	283.01614	285.01319	0.005

Table S2.6 - The LC-MS/MS apparatus.

	Multi-residues	**Glyphosate and AMPA**
Type of LC	TQ-S mass spectrometer (Waters, U.K.) coupled to an Acquity UPLC system (Waters, U.K.)	Quattro Ultima mass spectrometer (Micromass, U.K.) coupled to an Acquity UPLC system (Waters, U.K.)
ESI mode	Positive	Negative
Column	ACQUITY UPLC HSS T3 1.8 µm particle size column, 100 x 2.1 mm i.d. (Waters, The Netherlands)	XBridge™ Shield RP C18 3.5 µm particle size column, 150 x 2.1 mm i.d. (Waters, The Netherlands)
Column temperature	45 °C	35 °C
Mobile phases	A: ammonium formate 5mM and formic acid 0.1% in Milipore water B: ammonium formate 5 mM and formic acid 0.1% in Millipore water: methanol (5:95 v/v)	A: ammonium acetate 5 mM in Millipore water B: ammonium acetate 5 mM in Millipore water: methanol (10:90 v/v) Mobile phases were adjusted to pH 9 with ammonia solution
LC gradient	0–1st minute: 100% A 1st–8th minute: gradient linearly decreased to 0% A 8th–11th minute: 0% A 11th–12nd minute: gradient linearly increased to 100% A 12nd–14th minute: 100% A	0–1st minute: 100% A 1st–6th minute: gradient linearly decreased to 0% A 6th–8th minute: 0% A 8th–9th minute: gradient linearly increased to 100% A 9th–14th minute: 100% A
Flow rate	0.4 ml/ min	0.4 ml/ min
Mass spectrometer conditions: capillary source temperature desolvation temperature cone gas flow desolvation gas flow	 3.0 kV 150 °C 450 °C 150 L/h 800 L/h	 3.5 kV 120 °C 400 °C 160–200 L/h 580–600 L/h
Injection volume	5 µl	5 µl

Table S2.7 - GC-HRMS apparatus.

Type of GC	GC-EI-Q-Orbitrap system (Exactive GC; Thermo Scientific)
Scan range	50 to 500 m/z
Resolution	60 000
Column	TraceGOLD™ TG-OCP I 0.25 µm particle size column, 30 m × 0.25 mm i.d. (Thermo Scientific)
Inlet	SSL inlet with CarboFrit Splitless injection 290 °C
Oven temperature program	70 °C for 1.5 minutes The temperature was increased 50°C/min to 135 °C The temperature was increased 10°C/min to 300 °C 300 °C for 7 minutes
Carrier gas	Helium 5.0 (99.999%, Linde Gas, Schiedam, The Netherlands)
Flow rate	1.2 ml/min
Mass spectrometer conditions: transfer line temperature ion source temperature	 280 °C 230 °C
Injection volume	1 µl

Table S2.8 - Frequency and median and maximum contents of the pesticide residues detected in the tested European agricultural topsoils (0–15/20 cm). Compounds are presented in decreasing order of frequency (number of soil samples in which the compound was ≥ respective limit of quantification, LOQ). Only contents ≥ LOQ were considered in median calculations. NA*-not applicable, no quantitative data are provided for phthalimide because of artifacts. DDTs=sum of DDE op, DDE pp, DDD op, DDD pp, DDT op and DDT pp. n–number of soils containing pesticide residues, nq–number of soils containing quantifiable pesticide residues (i.e. the number of samples containing pesticide residues minus the number of samples with just phthalimide).

Compound	LOQ (mg/kg)	Number of soils ≥LOQ (% of the 317 tested soils)	Median content (mg/kg)	Maximum content (mg/kg)
AMPA	0.05	133 (42%)	0.15	1.92
Boscalid (BOS)	0.01	87 (27%)	0.04	0.41
Epoxiconazole (EPI)	0.01	75 (24%)	0.02	0.16
DDE pp	0.005	72 (23%)	0.02	0.31
Glyphosate (GLY)	0.05	67 (21%)	0.14	2.05
Phthalimide (PTI)	0.005	59 (19%)	NA*	NA*
Tebuconazole (TEB)	0.01	39 (12%)	0.02	0.19
DDD op	0.005	23 (7%)	0.01	0.04
DDT pp	0.005	23 (7%)	0.01	0.05
Imidacloprid (IMI)	0.01	23 (7%)	0.02	0.06
Prothioconazole (PTC)	0.01	23 (7%)	0.04	0.14
Folpet (FOL)	0.005	22 (7%)	0.01	0.03
Azoxystrobin (AZO)	0.01	22 (7%)	0.03	0.25
Linuron (LIN)	0.01	21 (7%)	0.03	0.28
Metamitron (MTM)	0.01	16 (5%)	0.02	0.07
Dieldrin (DIE)	0.005	15 (5%)	0.01	0.06
Dimethomorph (DIM)	0.01	12 (4%)	0.02	0.08
Difenoconazole (DIF)	0.01	11 (3%)	0.03	0.24
DDD pp	0.005	10 (3%)	0.01	0.04
Carbofuran (CAR)	0.01	8 (3%)	0.01	0.02
Propiconazole (PPC)	0.01	8 (3%)	0.02	0.04
Terbuthylazine (TER)	0.01	8 (3%)	0.02	0.02
Fenpropimorph (FEN)	0.01	7 (2%)	0.02	0.09
Cyproconazole (CPC)	0.01	7 (2%)	0.02	0.04
Cyprodinil (CYP)	0.01	6 (2%)	0.03	0.06
Cymoxanil (CYM)	0.01	5 (2%)	0.02	0.14
Myclobutanil (MYC)	0.01	5 (2%)	0.02	0.10
Quinoxyfen (QUI)	0.01	5 (2%)	0.03	0.10
Prochloraz (PCL)	0.01	5 (2%)	0.05	0.07
Chlorpyrifos (CHL)	0.01	4 (1%)	0.03	0.11
Metalaxyl (MET)	0.01	4 (1%)	0.04	0.05
Penconazole (PCZ)	0.01	4 (1%)	0.02	0.13
Isoproturon (ISO)	0.01	4 (1%)	0.02	0.02
Chlordane alpha (CHDα)	0.005	2 (1%)	0.01	0.01
Pyraclostrobin (PYR)	0.01	2 (1%)	0.04	0.06
Chlordane gamma (CHDγ)	0.005	1 (<1%)	0.01	0.01
DDE op	0.005	1 (<1%)	0.02	0.02
DDT op	0.005	1 (<1%)	0.01	0.01
Heptachlor (HPT)	0.005	1 (<1%)	0.01	0.01
Hexachlorobenzene (HCB)	0.005	1 (<1%)	0.01	0.01
Procymidone (PCM)	0.005	1 (<1%)	0.01	0.01
Atrazine (ATR)	0.01	1 (<1%)	0.01	0.01
Triadimenol (TRI)	0.01	1 (<1%)	0.01	0.01
DDTs		78 (25%)	0.03	0.31
Total (Σ pesticides per sample)		n:263 (83%), nq: 246 (78%)	nq:0.15	2.87

Table S2.9 - Pesticide composition of the EU agricultural topsoil samples. For individual pesticide abbreviations please see *Table S2.8*. N–number of soil samples presenting the respective pesticide combination; Range–minimum-maximum mixture content; * PTI (phthalimide) was considered in the number of residues present in the soil but not in the total pesticide content.

Number of pesticide residues in soil ≥LOQ	N	Range (mg/kg)	
0 residues	54		
1 residue	78		
AMPA	21	0.062-0.728	
PTI	17		*
DDE pp	8	0.005-0.056	
EPI	6	0.010-0.019	
TER	5	0.012-0.021	
BOS	4	0.015-0.037	
FOL	4	0.009-0.013	
GLY	3	0.062-0.175	
PTC	3	0.012-0.138	
ATR	1	0.011	
CYM	1	0.013	
DIE	1	0.011	
DIM	1	0.048	
ENDα	1	0.006	
IMI	1	0.022	
TEB	1	0.018	
2 residues	53		
AMPA + GLY	7	0.169-2.561	
AMPA + PTI	5	0.053-0.132	*
DDE pp + PTI	5	0.005-0.041	*
AMPA+ BOS	3	0.123-0.560	
FOL + PTI	3	0.006-0.011	*
BOS + PTC	2	0.034-0.050	
AMPA + DDE pp	2	0.120-0.168	
DDE pp + CARh	2	0.017-0.068	
DDE pp + EPI	2	0.022-0.042	
AMPA + EPI	1	0.079	
AMPA + FOL	1	0.086	
AMPA + TEB	1	0.086	
GLY + BOS	1	0.093	
GLY + CYM	1	0.074	
GLY + DDE pp	1	0.142	
GLY + EPI	1	0.233	
GLY + PTI	1	1.136	*
BOS + EPI	1	0.042	
BOS + IMI	1	0.052	
BOS + MET	1	0.051	
BOS + PTI	1	0.019	*
DDE pp + DDD op	1	0.052	
DDE pp + FOL	1	0.012	
EPI + FEN	1	0.067	
EPI + PTI	1	0.013	*
EPI + TEB	1	0.033	
PTC + DIM	1	0.057	
PTC + PTI	1	0.050	*
PTC + TER	1	0.110	
CHL + DIM	1	0.091	
CHL + MTM	1	0.138	

Table S2.9 (cont.) - Pesticide composition of the EU agricultural topsoil samples. For individual pesticide abbreviations please see *Table S2.8*. N–number of soil samples presenting the respective pesticide combination; Range–minimum-maximum mixture content; * PTI (phthalimide) was considered in the number of residues present in the soil but not in the total pesticide content.

Number of pesticide residues in soil ≥LOQ	N	Range (mg/kg)	
3 residues	41		
AMPA + GLY + PTI	7	0.113-2.868	*
AMPA + GLY + PTC	2	0.315-0.333	
AMPA + GLY + DDD op	2	0.314-1.319	
AMPA + GLY + DDE pp	2	0.349-0.838	
AMPA + DDE pp + FOL	2	0.262-0.645	
AZO + LIN + EPI	2	0.078-0.079	
AMPA + BOS + DDD op	1	0.079	
AMPA + BOS + DDE pp	1	0.264	
AMPA + BOS + DIM	1	0.328	
AMPA + BOS + FOL	1	0.079	
AMPA + DDE pp + DIM	1	0.199	
AMPA + DDE pp + IMI	1	0.083	
AMPA + DDE pp + PTI	1	0.224	*
AMPA + DDE pp + PCM	1	0.164	
AMPA + GLY + BOS	1	0.192	
AMPA + GLY + FOL	1	0.285	
AMPA + GLY + TEB	1	0.199	
AMPA + CARh + EPI	1	0.209	
AMPA + IMI + MTM	1	0.181	
BOS + IMI + CYP	1	0.204	
BOS + IMI + TRI	1	0.160	
BOS + PTI + TEB	1	0.073	*
DDE pp + DDT pp + DDD op	1	0.024	
DDE pp + DIE + PTI	1	0.080	*
DDE pp + MTM + EPI	1	0.226	
EPI + GLY + IMI	1	0.079	
EPI + TEB + MTM	1	0.207	
AZO+ IMI + LIN	1	0.487	
CARh + CHL + MTM	1	0.085	
CYM + MYC + QUI	1	0.192	
4 residues	23		
AMPA + BOS + EPI + DDE pp	2	0.099-0.247	
AMPA + BOS + EPI + AZO	1	0.233	
AMPA + BOS + EPI + DIE	1	0.336	
AMPA + BOS + EPI + ISO	1	0.181	
AMPA + BOS + EPI + PTC	1	0.323	
AMPA + BOS + EPI +TEB	1	0.146	
AMPA + BOS + GLY + DDE pp	1	0.389	
AMPA + BOS + GLY + LIN	1	0.388	
AMPA + BOS + TEB + IMI	1	0.215	
AMPA + GLY + DIM + TER	1	0.350	
BOS + EPI + TEB + CARh	1	0.080	
BOS + EPI + TEB + DIE	1	0.079	
BOS + EPI + TEB + PYR	1	0.305	
BOS + EPI + DIF + LIN	1	0.407	
BOS + EPI + AZO + DIM	1	0.313	
DDE pp + BOS + DDD op + IMI	1	0.099	
DDE pp + BOS + EPI + LIN	1	0.122	
DDE pp + BOS + TEB + PCL	1	0.290	
DDE pp + DDD op + DDT pp + AMPA	1	0.167	
DDE pp + DDD op + DDT pp + LIN	1	0.327	
DDE pp + EPI + DIE + MTM	1	0.107	

Table S2.9 (cont.) - Pesticide composition of the EU agricultural topsoil samples. For individual pesticide abbreviations please see *Table S2.8*. N–number of soil samples presenting the respective pesticide combination; Range–minimum-maximum mixture content; * PTI (phthalimide) was considered in the number of residues present in the soil but not in the total pesticide content.

Number of pesticide residues in soil ≥LOQ	N	Range (mg/kg)	
4 residues			
EPI + TEB + MTM + PCL	1	0.085	
5 residues	26		
AMPA + GLY + DDE pp + FOL + PTI	2	0.525-1.070	*
AMPA + GLY + BOS + EPI + AZO	1	0.739	
AMPA + GLY + BOS + EPI + FOL	1	0.514	
AMPA + GLY + BOS + EPI + PTC	1	1.107	
AMPA + GLY + BOS + EPI + PTI	1	0.512	*
AMPA + GLY + BOS + MET + IMI	1	0.773	
AMPA + GLY + BOS + PTI + FOL	1	0.297	*
AMPA + GLY + PTI + FOL + PTC	1	0.255	*
AMPA + GLY + PTI + TEB + AZO	1	0.261	*
AMPA + GLY + PTI + TEB + QUI	1	0.365	*
AMPA + GLY + TEB + DDE pp + MYC	1	0.803	
AMPA + GLY + DDE pp + DDT pp + DDD pp	1	0.427	
AMPA + BOS + EPI + DIM + LIN	1	0.184	
AMPA + BOS + EPI + TEB + PCL	1	0.411	
AMPA + BOS + PCZ + QUI + PTC	1	0.357	
AMPA + BOS + PTI + EPI + IMI	1	0.201	*
AMPA + EPI + TEB + CYP + PPC	1	0.618	
BOS + EPI + DDE pp + DDT pp + DDD op	1	0.105	
BOS + EPI + DDE pp + TEB + PTC	1	0.128	
BOS + EPI + CARh + MTM + FEN	1	0.105	
BOS + EPI + IMI + LIN + PTC	1	0.181	
BOS + EPI + TEB + PPC + PCP	1	0.145	
BOS + TEB + PTI + CYM + MET	1	0.508	*
EPI + DDD op + DDD pp + DDE pp + DDT pp	1	0.149	
EPI + TEB + AZO+ PPC + FEN	1	0.286	
6 residues	15		
AMPA + GLY + BOS + TEB + EPI + DIF	1	0.782	
AMPA + GLY + BOS + TEB + EPI + ISO	1	0.800	
AMPA + GLY + BOS + TEB + CYP + PCZ	1	0.661	
AMPA + GLY + BOS + DDE pp + DDD op + DIE	1	0.450	
AMPA + GLY + CHL + MYC + PCZ + DIF	1	1.843	
AMPA + GLY + DDE pp + PTI + DDT pp + PTC	1	0.534	*
AMPA + GLY + DDE pp + PTI + FOL + IMI	1	1.003	*
AMPA + BOS + DDT pp + DDE pp + DDD op + DDD pp	1	0.533	
AMPA + BOS + DDT pp + DDE pp + DDD op + EPI	1	0.376	
AMPA + BOS + DDT pp + EPI + FEN + LIN	1	0.207	
AMPA + BOS + AZO+ MTM + LIN + PCP	1	0.213	
AMPA + BOS + PCZ + IMI + TEB + DIE	1	0.180	
AMPA + DDE pp + PTI + PPC + TEB + PCL	1	0.330	*
BOS + EPI + PTC + DIF + AZO + LIN	1	0.154	
BOS + EPI + PTC + DIF + CYM + TEB	1	0.164	
7 residues	9		
AMPA + GLY + BOS + DDT pp + DIE + MET + IMI	1	0.348	
AMPA + GLY + BOS + EPI + DIE + FOL + IMI	1	0.975	
AMPA + GLY + BOS + CYP + DIM + MYC + QUI	1	0.577	
AMPA + GLY + TEB + PCL + DIF + FOL + CYP	1	0.805	
AMPA + GLY + TEB + EPI + AZO+ PPC + FEN	1	1.054	
AMPA + BOS + CARh + AZO+ MTM + LIN + PCP	1	0.214	
BOS + EPI + AZO+ DIM + TER + LIN + PTC	1	0.434	
BOS + EPI + AZO+ PPC + IMI + TEB + MTM	1	0.338	

Table S2.9 (cont.) - Pesticide composition of the EU agricultural topsoil samples. For individual pesticide abbreviations please see *Table S2.8*. N–number of soil samples presenting the respective pesticide combination; Range–minimum-maximum mixture content; * PTI (phthalimide) was considered in the number of residues present in the soil but not in the total pesticide content.

Number of pesticide residues in soil ≥LOQ	N	Range (mg/kg)	
7 residues (cont.)			
DDD op + DDD pp + DDE pp + DDE op + DDT op + DIE + TEB	1	0.189	
8 residues	7		
AMPA + BOS + DDE pp + EPI + DDT pp + DDD op + AZO+ LIN	1	0.380	
AMPA + BOS + DDE pp + CHD + DIE + ENDα + HPT + IMI	1	0.346	
AMPA + GLY + BOS + DDE pp + PTI + EPI + TEB + PPC	1	1.296	*
AMPA + GLY + BOS + DDE pp + PTI + EPI + DDT pp + AZO	1	0.739	*
AMPA + GLY + BOS + DDE pp + TEB + CYP + DIM + DIF	1	1.061	
AMPA + DDE pp + EPI + DDT pp + DDD pp + ISO + LIN + PCP	1	0.189	
BOS + DDE pp + EPI + DDT pp + DDD op + MTM + FEN + DIF	1	0.150	
9 residues	7		
AMPA + GLY + BOS + EPI + DDD op + DDE pp + DDT pp + DDD pp + DIE	1	1.748	
AMPA + GLY + BOS + DDE pp + FOL + MYC + QUI + TEB + DIF	1	0.529	
AMPA + GLY + EPI + DIF + AZO+ PYR + TEB + MTM + LIN	1	0.859	
AMPA + BOS + EPI + AZO + IMI + TEB + ISO + FEN + PCP	1	0.407	
AMPA + BOS + EPI + DDT pp + DIE + TEB + MTM + PCP + PTC	1	0.362	
BOS + EPI + DDE pp + DDT pp + DDD op + DDD pp + AZO + IMI + LIN	1	0.353	
BOS + EPI + DDE pp + DDT pp + DDD op + AZO+ DIM + LIN + DIF	1	0.637	
10 residues	2		
AMPA + BOS + EPI + DDD op + DDD pp + DDE pp + DDT pp + PTI + AZO + LIN	1	0.221	*
AMPA + BOS + EPI + DDD op + DDE pp + DDT pp + AZO + IMI + LIN + PTC	1	0.536	
11 residues	1		
AMPA + GLY + EPI + DDE pp + DDD op + DDD pp + DDT pp + DIE + MTM + PCP + PTC	1	0.921	
13 residues	1		
AMPA + EPI + DDE pp + TEB + DDD op + DDD pp + DDT pp + DIE + HCB + CARh + PPC + IMI + MTM	1	0.486	

Table S2.10 - Pesticide composition of the EU agricultural topsoil samples by EU region. For individual pesticide abbreviations please see *Table S2.8*. N–number of soil samples presenting the respective pesticide combination; Range–minimum-maximum mixture content; * PTI (phthalimide) was considered in the number of residues present in the soil but not in the total pesticide content.

Number of pesticide residues in soil ≥LOQ	N	Range (mg/kg)	
NORTH EU			
0 residues	*6*		
1 residue	*11*		
AMPA	6	0.062-0.166	
BOS	1	0.037	
EPI	1	0.011	
FOL	1	0.009	
GLY	1	0.062	
PTI	1		*
2 residues	*11*		
AMPA + DDE pp	2	0.120-0.168	
AMPA + PTI	2	0.053	*
AMPA + BOS	1	0.132-0.560	
AMPA + FOL	1	0.086	
AMPA + GLY	1	0.493	
BOS + PTI	1	0.019	*
DDE pp + PTI	1	0.016	*
EPI + FEN	1	0.067	
PTC + PTI	1	0.050	*
3 residues	*10*		
AMPA + DDE pp + FOL	2	0.262-0.645	
AMPA + BOS + DDE pp	1	0.264	
AMPA + BOS + FOL	1	0.079	
AMPA + DDE pp + PTI	1	0.224	*
AMPA + GLY + DDE pp	1	0.349	
AMPA + GLY + PTC	1	0.333	
AMPA + GLY + PTI	1	0.279	*
AMPA + IMI + MTM	1	0.181	
BOS + PTI + TEB	1	0.073	*
4 residues	*5*		
AMPA + BOS + EPI + DDE pp	1	0.247	
AMPA + BOS + EPI + ISO	1	0.181	
AMPA + BOS + EPI + PTC	1	0.323	
AMPA + BOS + EPI +TEB	1	0.146	
EPI + TEB + MTM + PCL	1	0.085	
5 residues	*7*		
AMPA + BOS + EPI + DIM + LIN	1	0.184	
AMPA + BOS + PTI + EPI + IMI	1	0.201	*
AMPA + GLY + DDE pp + DDT pp + DDD pp	1	0.427	
AMPA + GLY + BOS + EPI + AZO	1	0.739	
AMPA + GLY + BOS + EPI + PTI	1	0.512	*
AMPA + GLY + DDE pp + FOL + PTI	1	0.525	*
AMPA + GLY + PTI + TEB + AZO	1	0.261	*
6 residues	*4*		
AMPA + GLY + BOS + TEB + EPI + DIF	1	0.782	
AMPA + GLY + BOS + TEB + EPI + ISO	1	0.800	
AMPA + GLY + DDE pp + PTI + DDT pp + PTC	1	0.534	*
BOS + EPI + PTC + DIF + AZO + LIN	1	0.154	
8 residues	*2*		
AMPA + DDE pp + EPI + DDT pp + DDD pp + ISO + LIN + PCP	1	0.189	
AMPA + GLY + BOS + DDE pp + PTI + EPI + TEB + PPC	1	1.296	*

Table S2.10 (cont.) - Pesticide composition of the EU agricultural topsoil samples by EU region. For individual pesticide abbreviations please see *Table S2.8*. N–number of soil samples presenting the respective pesticide combination; Range–minimum-maximum mixture content; * PTI (phthalimide) was considered in the number of residues present in the soil but not in the total pesticide content.

Number of pesticide residues in soil ≥LOQ	N	Range (mg/kg)	
9 residues	*2*		
AMPA + BOS + EPI + AZO + IMI + TEB + ISO + FEN + PCP	1	0.407	
AMPA + GLY + EPI + DIF + AZO+ PYR + TEB + MTM + LIN	1	0.859	
10 residues	*1*		
AMPA + BOS + EPI + DDD op + DDD pp + DDE pp + DDT pp + PTI + AZO + LIN	1	0.221	*
11 residues	*1*		
AMPA + GLY + EPI + DDE pp + DDD op + DDD pp + DDT pp + DIE + MTM + PCP + PTC	1	0.921	
SOUTH EU			
0 residues	*28*		
1 residue	*27*		
PTI	8		*
AMPA	4	0.083-0.728	
DDE pp	4	0.006-0.056	
FOL	3	0.009-0.013	
PTC	3	0.012-0.138	
GLY	2	0.120-0.175	
BOS	1	0.023	
DIM	1	0.048	
TER	1	0.012	
2 residues	*22*		
AMPA + GLY	6	0.169-2.561	
FOL + PTI	3	0.006-0.011	*
DDE pp + CARh	2	0.017-0.068	
AMPA + TEB	1	0.086	
BOS + PTC	1	0.034	
CHL + DIM	1	0.091	
CHL + MTM	1	0.138	
DDE pp + EPI	1	0.022	
DDE pp + FOL	1	0.012	
DDE pp + PTI	1	0.041	*
GLY + DDE pp	1	0.142	
GLY + EPI	1	0.233	
GLY + PTI	1	1.136	*
PTC + DIM	1	0.057	
3 residues	*13*		
AMPA + GLY + PTI	5	1.531-2.868	*
AMPA + BOS + DIM	1	0.328	
AMPA + DDE pp + IMI	1	0.083	
AMPA + GLY + BOS	1	0.192	
AMPA + GLY + DDE pp	1	0.838	
AZO + LIN + EPI	1	0.079	
BOS + IMI + CYP	1	0.204	
CYM + MYC + QUI	1	0.192	
DDE pp + MTM + EPI	1	0.226	
4 residues	*6*		
AMPA + BOS + TEB + IMI	1	0.215	
AMPA + GLY + DIM + TER	1	0.350	
BOS + EPI + TEB + CARh	1	0.080	
BOS + EPI + TEB + PYR	1	0.305	
DDE pp + DDD op + DDT pp + AMPA	1	0.167	
DDE pp + EPI + DIE + MTM	1	0.107	

Table S2.10 (cont.) - Pesticide composition of the EU agricultural topsoil samples by EU region. For individual pesticide abbreviations please see *Table S2.8*. N–number of soil samples presenting the respective pesticide combination; Range–minimum-maximum mixture content; * PTI (phthalimide) was considered in the number of residues present in the soil but not in the total pesticide content.

Number of pesticide residues in soil ≥LOQ	N	Range (mg/kg)	
5 residues	*6*		
AMPA + BOS + EPI + TEB + PCL	1	0.411	
AMPA + GLY + BOS + EPI + PTC	1	1.107	
AMPA + GLY + TEB + DDE pp + MYC	1	0.803	
BOS + EPI + TEB + PPC + PCP	1	0.145	
EPI + DDD op + DDD pp + DDE pp + DDT pp	1	0.149	
EPI + TEB + AZO + PPC + FEN	1	0.286	
6 residues	*2*		
AMPA + GLY + CHL + MYC + PCZ + DIF	1	1.843	
AMPA + GLY + DDE pp + PTI + FOL + IMI	1	1.003	*
7 residues	*1*		
BOS + EPI + AZO + PPC + IMI + TEB + MTM	1	0.338	
8 residues	*2*		
AMPA + BOS + DDE pp + CHD + DIE + ENDα + HPT + IMI	1	0.346	
AMPA + GLY + BOS + DDE pp + TEB + CYP + DIM + DIF	1	1.061	
EAST EU			
0 residues	*4*		
1 residue	*16*		
PTI	5		*
TER	4	0.012-0.021	
EPI	3	0.012-0.019	
AMPA	2	0.142-0.145	
DDE pp	1	0.005	
TEB	1	0.018	
2 residues	*8*		
DDE pp + PTI	3	0.005-0.025	*
AMPA + EPI	1	0.079	
BOS + EPI	1	0.042	
DDE pp + DDD op	1	0.052	
EPI + PTI	1	0.013	*
PTC + TER	1	0.110	
3 residues	*9*		
AMPA + GLY + DDD op	2	0.314-1.319	
AMPA + BOS + DDD op	1	0.079	
AMPA + DDE pp + DIM	1	0.199	
AMPA + DDE pp + PCM	1	0.164	
AMPA + GLY + TEB	1	0.199	
AZO + IMI + LIN	1	0.487	
DDE pp + DDT pp + DDD op	1	0.024	
DDE pp + DIE + PTI	1	0.080	*
4 residues	*7*		
AMPA + BOS + EPI + AZO	1	0.233	
AMPA + BOS + EPI + DDE pp	1	0.099	
AMPA + BOS + GLY + DDE pp	1	0.389	
BOS + EPI + DIF + LIN	1	0.407	
DDE pp + BOS + DDD op + IMI	1	0.099	
DDE pp + BOS + EPI + LIN	1	0.122	
DDE pp + BOS + TEB + PCL	1	0.290	
5 residues	*2*		
BOS + EPI + DDE pp + DDT pp + DDD op	1	0.105	
BOS + EPI + CARh + MTM + FEN	1	0.105	

Table S2.10 (cont.) - Pesticide composition of the EU agricultural topsoil samples by EU region. For individual pesticide abbreviations please see *Table S2.8*. N–number of soil samples presenting the respective pesticide combination; Range–minimum-maximum mixture content; * PTI (phthalimide) was considered in the number of residues present in the soil but not in the total pesticide content.

Number of pesticide residues in soil ≥LOQ	N	Range (mg/kg)	
6 residues	*6*		
AMPA + BOS + AZO + MTM + LIN + PCP	1	0.213	
AMPA + BOS + DDT pp + DDE pp + DDD op + EPI	1	0.376	
AMPA + BOS + DDT pp + EPI + FEN + LIN	1	0.207	
AMPA + DDE pp + PTI + PPC + TEB + PCL	1	0.330	*
AMPA + GLY + BOS + TEB + CYP + PCZ	1	0.661	
BOS + EPI + PTC + DIF + CYM + TEB	1	0.164	
7 residues	*2*		
BOS + EPI + AZO + DIM + TER + LIN + PTC	1	0.434	
DDD op + DDD pp + DDE pp + DDE op + DDT op + DIE + TEB	1	0.189	
8 residues	*3*		
AMPA + BOS + DDE pp + EPI + DDT pp + DDD op + AZO + LIN	1	0.380	
AMPA + GLY + BOS + DDE pp + PTI + EPI + DDT pp + AZO	1	0.739	*
BOS + DDE pp + EPI + DDT pp + DDD op + MTM + FEN + DIF	1	0.150	
9 residues	*2*		
BOS + EPI + DDE pp + DDT pp + DDD op + AZO + DIM + LIN + DIF	1	0.637	
BOS + EPI + DDE pp + DDT pp + DDD op + DDD pp + AZO + IMI + LIN	1	0.353	
10 residues	1		
AMPA + BOS + EPI + DDD op + DDE pp + DDT pp + AZO + IMI + LIN + PTC	1	0.536	
WEST EU			
0 residues	*16*		
1 residue	*24*		
AMPA	9	0.070-0.232	
DDE pp	3	0.005-0.011	
PTI	3		*
BOS	2	0.015-0.032	
EPI	2	0.010-0.018	
ATR	1	0.011	
CYM	1	0.013	
DIE	1	0.011	
ENDα	1	0.006	
IMI	1	0.022	
2 residues	*12*		
AMPA + PTI	4	0.063-0.132	*
AMPA+ BOS	1	0.123	
BOS + IMI	1	0.052	
BOS + MET	1	0.051	
BOS + PTC	1	0.050	
DDE pp + EPI	1	0.042	
EPI + TEB	1	0.033	
GLY + BOS	1	0.093	
GLY + CYM	1	0.074	
3 residues	*9*		
AMPA + CARh + EPI	1	0.209	
AMPA + GLY + FOL	1	0.285	
AMPA + GLY + PTC	1	0.315	
AMPA + GLY + PTI	1	0.113	*
AZO + LIN + EPI	1	0.078	
BOS + IMI + TRI	1	0.160	
CARh + CHL + MTM	1	0.085	
EPI + GLY + IMI	1	0.079	
EPI + GLY + IMI	1	0.207	

Table S2.10 (cont.) - Pesticide composition of the EU agricultural topsoil samples by EU region. For individual pesticide abbreviations please see *Table S2.8*. N–number of soil samples presenting the respective pesticide combination; Range–minimum-maximum mixture content; * PTI (phthalimide) was considered in the number of residues present in the soil but not in the total pesticide content.

Number of pesticide residues in soil ≥LOQ	N	Range (mg/kg)	
4 residues	*5*		
AMPA + BOS + EPI + DIE	1	0.336	
AMPA + BOS + GLY + LIN	1	0.388	
BOS + EPI + AZO + DIM	1	0.313	
BOS + EPI + TEB + DIE	1	0.079	
DDE pp + DDD op + DDT pp + LIN	1	0.327	
5 residues	*11*		
AMPA + GLY + BOS + EPI + FOL	2	0.297-0.514	
AMPA + BOS + PCZ + QUI + PTC	1	0.357	
AMPA + EPI + TEB + CYP + PPC	1	0.618	
AMPA + GLY + BOS + MET + IMI	1	0.773	
AMPA + GLY + DDE pp + FOL + PTI	1	1.070	*
AMPA + GLY + PTI + FOL + PTC	1	0.255	*
AMPA + GLY + PTI + TEB + QUI	1	0.365	*
BOS + EPI + DDE pp + TEB + PTC	1	0.128	
BOS + EPI + IMI + LIN + PTC	1	0.181	
BOS + TEB + PTI + CYM + MET	1	0.508	*
6 residues	*3*		
AMPA + BOS + DDT pp + DDE pp + DDD op + DDD pp	1	0.533	
AMPA + BOS + PCZ + IMI + TEB + DIE	1	0.180	
AMPA + GLY + BOS + DDE pp + DDD op + DIE	1	0.450	
7 residues	*6*		
AMPA + BOS + CARh + AZO + MTM + LIN + PCP	1	0.214	
AMPA + GLY + BOS + CYP + DIM + MYC + QUI	1	0.577	
AMPA + GLY + BOS + DDT pp + DIE + MET + IMI	1	0.348	
AMPA + GLY + BOS + EPI + DIE + FOL + IMI	1	0.975	
AMPA + GLY + TEB + EPI + AZO + PPC + FEN	1	1.054	
AMPA + GLY + TEB + PCL + DIF + FOL + CYP	1	0.805	
9 residues	*3*		
AMPA + BOS + EPI + DDT pp + DIE + TEB + MTM + PCP + PTC	1	0.362	
AMPA + GLY + BOS + DDE pp + FOL + MYC + QUI + TEB + DIF	1	0.529	
AMPA + GLY + BOS + EPI + DDD op + DDE pp + DDT pp + DDD pp + DIE	1	1.748	
13 residues	*1*		
AMPA + EPI + DDE pp + TEB + DDD op + DDD pp + DDT pp + DIE + HCB + CARh + PPC + IMI + MTM	1	0.486	

Table S2.11 - Pesticide composition of the EU agricultural topsoil samples by country. For individual pesticide abbreviations please see *Table S2.8*. N–number of soil samples presenting the respective pesticide combination; Range–minimum-maximum mixture content; * PTI (phthalimide) was considered in the number of residues present in the soil but not in the total pesticide content.

Number of pesticide residues in soil ≥LOQ	N	Range (mg/kg)	
UNITED KINGDOM			
0 residues	*5*		
1 residue	*5*		
AMPA	3	0.065-0.067	
EPI	1	0.011	
PTI	1		*
2 residues	*3*		
AMPA + GLY	1	0.493	
EPI + FEN	1	0.067	
PTC + PTI	1	0.050	*
3 residues	*1*		
BOS + PTI + TEB	1	0.073	*
4 residues	*4*		
AMPA + BOS + EPI + ISO	1	0.181	
AMPA + BOS + EPI + PTC	1	0.323	
AMPA + BOS + EPI +TEB	1	0.146	
EPI + TEB + MTM + PCL	1	0.085	
5 residues	*3*		
AMPA + BOS + EPI + DIM + LIN	1	0.184	
AMPA + GLY + DDE pp + DDT pp + DDD pp	1	0.427	
AMPA + GLY + BOS + EPI + AZO	1	0.739	
6 residues	*4*		
AMPA + GLY + BOS + TEB + EPI + DIF	1	0.782	
AMPA + GLY + BOS + TEB + EPI + ISO	1	0.800	
AMPA + GLY + DDE pp + PTI + DDT pp + PTC	1	0.534	*
BOS + EPI + PTC + DIF + AZO + LIN	1	0.154	
8 residues	*1*		
AMPA + DDE pp + EPI + DDT pp + DDD pp + ISO + LIN + PCP	1	0.189	
9 residues	*2*		
AMPA + BOS + EPI + AZO + IMI + TEB + ISO + FEN + PCP	1	0.407	
AMPA + GLY + EPI + DIF + AZO+ PYR + TEB + MTM + LIN	1	0.859	
10 residues	*1*		
AMPA + BOS + EPI + DDD op + DDD pp + DDE pp + DDT pp + PTI + AZO + LIN	1	0.221	*
11 residues	*1*		
AMPA + GLY + EPI + DDE pp + DDD op + DDD pp + DDT pp + DIE + MTM + PCP + PTC	1	0.921	
DENMARK			
0 residues	*1*		
1 residue	*6*		
AMPA	3	0.062-0.166	
BOS	1	0.037	
FOL	1	0.009	
GLY	1	0.062	

Table S2.11 (cont.) - Pesticide composition of the EU agricultural topsoil samples by country. For individual pesticide abbreviations please see *Table S2.8*. N–number of soil samples presenting the respective pesticide combination; Range–minimum-maximum mixture content; * PTI (phthalimide) was considered in the number of residues present in the soil but not in the total pesticide content.

Number of pesticide residues in soil ≥LOQ	N	Range (mg/kg)	
2 residues	*8*		
AMPA + DDE pp	2	0.120-0.168	
AMPA+ BOS	2	0.132-0.560	
AMPA + FOL	1	0.086	
AMPA + PTI	1	0.053	*
BOS + PTI	1	0.019	*
DDE pp + PTI	1	0.016	*
3 residues	*9*		
AMPA + DDE pp + FOL	2	0.262-0.645	
AMPA + BOS + DDE pp	1	0.264	
AMPA + BOS + FOL	1	0.079	
AMPA + DDE pp + PTI	1	0.224	*
AMPA + GLY + DDE pp	1	0.349	
AMPA + GLY + PTC	1	0.333	
AMPA + GLY + PTI	1	0.279	*
AMPA + IMI + MTM	1	0.181	
4 residues	*1*		
AMPA + BOS + EPI + DDE pp	1	0.247	
5 residues	*4*		
AMPA + BOS + PTI + EPI + IMI	1	0.201	*
AMPA + GLY + BOS + EPI + PTI	1	0.512	*
AMPA + GLY + DDE pp + FOL + PTI	1	0.525	*
AMPA + GLY + PTI + TEB + AZO	1	0.261	*
8 residues	*1*		
AMPA + GLY + BOS + DDE pp + PTI + EPI + TEB + PPC	1	1.296	*
ITALY			
0 residues	*14*		
1 residue	*8*		
GLY	2	0.120-0.175	
PTC	2	0.027-0.138	
AMPA	1	0.103	
BOS	1	0.023	
DDE pp	1	0.016	
DIM	1	0.048	
2 residues	*3*		
DDE pp + CARh	1	0.017	
GLY + DDE pp	1	0.142	
PTC + DIM	1	0.057	
3 residues	*4*		
AMPA + BOS + DIM	1	0.328	
AMPA + DDE pp + IMI	1	0.083	
AMPA + GLY + BOS	1	0.192	
CYM + MYC + QUI	1	0.192	
6 residues	*1*		
AMPA + GLY + CHL + MYC + PCZ + DIF	1	1.843	

Table S2.11 (cont.) - Pesticide composition of the EU agricultural topsoil samples by country. For individual pesticide abbreviations please see *Table S2.8*. N–number of soil samples presenting the respective pesticide combination; Range–minimum-maximum mixture content; * PTI (phthalimide) was considered in the number of residues present in the soil but not in the total pesticide content.

Number of pesticide residues in soil ≥LOQ	N	Range (m/ kg)	
GREECE			
0 residues	*6*		
1 residue	*9*		
FOL	3	0.009-0.013	
PTI	3		*
DDE pp	2	0.008-0.056	
PTC	1	0.012	
2 residues	*8*		
FOL + PTI	3	0.006-0.011	*
BOS + PTC	1	0.034	
CHL + DIM	1	0.091	
DDE pp + CARh	1	0.068	
DDE pp + FOL	1	0.012	
DDE pp + PTI	1	0.041	*
3 residues	*1*		
BOS + IMI + CYP	1	0.204	
4 residues	*2*		
AMPA + BOS + TEB + IMI	1	0.215	
BOS + EPI + TEB + PYR	1	0.305	
5 residues	*1*		
AMPA + GLY + TEB + DDE pp + MYC	1	0.803	
6 residues	*1*		
AMPA + GLY + DDE pp + PTI + FOL + IMI	1	1.003	*
7 residues	*2*		
AMPA + BOS + DDE pp + CHD + DIE + ENDα + HPT + IMI	1	0.346	
AMPA + GLY + BOS + DDE pp + TEB + CYP + DIM + DIF	1	1.061	
SPAIN			
0 residues	*6*		
1 residue	*4*		
AMPA	2	0.083-0.092	
DDE pp	1	0.006	
TER	1	0.012	
2 residues	*7*		
AMPA + GLY	3	0.169-0.702	
AMPA + TEB	1	0.086	
CHL + MTM	1	0.138	
DDE pp + EPI	1	0.022	
GLY + EPI	1	0.233	
3 residues	*3*		
AMPA + GLY + DDE pp	1	0.838	
AZO + LIN + EPI	1	0.079	
DDE pp + MTM + EPI	1	0.226	
4 residues	*4*		
AMPA + GLY + DIM + TER	1	0.350	
BOS + EPI + TEB + CARh	1	0.080	
DDE pp + DDD op + DDT pp + AMPA	1	0.167	
DDE pp + EPI + DIE + MTM	1	0.107	

Table S2.11 (cont.) - Pesticide composition of the EU agricultural topsoil samples by country. For individual pesticide abbreviations please see *Table S2.8*. N–number of soil samples presenting the respective pesticide combination; Range–minimum-maximum mixture content; * PTI (phthalimide) was considered in the number of residues present in the soil but not in the total pesticide content.

Number of pesticide residues in soil ≥LOQ	N	Range (mg/kg)	
5 residues	*5*		
AMPA + BOS + EPI + TEB + PCL	1	0.411	
AMPA + GLY + BOS + EPI + PTC	1	1.107	
BOS + EPI + TEB + PPC + PCP	1	0.145	
EPI + DDD op + DDD pp + DDE pp + DDT pp	1	0.149	
EPI + TEB + AZO + PPC + FEN	1	0.286	
7 residues	*1*		
BOS + EPI + AZO + PPC + IMI + TEB + MTM	1	0.338	
PORTUGAL			
0 residues	*2*		
1 residue	*6*		
PTI	5		*
AMPA	1	0.728	
2 residues	*4*		
AMPA + GLY	3	0.842-2.561	
GLY + PTI	1	1.136	*
3 residues	*5*		
AMPA + GLY + PTI	5	1.531-2.868	*
HUNGARY			
0 residues	*4*		
1 residue	*11*		
PTI	5		*
TER	4	0.012-0.021	
EPI	1	0.017	
TEB	1	0.018	
2 residues	*6*		
DDE pp + PTI	3	0.005-0.025	*
DDE pp + DDD op	1	0.052	
EPI + PTI	1	0.013	*
PTC + TER	1	0.110	
3 residues	*5*		
AMPA + GLY + DDD op	2	0.314-1.319	
AMPA + BOS + DDD op	1	0.079	
AMPA + GLY + TEB	1	0.199	
DDE pp + DIE + PTI	1	0.080	*
6 residues	*3*		
AMPA + DDE pp + PTI + PPC + TEB + PCL	1	0.330	*
AMPA + GLY + BOS + TEB + CYP + PCZ	1	0.661	
BOS + EPI + PTC + DIF + CYM + TEB	1	0.164	
7 residues	*1*		
DDD op + DDD pp + DDE pp + DDE op + DDT op + DIE + TEB	1	0.189	
POLAND			
0 residues			
1 residue	*5*		
AMPA	2	0.142-0.145	
EPI	2	0.012-0.019	
DDE pp	1	0.005	
2 residues	*2*		
AMPA + EPI	1	0.079	
BOS + EPI	1	0.042	

Table S2.11 (cont.) - Pesticide composition of the EU agricultural topsoil samples by country. For individual pesticide abbreviations please see *Table S2.8*. N–number of soil samples presenting the respective pesticide combination; Range–minimum-maximum mixture content; * PTI (phthalimide) was considered in the number of residues present in the soil but not in the total pesticide content.

Number of pesticide residues in soil ≥LOQ	N	Range (mg/kg)	
3 residues	*4*		
AMPA + DDE pp + DIM	1	0.199	
AMPA + DDE pp + PCM	1	0.164	
AZO + IMI + LIN	1	0.487	
DDE pp + DDT pp + DDD op	1	0.024	
4 residues	*7*		
AMPA + BOS + EPI + AZO	1	0.233	
AMPA + BOS + EPI + DDE pp	1	0.099	
AMPA + BOS + GLY + DDE pp	1	0.389	
BOS + EPI + DIF + LIN	1	0.407	
DDE pp + BOS + DDD op + IMI	1	0.099	
DDE pp + BOS + EPI + LIN	1	0.122	
DDE pp + BOS + TEB + PCL	1	0.290	
5 residues	*2*		
BOS + EPI + DDE pp + DDT pp + DDD op	1	0.105	
BOS + EPI + CARh + MTM + FEN	1	0.105	
6 residues	*3*		
AMPA + BOS + AZO + MTM + LIN + PCP	1	0.213	
AMPA + BOS + DDT pp + DDE pp + DDD op + EPI	1	0.376	
AMPA + BOS + DDT pp + EPI + FEN + LIN	1	0.207	
7 residues	*1*		
BOS + EPI + AZO + DIM + TER + LIN + PTC	1	0.434	
8 residues	*3*		
AMPA + BOS + DDE pp + EPI + DDT pp + DDD op + AZO + LIN	1	0.380	
AMPA + GLY + BOS + DDE pp + PTI + EPI + DDT pp + AZO	1	0.739	*
BOS + DDE pp + EPI + DDT pp + DDD op + MTM + FEN + DIF	1	0.150	
9 residues	*2*		
BOS + EPI + DDE pp + DDT pp + DDD op + AZO + DIM + LIN + DIF	1	0.637	
BOS + EPI + DDE pp + DDT pp + DDD op + DDD pp + AZO + IMI + LIN	1	0.353	
10 residues	*1*		
AMPA + BOS + EPI + DDD op + DDE pp + DDT pp + AZO + IMI + LIN + PTC	1	0.536	
THE NETHERLANDS			
0 residues	*3*		
1 residue	*5*		
AMPA	1	0.077	
ATR	1	0.011	
DIE	1	0.011	
ENDα	1	0.006	
IMI	1	0.022	
2 residues	*3*		
AMPA + BOS	1	0.123	
BOS + MET	1	0.051	
BOS + PTC	1	0.050	
3 residues	*6*		
AMPA + GLY + PTC	1	0.315	
AZO + LIN + EPI	1	0.078	
BOS + IMI + TRI	1	0.160	
CARh + CHL + MTM	1	0.085	
EPI + GLY + IMI	1	0.079	
EPI + TEB + MTM	1	0.207	

Table S2.11 (cont.) - Pesticide composition of the EU agricultural topsoil samples by country. For individual pesticide abbreviations please see *Table S2.8*. N–number of soil samples presenting the respective pesticide combination; Range–minimum-maximum mixture content; * PTI (phthalimide) was considered in the number of residues present in the soil but not in the total pesticide content.

Number of pesticide residues in soil ≥LOQ	N	Range (mg/kg)	
4 residues	*4*		
AMPA + BOS + GLY + LIN	1	0.388	
BOS + EPI + AZO + DIM	1	0.313	
BOS + EPI + TEB + DIE	1	0.079	
DDE pp + DDD op + DDT pp + LIN	1	0.327	
5 residues	*2*		
AMPA + GLY + BOS + MET + IMI	1	0.773	
BOS + EPI + IMI + LIN + PTC	1	0.181	
6 residues	*1*		
AMPA + BOS + PCZ + IMI + TEB + DIE	1	0.180	
7 residues	*3*		
AMPA + BOS + CARh + AZO + MTM + LIN + PCP	1	0.214	
AMPA + GLY + BOS + DDT pp + DIE + MET + IMI	1	0.348	
AMPA + GLY + TEB + EPI + AZO + PPC + FEN	1	1.054	
9 residues	*2*		
AMPA + BOS + EPI + DDT pp + DIE + TEB + MTM + PCP + PTC	1	0.362	
AMPA + GLY + BOS + EPI + DDD op + DDE pp + DDT pp + DDD pp + DIE	1	1.748	
13 residues	*1*		
AMPA + EPI + DDE pp + TEB + DDD op + DDD pp + DDT pp + DIE + HCB + CARh + PPC + IMI + MTM	1	0.486	
FRANCE			
0 residues	*6*		
1 residue	*9*		
AMPA	3	0.085-0.232	
PTI	3		*
DDE pp	2	0.007-0.011	
CYM	1	0.013	
2 residues	*6*		
AMPA + PTI	4	0.063-0.132	*
BOS + IMI	1	0.052	
GLY + CYM	1	0.074	
3 residues	*2*		
AMPA + GLY + FOL	1	0.285	
AMPA + GLY + PTI	1	0.113	*
5 residues	*5*		
AMPA + GLY + BOS + EPI + FOL	1	0.297	
AMPA + GLY + DDE pp + FOL + PTI	1	1.070	*
AMPA + GLY + PTI + FOL + PTC	1	0.255	*
AMPA + GLY + PTI + TEB + QUI	1	0.365	*
BOS + TEB + PTI + CYM + MET	1	0.508	*
6 residues	*1*		
AMPA + GLY + BOS + DDE pp + DDD op + DIE	1	0.450	
7 residues	*1*		
AMPA + GLY + BOS + EPI + DIE + FOL + IMI	1	0.975	

Table S2.11 (cont.) - Pesticide composition of the EU agricultural topsoil samples by country. For individual pesticide abbreviations please see *Table S2.8*. N–number of soil samples presenting the respective pesticide combination; Range–minimum-maximum mixture content; * PTI (phthalimide) was considered in the number of residues present in the soil but not in the total pesticide content.

Number of pesticide residues in soil ≥LOQ	N	Range (mg/kg)
GERMANY		
0 residues	*7*	
1 residue	*10*	
AMPA	5	0.070-0.135
BOS	2	0.015-0.032
EPI	2	0.010-0.018
DDE pp	1	0.005
2 residues	*3*	
DDE pp + EPI	1	0.042
EPI + TEB	1	0.033
GLY + BOS	1	0.093
3 residues	*1*	
AMPA + CARh + EPI	1	0.209
4 residues	*1*	
AMPA + BOS + EPI + DIE	1	0.336
5 residues	*4*	
AMPA + BOS + PCZ + QUI + PTC	1	0.357
AMPA + EPI + TEB + CYP + PPC	1	0.618
AMPA + GLY + BOS + EPI + FOL	1	0.514
BOS + EPI + DDE pp + TEB + PTC	1	0.128
6 residues	*1*	
AMPA + BOS + DDT pp + DDE pp + DDD op + DDD pp	1	0.533
7 residues	*2*	
AMPA + GLY + BOS + CYP + DIM + MYC + QUI	1	0.577
AMPA + GLY + TEB + PCL + DIF + FOL + CYP	1	0.805
9 residues	*1*	
AMPA + GLY + BOS + DDE pp + FOL + MYC + QUI + TEB + DIF	1	0.529

Table S2.12 - Pesticide composition of the EU agricultural topsoil samples by cropping system. For individual pesticide abbreviations please see *Table S2.8*. N–number of soil samples presenting the respective pesticide combination; Range–minimum-maximum mixture content; * PTI (phthalimide) was considered in the number of residues present in the soil but not in the total pesticide content.

Number of pesticide residues in soil ≥LOQ	N	Range (mg /kg)	
CEREALS			
0 residues	*18*		
1 residue	*29*		
AMPA	7	0.062-0.143	
PTI	6		*
FOL	3	0.009-0.012	
TER	3	0.012-0.018	
DDE pp	2	0.005-0.005	
EPI	2	0.017-0.018	
PTC	2	0.027-0.138	
BOS	1	0.037	
DIE	1	0.011	
GLY	1	0.062	
TEB	1	0.018	
2 residues	*20*		
DDE pp + PTI	4	0.005-0.025	*
AMPA + DDE pp	1	0.120	
AMPA + EPI	1	0.079	
AMPA + GLY	1	0.493	
AMPA + PTI	1	0.053	*
AMPA + TEB	1	0.086	
AMPA+ BOS	1	0.132	
BOS + PTI	1	0.019	*
CHL + MTM	1	0.138	
DDE pp + CARh	1	0.017	
DDE pp + DDD op	1	0.052	
DDE pp + EPI	1	0.042	
EPI + PTI	1	0.013	*
EPI + TEB	1	0.033	
GLY + EPI	1	0.233	
PTC + PTI	1	0.050	*
PTC + TER	1	0.110	
3 residues	*15*		
AMPA + DDE pp + FOL	2	0.262-0.645	
AMPA + BOS + DDE pp	1	0.264	
AMPA + BOS + FOL	1	0.079	
AMPA + CARh + EPI	1	0.209	
AMPA + DDE pp + DIM	1	0.199	
AMPA + GLY + BOS	1	0.192	
AMPA + GLY + DDE pp	1	0.838	
AMPA + GLY + FOL	1	0.285	
AMPA + GLY + PTC	1	0.333	
AMPA + GLY + PTI	1	0.279	*
AMPA + GLY + TEB	1	0.199	
AZO + LIN + EPI	1	0.079	
DDE pp + DDT pp + DDD op	1	0.024	
DDE pp + DIE + PTI	1	0.080	*

Table S2.12 - Pesticide composition of the EU agricultural topsoil samples by cropping system. For individual pesticide abbreviations please see *Table S2.8*. N–number of soil samples presenting the respective pesticide combination; Range–minimum-maximum mixture content; * PTI (phthalimide) was considered in the number of residues present in the soil but not in the total pesticide content.

Number of pesticide residues in soil ≥LOQ	N	Range (mg/kg)	
4 residues	*9*		
AMPA + BOS + EPI + DDE pp	2	0.099-0.247	
AMPA + BOS + EPI + AZO	1	0.233	
AMPA + BOS + EPI + ISO	1	0.181	
BOS + EPI + TEB + CARh	1	0.080	
DDE pp + BOS + DDD op + IMI	1	0.099	
DDE pp + BOS + EPI + LIN	1	0.122	
DDE pp + DDD op + DDT pp + LIN	1	0.327	
EPI + TEB + MTM + PCL	1	0.085	
5 residues	*10*		
AMPA + BOS + PTI + EPI + IMI	1	0.201	*
AMPA + EPI + TEB + CYP + PPC	1	0.618	
AMPA + GLY + DDE pp + DDT pp + DDD pp	1	0.427	
AMPA + GLY + BOS + EPI + FOL	1	0.514	
AMPA + GLY + DDE pp + FOL + PTI	1	0.525	*
AMPA + GLY + PTI + FOL + PTC	1	0.255	*
AMPA + GLY + PTI + TEB + AZO	1	0.261	*
BOS + EPI + DDE pp + TEB + PTC	1	0.128	
EPI + DDD op + DDD pp + DDE pp + DDT pp	1	0.149	
EPI + TEB + AZO + PPC + FEN	1	0.286	
6 residues	*3*		
AMPA + BOS + AZO + MTM + LIN + PCP	1	0.213	
AMPA + BOS + DDT pp + DDE pp + DDD op + EPI	1	0.376	
AMPA + DDE pp + PTI + PPC + TEB + PCL	1	0.330	*
7 residues	*3*		
AMPA + GLY + TEB + EPI + AZO + PPC + FEN	1	1.054	
AMPA + GLY + TEB + PCL + DIF + FOL + CYP	1	0.805	
BOS + EPI + AZO + DIM + TER + LIN + PTC	1	0.434	
8 residues	*1*		
AMPA + GLY + BOS + DDE pp + PTI + EPI + TEB + PPC	1	1.296	*
9 residues	*2*		
AMPA + BOS + EPI + AZO + IMI + TEB + ISO + FEN + PCP	1	0.407	
AMPA + GLY + EPI + DIF + AZO+ PYR + TEB + MTM + LIN	1	0.859	
10 residues	*2*		
AMPA + BOS + EPI + DDD op + DDD pp + DDE pp + DDT pp + PTI + AZO + LIN	1	0.221	*
AMPA + BOS + EPI + DDD op + DDE pp + DDT pp + AZO + IMI + LIN + PTC	1	0.536	
PERMANENT CROPS			
0 residues	*22*		
1 residue	*23*		
DDE pp	6	0.006-0.056	
PTI	6		*
AMPA	3	0.092-0.728	
BOS	2	0.023-0.032	
GLY	2	0.120-0.175	
CYM	1	0.013	
DIM	1	0.048	
EPI	1	0.019	
PTC	1	0.012	

Table S2.12 - Pesticide composition of the EU agricultural topsoil samples by cropping system. For individual pesticide abbreviations please see *Table S2.8*. N–number of soil samples presenting the respective pesticide combination; Range–minimum-maximum mixture content; * PTI (phthalimide) was considered in the number of residues present in the soil but not in the total pesticide content.

Number of pesticide residues in soil ≥LOQ	N	Range (mg/kg)	
2 residues	*20*		
AMPA + GLY	5	0.169-2.561	
AMPA + PTI	4	0.063-0.132	*
FOL + PTI	3	0.006-0.011	*
BOS + PTC	1	0.034	
DDE pp + CARh	1	0.068	
DDE pp + FOL	1	0.012	
DDE pp + PTI	1	0.041	*
GLY + BOS	1	0.093	
GLY + DDE pp	1	0.142	
GLY + PTI	1	1.136	*
PTC + DIM	1	0.057	
3 residues	*12*		
AMPA + GLY + PTI	5	1.531-2.868	*
AMPA + BOS + DDD op	1	0.079	
AMPA + BOS + DIM	1	0.328	
AMPA + DDE pp + IMI	1	0.083	
AMPA + DDE pp + PCM	1	0.164	
AMPA + GLY + DDD op	1	1.319	
BOS + IMI + CYP	1	0.204	
CYM + MYC + QUI	1	0.192	
4 residues	*5*		
AMPA + BOS + TEB + IMI	1	0.215	
AMPA + BOS + GLY + DDE pp	1	0.389	
AMPA + GLY + DIM + TER	1	0.350	
BOS + EPI + DIF + LIN	1	0.407	
DDE pp + EPI + DIE + MTM	1	0.107	
5 residues	*6*		
AMPA + BOS + EPI + TEB + PCL	1	0.411	
AMPA + GLY + BOS + EPI + FOL	1	0.297	
AMPA + GLY + DDE pp + FOL + PTI	1	1.070	*
AMPA + GLY + PTI + TEB + QUI	1	0.365	*
AMPA + GLY + TEB + DDE pp + MYC	1	0.803	
BOS + TEB + PTI + CYM + MET	1	0.508	*
6 residues	*6*		
AMPA + BOS + DDT pp + DDE pp + DDD op + DDD pp	1	0.533	
AMPA + GLY + BOS + TEB + CYP + PCZ	1	0.661	
AMPA + GLY + BOS + TEB + EPI + DIF	1	0.782	
AMPA + GLY + BOS + DDE pp + DDD op + DIE	1	0.450	
AMPA + GLY + CHL + MYC + PCZ + DIF	1	1.843	
AMPA + GLY + DDE pp + PTI + FOL + IMI	1	1.003	*
7 residues	*1*		
AMPA + GLY + BOS + CYP + DIM + MYC + QUI	1	0.577	
8 residues	*4*		
AMPA + BOS + DDE pp + CHD + DIE + ENDα + HPT + IMI	1	0.346	
AMPA + BOS + DDE pp + EPI + DDT pp + DDD op + AZO + LIN	1	0.380	
AMPA + GLY + BOS + DDE pp + TEB + CYP + DIM + DIF	1	1.061	
BOS + DDE pp + EPI + DDT pp + DDD op + MTM + FEN + DIF	1	0.150	
9 residues	*2*		
AMPA + GLY + BOS + DDE pp + FOL + MYC + QUI + TEB + DIF	1	0.529	
BOS + EPI + DDE pp + DDT pp + DDD op + DDD pp + AZO + IMI + LIN	1	0.353	

Table S2.12 - Pesticide composition of the EU agricultural topsoil samples by cropping system. For individual pesticide abbreviations please see *Table S2.8*. N–number of soil samples presenting the respective pesticide combination; Range–minimum-maximum mixture content; * PTI (phthalimide) was considered in the number of residues present in the soil but not in the total pesticide content.

Number of pesticide residues in soil ≥LOQ	N	Range (mg/kg)	
ROOT CROPS			
1 residue	*4*		
AMPA	1	0.103	
EPI	1	0.011	
IMI	1	0.022	
TER	1	0.020	
2 residues	*3*		
AMPA + GLY	1	0.702	
BOS + EPI	1	0.042	
BOS + PTC	1	0.050	
3 residues	*5*		
AMPA + GLY + DDE pp	1	0.349	
AMPA + IMI + MTM	1	0.181	
AZO + IMI + LIN	1	0.487	
BOS + IMI + TRI	1	0.160	
CARh + CHL + MTM	1	0.085	
4 residues	*4*		
AMPA + BOS + EPI +TEB	1	0.146	
BOS + EPI + AZO + DIM	1	0.313	
BOS + EPI + TEB + DIE	1	0.079	
BOS + EPI + TEB + PYR	1	0.305	
5 residues	*2*		
AMPA + GLY + BOS + MET + IMI	1	0.773	
BOS + EPI + IMI + LIN + PTC	1	0.181	
6 residues	*2*		
AMPA + BOS + DDT pp + EPI + FEN + LIN	1	0.207	
AMPA + BOS + PCZ + IMI + TEB + DIE	1	0.180	
7 residues	*2*		
AMPA + BOS + CARh + AZO + MTM + LIN + PCP	1	0.214	
AMPA + GLY + BOS + DDT pp + DIE + MET + IMI	1	0.348	
8 residues	*1*		
AMPA + GLY + BOS + DDE pp + PTI + EPI + DDT pp + AZO	1	0.739	*
9 residues	*3*		
AMPA + BOS + EPI + DDT pp + DIE + TEB + MTM + PCP + PTC	1	0.362	
AMPA + GLY + BOS + EPI + DDD op + DDE pp + DDT pp + DDD pp + DIE	1	1.748	
BOS + EPI + DDE pp + DDT pp + DDD op + AZO + DIM + LIN + DIF	1	0.637	
13 residues	*1*		
AMPA + EPI + DDE pp + TEB + DDD op + DDD pp + DDT pp + DIE + HCB + CARh + PPC + IMI + MTM	1	0.486	
NON-PERMANENT INDUSTRIAL CROPS			
0 residues	*4*		
1 residue	*5*		
AMPA	2	0.135-0.232	
FOL	1	0.013	
PTI	1		*
TER	1	0.021	
2 residues	*2*		
AMPA + BOS	1	0.560	
BOS + IMI	1	0.052	

Table S2.12 - Pesticide composition of the EU agricultural topsoil samples by cropping system. For individual pesticide abbreviations please see *Table S2.8*. N–number of soil samples presenting the respective pesticide combination; Range–minimum-maximum mixture content; * PTI (phthalimide) was considered in the number of residues present in the soil but not in the total pesticide content.

Number of pesticide residues in soil ≥LOQ	N	Range (mg/kg)	
3 residues	*3*		
AMPA + DDE pp + PTI	1	0.224	*
AMPA + GLY + PTI	1	0.113	*
BOS + PTI + TEB	1	0.073	*
4 residues	*4*		
AMPA + BOS + EPI + DIE	1	0.336	
AMPA + BOS + EPI + PTC	1	0.323	
AMPA + BOS + GLY + LIN	1	0.388	
DDE pp + BOS + TEB + PCL	1	0.290	
5 residues	*3*		
AMPA + GLY + BOS + EPI + AZO	1	0.739	
AMPA + GLY + BOS + EPI + PTI	1	0.512	*
BOS + EPI + CARh + MTM + FEN	1	0.105	
6 residues	*1*		
BOS + EPI + PTC + DIF + CYM + TEB	1	0.164	
11 residues	*1*		
AMPA + GLY + EPI + DDE pp + DDD op + DDD pp + DDT pp + DIE + MTM + PCP + PTC	1	0.921	
DRY PULSES & FODDER CROPS			
0 residues	*6*		
1 residue	*8*		
AMPA	3	0.093-0.166	
EPI	2	0.010-0.012	
ATR	1	0.011	
ENDα	1	0.006	
PTI	1		*
2 residues	*3*		
AMPA + DDE pp	1	0.168	
AMPA + FOL	1	0.086	
GLY + CYM	1	0.074	
3 residues	*1*		
AZO + LIN + EPI	1	0.078	
5 residues	*2*		
AMPA + BOS + PCZ + QUI + PTC	1	0.357	
BOS + EPI + DDE pp + DDT pp + DDD op	1	0.105	
6 residues	*1*		
BOS + EPI + PTC + DIF + AZO + LIN	1	0.154	
VEGETABLES			
0 residues	*1*		
1 residue	*1*		
BOS	1	0.015	
2 residues	*1*		
EPI + FEN	1	0.067	
3 residues	*3*		
AMPA + GLY + PTC	1	0.315	
DDE pp + MTM + EPI	1	0.226	
EPI + TEB + MTM	1	0.207	
5 residues	*1*		
BOS + EPI + TEB + PPC + PCP	1	0.145	
6 residues	*1*		
AMPA + GLY + DDE pp + PTI + DDT pp + PTC	1	0.534	*
8 residues	*1*		
AMPA + DDE pp + EPI + DDT pp + DDD pp + ISO + LIN + PCP	1	0.189	

Table S2.12 - Pesticide composition of the EU agricultural topsoil samples by cropping system. For individual pesticide abbreviations please see *Table S2.8*. N–number of soil samples presenting the respective pesticide combination; Range–minimum-maximum mixture content; * PTI (phthalimide) was considered in the number of residues present in the soil but not in the total pesticide content.

Number of pesticide residues in soil ≥LOQ	N	Range (mg/kg)
OTHERS		
0 residues	*3*	
1 residue	*8*	
AMPA	5	0.065-0.145
PTI	3	*
2 residues	*4*	
AMPA+ BOS	1	0.123
BOS + MET	1	0.051
CHL + DIM	1	0.091
DDE pp + EPI	1	0.022
3 residues	*2*	
AMPA + GLY + DDD op	1	0.314
EPI + GLY + IMI	1	0.079
4 residues	*1*	
DDE pp + DDD op + DDT pp + AMPA	1	0.167
5 residues	*2*	
AMPA + BOS + EPI + DIM + LIN	1	0.184
AMPA + GLY + BOS + EPI + PTC	1	1.107
6 residues	*1*	
AMPA + GLY + BOS + TEB + EPI + ISO	1	0.800
7 residues	*3*	
AMPA + GLY + BOS + EPI + DIE + FOL + IMI	1	0.975
BOS + EPI + AZO + PPC + IMI + TEB + MTM	1	0.338
DDD op + DDD pp + DDE pp + DDE op + DDT op + DIE + TEB	1	0.189

Table S2.13 - Spearman's correlation coefficients between soil properties and the content of the most common pesticide residues in soil. OC–organic carbon content; nq–number of topsoil samples where the pesticide residues were quantified. Significant correlations (*p* <0.05) are marked in grey cells. Epox. = Epoxiconazole.

	% clay	% silt	soil pH	OC	AMPA	Boscalid	Epox.	DDE pp	Glyphosate	Tebuconazole
AMPA	0.04	0.04	-0.02	-0.04	1	0.06	0.02	-0.09	0.53	0.34
nq	133	133	133	133		52	35	37	58	23
Boscalid	0.05	-0.09	0.14	0.17		1	0.38	0.31	-0.08	0.01
nq	87	87	87	87			46	24	22	22
Epox.	0.05	-0.14	-0.02	0.13			1	0.29	-0.35	-0.37
nq	75	75	75	75				23	15	22
DDE pp	-0.06	-0.34	0.11	0.14				1	-0.01	-0.58
nq	72	72	72	72					17	9
Glyphosate	0.26	0.25	0.28	-0.33					1	-0.12
nq	67	67	67	67						13
Tebuconazole	-0.09	-0.32	0.00	-0.09						1
nq	39	39	39	39						

Table S2.14 - Maximum recommended application rates and predicted concentrations (PECs) in soil of the 7 most common compounds in the European agricultural topsoils, by the main crop uses. The range of contents in European topsoils are also indicated. Compounds are presented in decreasing order of frequency in the current study. Information on DDTs (total DDE, DDD and DDT) and folpet, parent and related compounds of 2 of the 7 most common compounds, were added to the bottom of the table, and marked in grey. PECs accumulated–sum of the PEC initial and plateau in soil; as–active substance, NA–not applicable; nd–not detected. If the range of DDTs was not available in the studies, or if it could not be obtained from the available data, the range of the individual residues was presented. In the concentration range of this study, 317 samples were considered for all crops: 112 for cereals, 101 for permanent crops, 23 for non-permanent industrial crops and 9 for vegetables.

Compound	Dominant use	Growth stage	Number of applications (min–max)	Recommended application rate (kg as/ha)	PECs in soil (0–100 days) (mg/kg)	PECs accumulated in soil (annual crops; permanent crops) (mg/kg)	Source	Range in soil (min–max) (mg/kg)	Country	Source
AMPA (metabolite of glyphosate)	NA	NA	NA	NA; (1.53 ▼)	2.04–1.82	3.07; 6.18	EFSA, 2015a	nd–1.92	11 EU Member States	This study, Silva et al., 2018
								nd–0.30	Finland	Laitinen et al., 2006
								nd–0.09	Finland	Laitinen et al., 2009
								nd–<0.25	Germany	Grunewald et al., 2001
Boscalid	All crops	NA	NA	NA	NA	NA	EC, 2008	nd–0.41	11 EU Member States	This study
							EFSA, 2006	nd–0.03	Czech Republic	Hvězdová et al., 2018
								0.12–0.53	Germany	Karlsson et al., 2016
	Oilseed rape	30, 63-65	2	0.25	NA	NA		nd–0.18	11 EU Member States	This study
	Vines	68-81	1	0.60	0.11, 0.12, 0.42	– ; 0.28, 0.50, 0.55, 0.79, 0.91		nd–0.41	11 EU Member States	This study
	Vegetables	60-69	2	0.50	0.27, 0.37, 0.73	0.48, 0.64, 0.78, 0.90, 0.94;–		nd–0.05	11 EU Member States	This study
Epoxiconazole	All/other crops	NA	NA	NA	NA	NA	EFSA, 2006, 2008, 2015b	nd–0.16	11 EU Member States	This study
								nd–0.03	Czech Republic	Hvezdova et al., 2018
								nd–0.02	Switzerland	Chiaia-Hernandez et al., 2017
	Cereals	25-69	1–2	0.13	0.13-0.09	0.03-0.06		nd–0.16	11 EU Member States	This study
	Sugar beets	39-49	1–2	0.09-0.13	NA	NA		nd–0.08	11 EU Member States	This study
DDE pp (metabolite of DDT pp)	NA	NA	NA	NA	NA	NA		nd–0.31	11 EU Member States	This study
								nd–0.59	Italy	Qu et al., 2016
								<0.01–0.01	Russia	Iwata et al., 1995
								<0.01–0.60	Czech Republic	Holoubek et al., 2009

Table S2.14 (cont.) - Maximum recommended application rates and predicted concentrations (PECs) in soil of the 7 most common compounds in the European agricultural topsoils, by the main crop uses. The range of contents in European topsoils are also indicated. Compounds are presented in decreasing order of frequency in the current study. Information on DDTs (total DDE, DDD and DDT) and folpet, parent and related compounds of 2 of the 7 most common compounds, were added to the bottom of the table, and marked in grey. PECs accumulated–sum of the PEC initial and plateau in soil; as–active substance, NA–not applicable; nd–not detected. If the range of DDTs was not available in the studies, or if it could not be obtained from the available data, the range of the individual residues was presented. In the concentration range of this study, 317 samples were considered for all crops: 112 for cereals, 101 for permanent crops, 23 for non-permanent industrial crops and 9 for vegetables.

Compound	Dominant use	Growth stage	Number of applications (min–max)	Recommended application rate (kg as/ha)	PECs in soil (0–100 days) (mg/kg)	PECs accumulated in soil (annual crops; permanent crops) (mg/kg)	Source	Range in soil (min–max) (mg/kg)	Country	Source
DDE pp (metabolite of DDT pp)	NA	NA	NA	NA	NA	NA		nd–0.02	France	Villanneau et al., 2011
								nd–10.40	Serbia	Skrbic et al., 2007
								<0.01–0.22	Poland	Maliszewska-Kordybach et al., 2013
								<0.01–0.22	Poland	Maliszewska-Kordybach et al., 2014
								nd–0.21	Poland	Łozowicka et al., 2016
								nd–<0.01	Spain	Fernandez-Alvarez et al., 2008
								nd–0.02	Spain	Fernandez-Alvarez et al., 2010
								nd–0.15	Spain	Plaza-Bolanos et al., 2012
								nd–0.13	Spain	Padilla-Sánchez et al., 2015
								nd–4.40	Romania	Ene et al., 2012
								nd–0.05	Romania	Ferencz and Balog, 2010
								<0.01–0.03	Romania	Tarcau et al., 2013
								nd–0.02	Germany	Rodil and Popp, 2006
								<0.01–0.02	Greece	Chrysikou et al., 2008
								<0.01–0.02	Portugal	Goncalves and Alpendurada, 2005
								<0.01–0.01	Albania	Mukaj et al., 2016
								nd–0.29	Switzerland	Hilber et al., 2008

Table S2.14 (cont.) - Maximum recommended application rates and predicted concentrations (PECs) in soil of the 7 most common compounds in the European agricultural topsoils, by the main crop uses. The range of contents in European topsoils are also indicated. Compounds are presented in decreasing order of frequency in the current study. Information on DDTs (total DDE, DDD and DDT) and folpet, parent and related compounds of 2 of the 7 most common compounds, were added to the bottom of the table, and marked in grey. PECs accumulated–sum of the PEC initial and plateau in soil; as–active substance, NA–not applicable; nd–not detected. If the range of DDTs was not available in the studies, or if it could not be obtained from the available data, the range of the individual residues was presented. In the concentration range of this study, 317 samples were considered for all crops: 112 for cereals, 101 for permanent crops, 23 for non-permanent industrial crops and 9 for vegetables.

Compound	Dominant use	Growth stage	Number of applications (min–max)	Recommended application rate (kg as/ha)	PECs in soil (0–100 days) (mg/kg)	PECs accumulated in soil (annual crops; permanent crops) (mg/kg)	Source	Range in soil (min–max) (mg/kg)	Country	Source
Glyphosate	All crops ■	Maximum ▲ Pre-planting Post-planting	1 1–2 1	4.32 0.36–2.16 0.36–1.08	5.76–1.76 4.75–1.68 1.44–0.44	5.97; 6.62 4.96; 5.57 1.49; 1.65	EFSA, 2015a	nd–2.05 nd–2.06 nd nd–<0.60	11 EU Member States Finland Finland Germany	This study, Silva et al., 2018 Laitinen et al., 2006 Laitinen et al., 2009 Grunewald et al., 2001
	Cereals	Crop maturity	1	0.72–2.16	0.29–0.09	0.30; –		nd–0.60	11 EU Member States	This study, Silva et al., 2018
	Oilseed rape	Crop maturity	1	0.72–2.16	0.58–0.18	0.60; –		nd–0.21	11 EU Member States	This study, Silva et al., 2018
	Orchard crops, vines, citrus & tree nuts	Post emergence of weeds	1–3	0.72–2.88	2.55–1.04 ● 3.82–1.56 ♦	– ; 3.06 ● – ; 4.60 ♦		nd–2.05	11 EU Member States	This study, Silva et al., 2018
Phthalimide (metabolite of folpet and potential artefact)	NA	NA	NA	NA	NA	NA	EFSA, 2009	NA	11 EU Member States	This study
Tebuconazole	All crops	NA	NA	NA	NA	NA	EFSA, 2014	nd–0.19 nd–<0.01 nd–<0.01 nd nd–0.03 nd–0.09	11 EU Member States Portugal, Spain Spain Czech Republic Switzerland	This study Sánchez-González et al., 2013 Masia et al., 2015 Hvězdová et al., 2018 Chiaia-Hernandez et al., 2017
	Cereals	Summer	1–2	0.25	0.19–0.09	NA		nd–0.13	11 EU Member States	This study

Table S2.14 (cont.) - Maximum recommended application rates and predicted concentrations (PECs) in soil of the 7 most common compounds in the European agricultural topsoils, by the main crop uses. The range of contents in European topsoils are also indicated. Compounds are presented in decreasing order of frequency in the current study. Information on DDTs (total DDE, DDD and DDT) and folpet, parent and related compounds of 2 of the 7 most common compounds, were added to the bottom of the table, and marked in grey. PECs accumulated–sum of the PEC initial and plateau in soil; as–active substance, NA–not applicable; nd–not detected. If the range of DDTs was not available in the studies, or if it could not be obtained from the available data, the range of the individual residues was presented. In the concentration range of this study, 317 samples were considered for all crops: 112 for cereals, 101 for permanent crops, 23 for non-permanent industrial crops and 9 for vegetables.

Compound	Dominant use	Growth stage	Number of applications (min–max)	Recommended application rate (kg as/ha)	PECs in soil (0–100 days) (mg/kg)	PECs accumulated in soil (annual crops; permanent crops) (mg/kg)	Source	Range in soil (min–max) (mg/kg)	Country	Source
Tebuconazole	Vines	Summer	1–3	0.10	0.12–0.06	NA	EFSA, 2014	nd–0.19	11 EU Member States	This study
								nd–0.01	Spain	Rial-Otero et al., 2004
								nd–<LOQ	Spain	Pose-Juan et al., 2015
	Oilseed rape □	Spring	1	0.25	0.07–0.03	0.14		nd–0.18	11 EU Member States	This study
Folpet	All crops						EFSA, 2009	nd–0.03	11 EU Member States	This study
	Cereals	NA	2	0.75	NA	NA		nd–0.03	11 EU Member States	This study
	Vegetables (tomatoes)	From beginning of fruit set	4	1.25	NA	NA		nd	11 EU Member States	This study
	Vines	Shoot emergence to veraison	10	1.5	1.48–<0.01	NA		nd–0.01	11 EU Member States	This study
DDTs	All crops	NA	NA	NA	NA	NA		nd–0.31	11 EU Member States	This study
								0.2–3.60	Central Europe	Ružicková et al., 2008
								<0.01–0.02 <0.01–0.06 0.02 <0.01–0.56	Belgium Italy Greece Romania	Covaci et al., 2002
								<0.01–1.23	Italy	Qu et al., 2016
								DDT/DDE: 0.04–0.46	Hungary	Székács et al., 2014
								<0.01–0.03	Russia	Iwata et al., 1995
								nd–0.72	Switzerland	Hilber et al., 2008
								<0.01–1.91	Czech Republic	Holoubek et al., 2009

Table S2.14 (cont.) - Maximum recommended application rates and predicted concentrations (PECs) in soil of the 7 most common compounds in the European agricultural topsoils, by the main crop uses. The range of contents in European topsoils are also indicated. Compounds are presented in decreasing order of frequency in the current study. Information on DDTs (total DDE, DDD and DDT) and folpet, parent and related compounds of 2 of the 7 most common compounds, were added to the bottom of the table, and marked in grey. PECs accumulated–sum of the PEC initial and plateau in soil; as–active substance, NA–not applicable; nd–not detected. If the range of DDTs was not available in the studies, or if it could not be obtained from the available data, the range of the individual residues was presented. In the concentration range of this study, 317 samples were considered for all crops: 112 for cereals, 101 for permanent crops, 23 for non-permanent industrial crops and 9 for vegetables.

Compound	Dominant use	Growth stage	Number of applications (min–max)	Recommended application rate (kg as/ha)	PECs in soil (0–100 days) (mg/kg)	PECs accumulated in soil (annual crops; permanent crops) (mg/kg)	Source	Range in soil (min–max) (mg/kg)	Country	Source
DDTs	All crops	NA	NA	NA	NA	NA		DDE: nd–0.02 DDD: nd–<0.01 DDT: nd–<0.01	France	Villanneau et al., 2011
								<0.01–0.11	Greece	Chrysikou et al., 2008
								<0.01–2.40	Poland	Falandysz et al., 2001
								<0.01–0.45	Poland	Maliszewska-Kordybach et al., 2013
								<0.01–0.39	Poland	Maliszewska-Kordybach et al., 2014
								nd–0.47	Poland	Łozowicka et al., 2016
								3.30–4.70	Spain	Vega et al., 2007
								nd–<0.01	Spain	Fernandez-Alvarez et al., 2008
								nd–0.02	Spain	Fernandez-Alvarez et al., 2010
								DDD op: nd–<0.01 DDE pp: nd–0.15 DDD pp + DDT op: nd–<0.01	Spain	Plaza-Bolanos et al., 2012
								DDD op: nd–<0.01 DDE pp: nd–0.13 DDD pp + DDT op: nd–<0.01	Spain	Padilla-Sánchez et al., 2015

Table S2.14 (cont.) - Maximum recommended application rates and predicted concentrations (PECs) in soil of the 7 most common compounds in the European agricultural topsoils, by the main crop uses. The range of contents in European topsoils are also indicated. Compounds are presented in decreasing order of frequency in the current study. Information on DDTs (total DDE, DDD and DDT) and folpet, parent and related compounds of 2 of the 7 most common compounds, were added to the bottom of the table, and marked in grey. PECs accumulated–sum of the PEC initial and plateau in soil; as–active substance, NA–not applicable; nd–not detected. If the range of DDTs was not available in the studies, or if it could not be obtained from the available data, the range of the individual residues was presented. In the concentration range of this study, 317 samples were considered for all crops: 112 for cereals, 101 for permanent crops, 23 for non-permanent industrial crops and 9 for vegetables.

Compound	Dominant use	Growth stage	Number of applications (min–max)	Recommended application rate (kg as/ha)	PECs in soil (0–100 days) (mg/kg)	PECs accumulated in soil (annual crops; permanent crops) (mg/kg)	Source	Range in soil (min–max) (mg/kg)	Country	Source
DDTs	All crops	NA	NA	NA	NA	NA		DDD pp + DDT op: nd–0.02	Spain	Vidal et al., 2010
								nd–10.40	Serbia	Skrbic et al., 2007
								nd–0.01	Albania	Mukaj et al., 2016
								<0.01–1.54	Romania	Covaci et al., 2001
								nd–5.83	Romania	Ene et al., 2012
								DDE: nd–0.05 DDT: nd–0.05	Romania	Ferencz and Balog, 2010
								<0.01–0.21	Romania	Dragan et al., 2006
								<0.01–0.67	Romania	Dranagan et al., 2007
								<0.01–0.08	Romania	Tarcau et al., 2013
								0.02–0.17	Germany	Manz et al., 2001
								nd–0.07	Germany	Rodil and Popp, 2006
								DDE pp: <0.01–0.02 DDD pp: <0.01	Portugal	Goncalves and Alpendurada, 2005

▼ assuming AMPA is formed at a maximum of 53.8% of applied glyphosate

■ includes vegetables, pulses, oil seeds, potatoes, sugar beet, ornamentals, cereals, trees, nursery plants

▲ maximum application rate per year: 4.32 kg as^{-1}, equivalent to the sum of pre-planting, pre-harvesting and post-harvesting

● applications made to intra-rows

♦ applications made to round base of trunks and to intra-rows

□ use as plant growth regulator

Table S2.15 - Toxicological endpoints of the most common residues in soil to in-soil organisms and respective toxicity/exposure ratios (TERs). Compounds are presented in decreasing order of frequency in the soils of the current study. LC_{50}–concentration responsible for a mortality of 50% of the individuals; NOEC–No Observed Effect Concentration, the highest concentration at which no statistically significant effect is observed, when compared to the control; NA–not available. Trigger value for acute exposures is 10, while for chronic exposures is 5. TERs below trigger values are marked in bold.

Compound	Group	Test organism	Test duration	Endpoint LC_{50} or NOEC or % effect (test substance)	TER	Source	Maximum content (this study)	TER (maximum measured content)
AMPA (metabolite of glyphosate)	Earthworms	*Eisenia andrei*	Acute (14 days)	LC_{50} >1000 mg/kg	59 ◊	EFSA, 2015a	1.92 mg/kg	520
		Eisenia fetida	Chronic (56 days)	NOEC=132 mg/kg	21			69
	Other soil macro-organisms	*Hypoaspis aculeifer*	Chronic (14 days)	NOEC=320 mg/kg	52			167
		Folsomia candida	Chronic (28 days)	NOEC=315 mg/kg	51			164
	Soil micro-organisms	Nitrogen mineralization	(28 days)	effect: 21% at 160 mg/kg	-			-
		Carbon mineralization	(28 days)	effect: 18% at 160 mg/kg	-			-
Boscalid	Earthworms	NA	Acute	LC_{50} >500 mg/kg * LC_{50} >500 mg/kg * (BAS 510 01 F)	-	EC, 2008 EFSA, 2006	0.41 mg/kg	1220 1220
		NA	Chronic-Reproductive	NOEC=1.20 mg/kg (BAS 510 01 F)	**1.41-4.81**			**2.9**
	Soil micro-organisms	Nitrogen mineralization	NA	effect: 0% at <8 mg/kg (BAS 510 01 F)	-			-
		Carbon mineralization	NA	effect: 0% at <8 mg/kg (BAS 510 01 F)	-			-
Epoxiconazole	Earthworms	NA	Acute	LC_{50} >500 mg/kg LC_{50} >62.5 mg/kg (BAS 480 27 F)	>3906 >488	EFSA, 2008, 2015b	0.16 mg/kg	>3125 >390
		NA	Chronic-Reproductive	NOEC=0.084 mg/kg NOEC=2x0.13 kg as/ha (extrapolation from enchytraeidae)▲ NOEC=2x0.13 kg as/ha ▪	**0.7** **1; >1** **>1**			**0.5** - -
	Other soil macro-organisms	Collembola	NA	NOEC=2x0.13 kg as/ha▲ NOEC=2x0.13 kg as/ha ▪	**<1; >1** **>1**			- -
	Soil micro-organisms	Nitrogen mineralization	NA	effect: 0% at 0.19 mg/kg effect: 0% at 1.88 mg/kg NOEC=0.33 g/kg▲	-			-
		Carbon mineralization	NA	effect: 0% at 0.19 mg/kg effect: 0% at 1.88 mg/kg	-			-
DDE pp (metabolite of DDT)	Earthworms	*Lumbricus terrestris*	Acute (14 days)	LC_{50} = 61 mg/kg	-	PPDB, 2017	0.31 mg/kg	197

Table S2.15 (cont.) – Toxicological endpoints of the most common residues in soil to in-soil organisms and respective toxicity/exposure ratios (TERs). Compounds are presented in decreasing order of frequency in the soils of the current study. LC_{50}–concentration responsible for a mortality of 50% of the individuals; NOEC–No Observed Effect Concentration, the highest concentration at which no statistically significant effect is observed, when compared to the control; NA–not available. Trigger value for acute exposures is 10, while for chronic exposures is 5. TERs below trigger values are marked in bold.

Compound	Group	Test organism	Test duration	Endpoint LC_{50} or NOEC or % effect (test substance) (test substance)	TER	Source	Maximum content (this study)	TER (maximum measured content)
Glyphosate	Earthworms	*Eisenia fetida*	Acute (14 days)	LC_{50}=5600 mg/kg (glyphosate acid) LC_{50} >388 mg/kg (MON 52276)*	846 59	EFSA, 2015a	2.05 mg/kg	2732 189
		Eisenia fetida	Chronic (56 days)	NOEC >473 mg/kg (MON 0139)*	72 ◊			231
	Other soil macro-organisms	*Hypoaspis aculeifer*	Chronic (14 days)	NOEC=473 mg/kg (Glyphosate IPA-salt)*	71			231
		Folsomia candida	Chronic (28 days)	NOEC=587 mg/kg (Glyphosate IPA-salt)*	89			286
	Soil micro-organisms	Nitrogen mineralization	(28 days)	effect: 6% at 33.1 mg/kg (MON 77973)* effect: 8% at 94 mg/kg (MON 52276)	-			-
		Carbon mineralization	(28 days)	effect: 9% at 6.4 mg/kg (Glyphosate acid) effect: 15% at 94 mg/kg (MON 52276)	-			-
Phthalimide (metabolite of folpet and potential artefact)	NA	NA	NA	NA	-	EFSA, 2009	NA	-
Tebuconazole	Earthworms	*Eisenia fetida*	Acute (14 days)	LC_{50}=1381 mg/kg LC_{50} >254 mg/kg (Folicur EW 250) NA □ NA (Folicur EW 250) □	3773 ● ◊ >693 ● ◊ 9331 □ >1789 □	EFSA, 2014	0.19 mg/kg	3634 ● > 668 ● - -
		Eisenia fetida	Chronic (8 weeks)	NOEC=10 mg/kg NOEC <1.5 mg/kg (Folicur EW 250) NA □ NA (Folicur EW 250) □	55 ◊ **< 4.1**● 70 <9.4			53 **<4.0** ● - -
	Other soil macro-organisms	*Hypoaspis aculeifer*	Chronic	NOEC=50 mg/kg NOEC=56.2 mg/kg (Folicur EW 250) NA □ NA (Folicur EW 250) □	273 ◊ 307 ◊ 704 792			263 296 - -
		Folsomia candida	Chronic	NOEC=250 mg/kg NA □	683 ◊ 1761 ●			658 ● -

Table S2.15 (cont.) - Toxicological endpoints of the most common residues in soil to in-soil organisms and respective toxicity/exposure ratios (TERs). Compounds are presented in decreasing order of frequency in the soils of the current study. LC_{50}–concentration responsible for a mortality of 50% of the individuals; NOEC–No Observed Effect Concentration, the highest concentration at which no statistically significant effect is observed, when compared to the control; NA–not available. Trigger value for acute exposures is 10, while for chronic exposures is 5. TERs below trigger values are marked in bold.

Compound	Group	Test organism	Test duration	Endpoint LC_{50} or NOEC or % effect (test substance)	TER	Source	Maximum content (this study)	TER (maximum measured content)
Tebuconazole	Soil micro-organisms	Nitrogen mineralization	(28 days)	effect: <10% at 8.3 mg/kg	-	EFSA, 2014	0.19 mg/kg	-
		Carbon mineralization	(28 days)	effect: <10% at 8.3 mg/kg	-			-
Folpet	Earthworms	NA	Acute – 14 days	LC_{50} >500 mg/kg * LC_{50} >414 mg/kg (FOLPAN 80 WDG) *	- 280	EFSA, 2009	0.03 mg/kg	16667 13800
		NA	Chronic (Reproductive)	NOEC=5.18 mg/kg (MON 0139)	**3.5**			173
	Soil micro-organisms	Nitrogen mineralization	NA	effect: <25% at 1.6 mg/kg effect: <25% at 15.9 mg/kg	-			-
		Carbon mineralization	NA	effect: <25% at 1.6 mg/kg effect: <25% at 15.9 mg/kg	-			-
DDTs	Earthworms	*Eisenia foetida*	56 days	LC_{50} >1000 mg/kg	-	PPDB, 2017	0.31 mg/kg	>3226

*expressed in mg acid equivalents kg^{-1} dry soil
▲ from a terrestrial model ecosystem (TEM) study, at an application rate of 2x0.13 kg as/ha.
■ from a field study with natural populations
● TER value divided by 2, to consider the 10% organic matter in the endpoint assessment and/or the substance log Pow >2.0.
□ use as plant growth regulator
◊ EFSA TER value slightly different from the value recalculated by us using the LC_{50} or the NOEC values and the PEC values in the EFSA conclusion report.

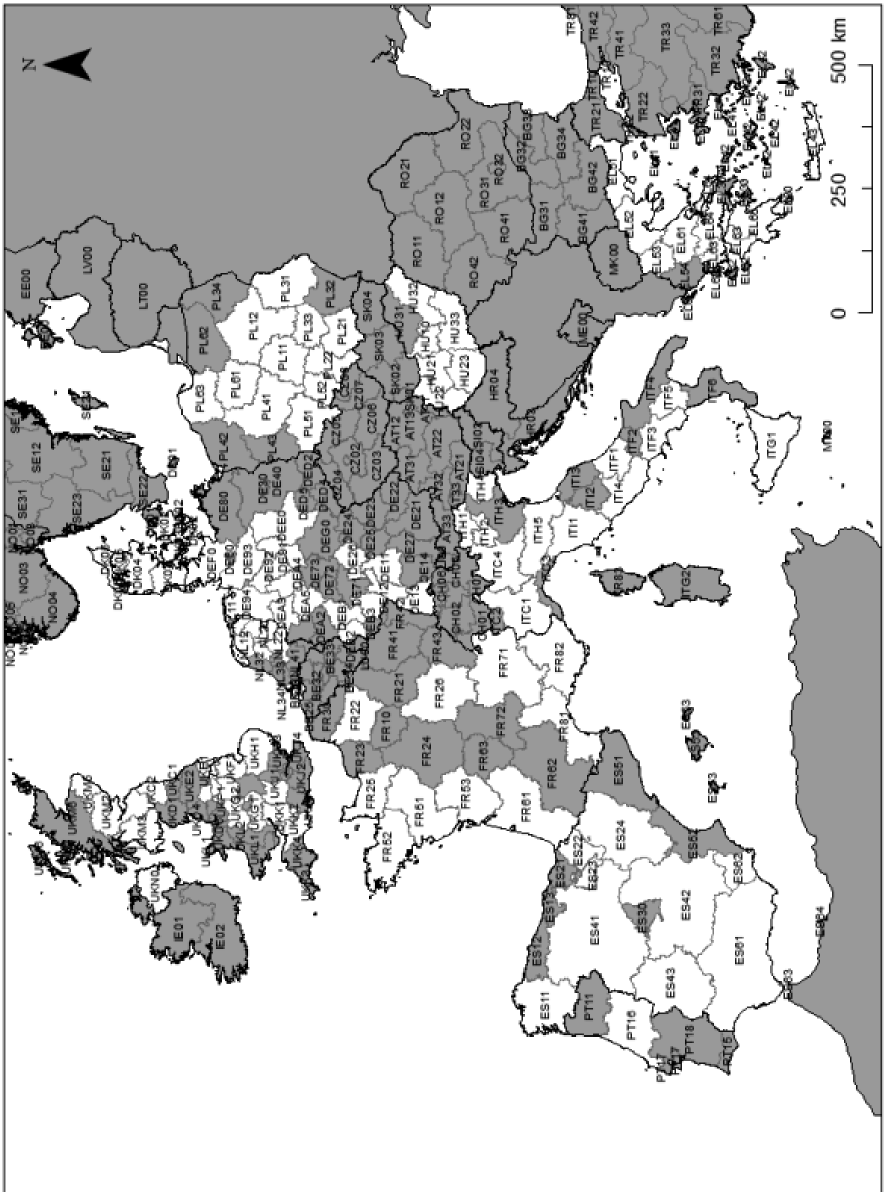


Figure S2.1 – Map of NUTS 2 regions. White and grey areas in the map represent the sampled and not-sampled NUTS2 regions, respectively.

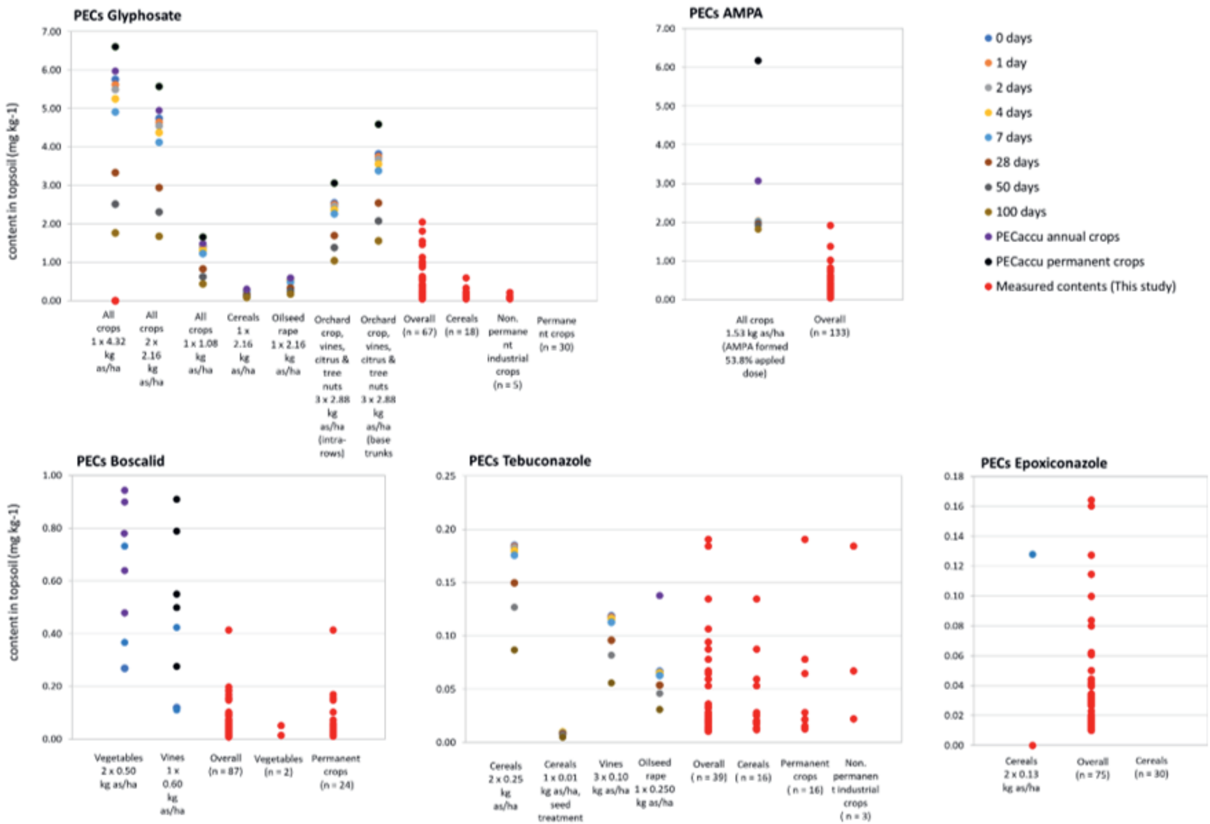


Figure S2.2 - Comparison between the predicted environmental concentrations (PEC) in soil, from EFSA, and the measured contents of glyphosate, AMPA, epoxiconazole, boscalid, and tebuconazole in the EU agricultural topsoils in 2015. The figure includes all of the available PECs for each compound (though, for reasons of consistency, the PECs for 14, 21 and 42 days after application, only available for tebuconazole, were not presented). Along with the overall distribution of the measured contents of each compound, the distribution of contents was also presented by major crop classes, namely those comparable to the compound dominant uses to which PECs are available. PECaccu=PEC accumulated (initial PEC in soil plus the plateau levels in soil). n=number of samples with residue content ≥LOQ (LOQ glyphosate and AMPA=0.05 mg/kg; LOQ boscalid, epoxiconazole and tebuconazole=0.01 mg/kg).

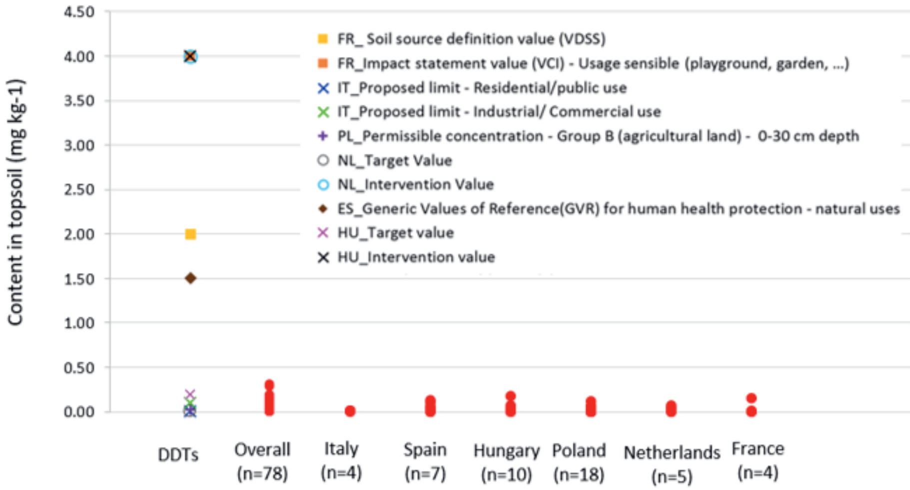


Figure S2.3 - Comparison between the soil screening values for DDTs for the sampled countries (from Carlon, 2007) and the measured DDTs content in EU agricultural topsoils in 2015. The distribution of measured content in the United Kingdom, Denmark, Greece and Germany is not presented since no threshold values are available in these countries. Portuguese soils did not contain DDTs. FR–France, IT–Italy, PL–Poland, NL–The Netherlands, ES–Spain, HU–Hungary. n–number of samples with DDTs ≥0.005 mg/kg. * – sum of DDT, DDE and DDD levels.

Supplementary material – Chapter 3

Table S3.1 – Distribution of topsoil samples per country, NUTS 2 region and crop system.

country	NUTS 2	cereals	root crops	non-permanent industrial crops	dry pulses and fodder crops	permanent crops	vegetables	others
United Kingdom	UKC2			1				
	UKE1	1						
	UKE3	1						
	UKE4							1
	UKF1				1			
	UKF3			1			1	
	UKG1	1					1	
	UKG2	1			1		1	
	UKH1	2						
	UKJ1	1						
	UKK1	2	1					
	UKK2	1						1
	UKM2	2		3	1			
	UKM3				1			
	UKM5	1						
	UKN0				1	1		
Denmark	DK02	5						1
	DK03	5	1	1				
	DK04	9	3	2				1
	DK05	2						
Portugal	PT16					17		
Italy	ITC1	2				3		
	ITC4	2		1		2		
	ITF1					1		
	ITF3					1		
	ITF5					1		
	ITG1					5		
	ITH1					1		
	ITH2					1		
	ITH4	1						
	ITH5	2	1	1				1
	ITI1				1	2		
	ITI4		1					
Greece	EL43					1		
	EL51	2	1					1
	EL52	2	1	1		6		
	EL53					1		
	EL61	1				1		
	EL63					1		
	EL64				1	3		
	EL65					7		
Spain	ES11	2	1					
	ES22	1						
	ES23					2		1
	ES24	1				2		
	ES41	3			1			
	ES42	1				4		
	ES43	1						
	ES61	1				1		
	ES62	1			4	1	2	

Table S3.1 (cont.) – Distribution of topsoil samples per country, NUTS 2 region and crop system.

country	NUTS 2	cereals	root crops	non-permanent industrial crops	dry pulses and fodder crops	permanent crops	vegetables	others
Hungary	HU10	1				1		
	HU21	2						
	HU22	4		3	1			
	HU23					1		
	HU32	7				1		1
	HU33	6			1	1		
Poland	PL11					1		
	PL12	1						1
	PL21					1		
	PL22	2						
	PL31	1			1	4		3
	PL33		1			1		
	PL41	2		1		1		1
	PL51	3		1				
	PL52	1						
	PL61	1						
	PL63	1	1					
The	NL11			1				4
Netherlands	NL12	1						2
	NL13	1						3
	NL21	1	1		2			
	NL22		1					
	NL23	1	2		1		1	4
	NL34	2					1	1
France	FR22				1			
	FR25		1					
	FR26					1		
	FR51			1				
	FR52	4			1	1		
	FR53			2		1		
	FR61					2		
	FR71			1	2	1		
	FR81					7		
	FR82		1			3		
Germany	DE11	1			1	1		
	DE12					1		
	DE13	1						
	DE26				1			
	DE91	1						
	DE92	1						
	DE93			1				
	DE94		2	1			1	
	DEA3	2	1					
	DEA4	1						
	DEA5	1						
	DEB1					1		
	DEB2	1				1		
	DEB3	1				4	1	
	DEE0	2						
	DEF0	1						

Table S3.2 – Distribution of glyphosate and AMPA in agricultural topsoils (0-15/20 cm) by EU region, country and crop system. Only samples containing glyphosate or AMPA (≥0.05 mg/kg) were considered for the range, median concentrations. For the AMPA proportion, samples containing only glyphosate or AMPA (≥0.05 mg/kg), with respectively an AMPA proportion of 0 or 100%, were considered in mean values. Different letters represent significant differences [(p<0.05): a>b] between regions, countries or crop systems. N – number of topsoil samples tested, Range – minimum-maximum concentrations, AMPA Prop. – AMPA proportion = [AMPA / (Glyphosate + AMPA)]*100.

	N	glyphosate				AMPA				AMPA prop.
		positive samples	range (mg/kg)	median		positive samples	range (mg/kg)	median		mean (%)
Overall	317	67 (21%)	0.05 – 2.05	0.14		133 (42%)	0.05 – 1.92	0.15		77
EU region										
North	60	16 (27%)	0.05 – 0.34	0.12	b	42 (70%)	0.05 – 0.61	0.14		87
South	107	24 (22%)	0.07 – 2.05	0.48	a	30 (28%)	0.06 – 1.92	0.19		54
East	60	6 (10%)	0.05 – 0.57	0.11	b	20 (33%)	0.06 – 0.73	0.15		91
West	90	21(23%)	0.05 – 0.59	0.1	b	41 (46%)	0.05 – 1.03	0.14		79
Country										
United Kingdom	30	8 (27%)	0.05 – 0.21	0.15	ab	18 (60%)	0.07 – 0.59	0.15	b	89
Denmark	30	9 (27%)	0.06 – 0.34	0.11	ab	24 (80%)	0.05 – 0.61	0.14	b	85
Portugal	17	9 (53%)	0.43 – 2.05	1.14	a	9 (53%)	0.42 – 1.92	0.73	a	42
Italy	30	5 (17%)	0.09 – 0.18	0.13	ab	5 (17%)	0.06 – 1.38	0.1	ab	54
Greece	30	3 (10%)	0.39 – 0.63	0.54	ab	5 (17%)	0.16 – 0.38	0.21	ab	61
Spain	30	7 (23%)	0.07 – 0.95	0.22	ab	11 (37%)	0.06 – 0.27	0.09	b	60
Hungary	30	4 (13%)	0.05 – 0.57	0.1	ab	6 (20%)	0.06 – 0.73	0.23	ab	79
Poland	30	2 (7%)	0.08 – 0.23	0.16	ab	14 (47%)	0.06 – 0.42	0.14	b	96
The Netherlands	30	7 (23%)	0.05 – 0.59	0.13	ab	12 (40%)	0.05 – 1.03	0.13	ab	75
France	30	10 (30%)	0.05 – 0.27	0.08	b	15 (50%)	0.06 – 0.78	0.13	ab	77
Germany	30	5 (17%)	0.07 – 0.24	0.13	ab	14 (47%)	0.07 – 0.54	0.15	b	83
Crop system										
Cereals	112	18 (16%)	0.05 – 0.60	0.11		46 (41%)	0.05 – 0.62	0.13		84
Root crops	27	6 (22%)	0.05 – 0.59	0.33		14 (52%)	0.05 – 1.03	0.12		80
Non-permanent industrial crops	23	5 (22%)	0.05 – 0.21	0.07		11 (48%)	0.06 – 0.59	0.16		86
Dry pulses and Fodder crops	21	1 (5%)	0.06			6 (29%)	0.07 – 0.17	0.11		86
Permanent crops	101	30 (30%)	0.07 – 2.05	0.17		41 (41%)	0.06 – 1.92	0.21		64
Vegetables	9	2 (22%)	0.13 – 0.14	0.14		3 (33%)	0.07 – 0.32	0.17		75
Others	24	5 (21%)	0.05 – 0.95	0.15		12 (50%)	0.06 – 0.74	0.08		79

Table S3.3 – **Distribution of glyphosate and AMPA in agricultural topsoils (0-15/20 cm) by NUTS 2 region.** Only NUTS 2 with at least one sample containing glyphosate and/or AMPA (≥0.05 mg/kg) were included in the table. Only samples containing glyphosate or AMPA were considered for the range and median concentrations. For the AMPA proportion, samples containing only glyphosate or AMPA (≥0.05 mg/kg), with respectively an AMPA proportion of 0 or 100%, were considered in mean values. N – number of topsoil samples tested, Range – minimum and maximum concentrations, AMPA Prop. – AMPA proportion = [AMPA/ (Glyphosate + AMPA)]*100.

NUTS 2	N	glyphosate			AMPA			AMPA prop.
		positive samples	range (mg/kg)	median	positive samples	range (mg/kg)	median	mean (%)
UKE3	1	0	-		1 (100%)	0.07		100
UKF1	1	1 (100%)	0.15		1 (100%)	0.29		65
UKF3	2	1 (50%)	0.21		1 (50%)	0.57		73
UKG1	2	1 (50%)	0.14		1 (50%)	0.31		69
UKG2	3	0	-		3 (100%)	0.07 – 0.08	0.07	100
UKJ1	1	0	-		1 (100%)	0.13		100
UKK1	3	0	-		1 (33%)	0.07		100
UKK2	2	0	-		1 (50%)	0.09		100
UKM2	6	3 (50%)	0.05 – 0.18	0.05	4 (67%)	0.16 – 0.59	0.33	86
UKM3	1	0	-		1 (100%)	0.07		100
UKM5	1	1 (100%)	0.19		1 (100%)	0.44		69
UKN0	2	1 (50%)	0.07		2 (100%)	0.09 – 0.43	0.26	93
DK02	6	0	-		5 (83%)	0.07 – 0.17	0.11	100
DK03	7	1 (14%)	0.10		5 (71%)	0.06 – 0.54	0.17	96
DK04	15	6 (40%)	0.06 – 0.33	0.12	13 (87%)	0.05 – 0.61	0.13	77
DK05	2	1 (50%)	0.06		1 (50%)	0.26		82
PT16	17	9 (53%)	0.43 – 2.05	1.14	9 (53%)	0.42 – 1.92	0.73	42
ITC1	5	1 (20%)	0.09		2 (40%)	0.07 – 0.15	0.11	71
ITF3	1	1 (100%)	0.12		0	-		0
ITG1	5	1 (20%)	0.13		1 (20%)	0.06		50
ITH1	1	1 (100%)	0.13		1 (100%)	1.38		91
ITH5	5	0	-		1 (20%)	0.10		100
ITI1	3	1 (33%)	0.18		0	-		0
EL52	10	1 (10%)	0.39		3 (30%)	0.16 – 0.38	0.18	83
EL61	2	1 (50%)	0.53		1 (50%)	0.20		28
EL65	7	1 (14%)	0.63		1 (14%)	0.26		29
ES11	3	1 (33%)	0.22		1 (33%)	0.07		50
ES23	3	2 (67%)	0.07 – 0.43	0.25	3 (100%)	0.12 – 0.27	0.15	69
ES41	4	0	-		1 (25%)	0.08		100
ES42	5	1 (20%)	0.11		2 (40%)	0.06 – 0.09	0.08	69
ES61	2	1 (50%)	0.16		1 (50%)	0.14		47
ES62	8	2 (25%)	0.6 – 0.95	0.78	3 (38%)	0.06 – 0.21	0.08	45
HU10	2	1 (50%)	0.57		1 (50%)	0.73		56
HU21	2	0	-		1 (50%)	0.23		100
HU22	8	1 (13%)	0.07		1 (13%)	0.23		77
HU32	9	2 (22%)	0.05 – 0.13	0.09	2 (22%)	0.12 – 0.36	0.24	71
HU33	8	0	-		1 (13%)	0.06		100

Table S3.3 (cont) – Distribution of glyphosate and AMPA in agricultural topsoils (0-15/20 cm) by NUTS 2 region. Only NUTS 2 with at least one sample containing glyphosate and/or AMPA (≥0.05 mg/kg) were included in the table. Only samples containing glyphosate or AMPA were considered for the range and median concentrations. For the AMPA proportion, samples containing only glyphosate or AMPA (≥0.05 mg/kg), with respectively an AMPA proportion of 0 or 100%, were considered in mean values. N – number of topsoil samples tested, Range – minimum and maximum concentrations, AMPA Prop. – AMPA proportion = [AMPA / (Glyphosate + AMPA)]*100.

NUTS 2	N	glyphosate			AMPA			AMPA prop.
		positive samples	range (mg/kg)	median	positive samples	range (mg/kg)	median	mean (%)
PL12	2	0	-		1 (50%)	0.08		100
PL22	2	0	-		1 (50%)	0.06		100
PL31	9	2 (22%)	0.08 – 0.23	0.16	7 (78%)	0.06 – 0.42	0.15	92
PL33	2	0	-		1 (50%)	0.08		100
PL41	5	0	-		1 (20%)	0.10		100
PL51	4	0	-		1 (25%)	0.20		100
PL52	1	0	-		1 (100%)	0.21		100
PL61	1	0	-		1 (100%)	0.07		100
NL11	5	2 (40%)	0.07 – 0.59	0.33	4 (80%)	0.06 – 1.02	0.18	85
NL13	4	3 (75%)	0.05 – 0.42	0.19	4 (100%)	0.09 – 0.62	0.22	70
NL21	4	0	-		2 (50%)	0.08 – 0.08	0.08	100
NL23	9	1 (11%)	0.05		1 (11%)	0.05		50
NL34	4	1 (25%)	0.13		1 (25%)	0.17		57
FR22	1	1 (100%)	0.17		1 (100%)	0.74		82
FR25	1	1 (100%)	0.06		0	-		0
FR51	1	0	-		1 (100%)	0.23		100
FR52	6	2 (33%)	0.09 – 0.10	0.10	4 (67%)	0.09 – 0.16	0.12	79
FR53	3	2 (67%)	0.05 – 0.07	0.06	2 (67%)	0.06 – 0.27	0.16	66
FR61	2	0	-		1 (50%)	0.13		100
FR81	7	3 (43%)	0.07 – 0.27	0.08	5 (71%)	0.06 – 0.78	0.09	80
FR82	4	0	-		1 (25%)	0.07		100
DE11	3	0	-		1 (33%)	0.11		100
DE91	1	1 (100%)	0.24		1 (100%)	0.38		62
DE92	1	1 (100%)	0.11		1 (100%)	0.31		73
DE93	1	0	-		1 (100%)	0.13		100
DE94	3	0	-		2 (67%)	0.10 – 0.16	0.13	100
DEA3	4	0	-		2 (50%)	0.13 – 0.19	0.16	100
DEA4	1	0	-		1 (100%)	0.07		100
DEA5	1	0	-		1 (100%)	0.54		100
DEB1	1	1 (100%)	0.13		1 (100%)	0.30		70
DEB2	2	0	-		1 (50%)			100
DEB3	6	2 (33%)	0.07 – 0.14	0.10	2 (33%)	0.12 – 0.21	0.16	49

Table S3.4 – Potential export of glyphosate by water and wind erosion by its concentration level in topsoils, EU region, country and crop system. Individual export rates were calculated every time glyphosate in soil ≥ 0.05 mg/kg and wind/water erosion > 0 Mg/ha/year. E – Number of samples with an export rate value.

	export by wind erosion			export by water erosion		
	E	mean (g/ha/year)	maximum (g/ha/year)	E	mean (g/ha/year)	maximum (g/ha/year)
Glyphosate content						
0.05–0.5 mg/kg	26	0.122	0.676	53	0.476	5.715
>0.5 mg/kg	3	0.215	0.645	14	2.516	5.182
EU region						
North	12	0.198	0.676	16	0.049	0.101
South	4	0.014	0.055	24	2.153	5.715
East	3	0.002	0.006	6	0.414	1.733
West	10	0.137	0.645	21	0.263	1.225
Country						
United Kingdom	7	0.093	0.283	8	0.051	0.101
Denmark	5	0.346	0.676	8	0.047	0.073
Portugal	0		-	9	3.475	5.182
Italy	1		~0	5	2.849	5.715
Greece	1		~0	3	0.531	1.056
Spain	2	0.027	0.055	7	0.650	1.073
Hungary	2	0.003	0.006	4	0.486	1.733
Poland	1		~0	2	0.270	0.291
The Netherlands	5	0.263	0.645	7	0.059	0.249
France	1		~0	9	0.386	1.225
Germany	4	0.014	0.040	5	0.326	0.697
Crop system						
Cereals	13	0.129	0.676	18	0.171	0.895
Root crops	3	0.338	0.645	6	0.280	1.073
Non-permanent industrial crops	3	0.137	0.283	5	0.025	0.047
Dry pulses and Fodder crops	0		-	1		0.215
Permanent crops	6	0.010	0.055	30	1.798	5.715
Vegetables	2	0.279	0.555	2	0.027	0.033
Others	2	0.046	0.091	5	0.270	0.990

Table S3.5 – **Potential export of AMPA by water and wind erosion by its concentration level in topsoils, EU region, country and crop system**. Individual export rates were calculated every time glyphosate in soil ≥ 0.05 mg/kg and wind/water erosion 0 Mg/ha/year. E – Number of samples with an export rate value.

	export by wind erosion			export by water erosion		
	E	mean (g/ha/year)	maximum (g/ha/year)	E	mean (g/ha/year)	maximum (g/ha/year)
AMPA content						
0.05–0.5 mg/kg	69	0.143	1.941	114	0.295	9.753
>0.5 mg/kg	5	1.135	3.045	19	4.157	47.666
EU region						
North	31	0.410	3.045	42	0.103	0.508
South	8	0.005	0.033	30	2.756	47.666
East	15	0.017	0.120	20	0.386	2.221
West	20	0.126	1.114	41	0.435	3.966
Country						
United Kingdom	12	0.335	3.045	18	0.131	0.508
Denmark	19	0.457	1.941	24	0.083	0.324
Portugal	0		-	9	2.331	8.266
Italy	1		~0	5	11.565	47.666
Greece	3	0.002	0.003	5	0.201	0.427
Spain	4	0.009	0.033	11	0.261	0.777
Hungary	3	0.012	0.019	6	0.503	2.221
Poland	12	0.018	0.120	14	0.336	1.033
The Netherlands	8	0.295	1.114	12	0.059	0.431
France	1		0.001	15	0.612	3.529
Germany	11	0.015	0.065	14	0.569	3.966
Crop system						
Cereals	34	0.221	1.941	46	0.248	3.966
Root crops	10	0.293	1.114	14	0.166	0.676
Non-permanent industrial crops	7	0.532	3.045	11	0.164	0.513
Dry pulses and Fodder crops	5	0.105	0.366	6	0.062	0.136
Permanent crops	12	0.006	0.033	41	2.317	47.666
Vegetables	3	0.251	0.732	3	0.040	0.073
Others	3	<0.001	0.002	12	0.134	0.436

Table S3.6 – **Potential export rates of glyphosate by water and wind erosion by NUTS 2 region.** Individual export rates were calculated every time glyphosate in soil ≥ 0.05 mg/kg and wind/water erosion 0 Mg/ha/year. E – Number of samples with an export rate value.

NUTS 2	export by wind erosion			export by water erosion		
	E	mean (g/ha/year)	maximum	E	mean (g/ha/year)	maximum
UKE3	0		-	0		-
UKF1	1		0.001	1		0.101
UKF3	1		0.104	1		0.009
UKG1	1		0.004	1		0.033
UKG2	0		-	0		-
UKJ1	0		-	0		-
UKK1	0		-	0		-
UKK2	0		-	0		-
UKM2	3	0.145	0.283	3	0.048	0.074
UKM3	0		-	0		-
UKM5	1		0.105	1		0.089
UKN0	0		-	1		0.031
DK02	0		-	0		-
DK03	0		-	1		0.052
DK04	5	0.346	0.676	6	0.041	0.052
DK05	0		-	1		0.073
PT16	0		-	9	3.475	5.182
ITC1	1		~0	1		0.093
ITF3	0		-	1		3.871
ITG1	0		-	1		0.117
ITH1	0		-	1		4.451
ITH5	0		-	0		-
ITI1	0		-	1		5.715
EL52	0		-	1		0.439
EL61	1		~0	1		1.056
EL65	0		-	1		0.096
ES11	0		-	1		0.294
ES23	0		-	2	0.623	1.073
ES41	0		-	0		-
ES42	1		0.055	1		0.238
ES61	0		-	1		0.884
ES62	1		~0	2	0.943	0.990
HU10	0		-	1		1.733
HU21	0		-	0		-
HU22	0		-	1		0.128
HU32	2	0.003	0.006	2	0.042	0.053
HU33	0	-		0	-	

Table S3.6 (cont.) – Potential export rates of glyphosate by water and wind erosion by NUTS 2 region. Individual export rates were calculated every time glyphosate in soil ≥ 0.05 mg/kg and wind/water erosion 0 Mg/ha/year. E – Number of samples with an export rate value.

NUTS 2	export by wind erosion			export by water erosion		
	E	mean (g/ha/year)	maximum (g/ha/year)	E	mean (g/ha/year)	maximum (g/ha/year)
PL12	0		-	0		-
PL22	0		-	0		-
PL31	1		~0	2	0.270	0.291
PL33	0		-	0		-
PL41	0		-	0		-
PL51	0		-	0		-
PL52	0		-	0		-
PL61	0		-	0		-
NL11	2	0.335	0.645	2	0.129	0.249
NL13	1		<0.001	3	0.026	0.040
NL21	0		-	0		-
NL23	1		0.091	1		0.050
NL34	1		0.555	1		0.022
FR22	0		-	1		0.080
FR25	0		-	1		0.215
FR51	0		-	0		-
FR52	1		0.001	2	0.581	0.684
FR53	0		-	2	0.036	0.055
FR61	0		-	0		-
FR81	0		-	3	0.649	1.225
FR82	0		-	0		-
DE11	0		-	0		-
DE91	1		0.040	1		0.067
DE92	1		0.016	1		0.052
DE93	0		-	0		-
DE94	0		-	0		-
DEA3	0		-	0		-
DEA4	0		-	0		-
DEA5	0		-	0		-
DEB1	1		~0	1		0.636
DEB2	0		-	0		-
DEB3	1		~0	2	0.437	0.697

Table S3.7 – Potential export rates of AMPA by water and wind erosion by NUTS 2 region. Individual export rates were calculated every time glyphosate in soil ≥ 0.05 mg/kg and wind/water erosion 0 Mg/ha/year. E – Number of samples with an export rate value.

NUTS 2	export by wind erosion			export by water erosion		
	E	mean (g/ha/year)	maximum (g/ha/year)	E	mean (g/ha/year)	maximum (g/ha/year)
UKE3	1		0.025	1		0.081
UKF1	1		0.002	1		0.191
UKF3	1		0.278	1		0.023
UKG1	1		0.008	1		0.073
UKG2	1		0.011	3	0.032	0.058
UKJ1	1		0.023	1		0.110
UKK1	0		-	1		0.009
UKK2	1		0.005	1		0.083
UKM2	4	0.857	3.045	4	0.285	0.508
UKM3	0		-	1		0.004
UKM5	1		0.237	1		0.202
UKN0	0		-	2	0.172	0.184
DK02	5	0.945	1.941	5	0.042	0.091
DK03	2	0.311	0.366	5	0.097	0.196
DK04	12	0.278	1.233	13	0.075	0.181
DK05	0		-	1		0.324
PT16	0		-	9	2.331	8.266
ITC1	1		~0	2	4.910	9.753
ITF3	0		-	0		-
ITG1	0		-	1		0.058
ITH1	0		-	1		47.666
ITH5	0		-	1		0.283
ITI1	0		-	0		-
EL52	2	0.003	0.003	3	0.187	0.427
EL61	1		~0	1		0.405
EL65	0		-	1		0.040
ES11	0		-	1		0.109
ES23	0		-	3	0.383	0.676
ES41	1		0.001	1		0.080
ES42	1		0.033	2	0.122	0.144
ES61	0		-	1		0.777
ES62	2	~0	~0	3	0.173	0.312
HU10	0		-	1		2.221
HU21	1		0.019	1		0.110
HU22	0		-	1		0.436
HU32	2	0.009	0.018	2	0.107	0.145
HU33	0		-	1		0.037

Table S3.7 (cont.) – Potential export rates of AMPA by water and wind erosion by NUTS 2 region. Individual export rates were calculated every time glyphosate in soil ≥ 0.05 mg/kg and wind/water erosion 0 Mg/ha/year. E – Number of samples with an export rate value.

NUTS 2	export by wind erosion			export by water erosion		
	E	mean (g/ha/year)	maximum (g/ha/year)	E	mean (g/ha/year)	maximum (g/ha/year)
PL12	1		~0	1		0.180
PL22	1		0.018	1		0.179
PL31	5	0.006	0.019	7	0.487	1.033
PL33	1		~0	1		0.468
PL41	1		0.023	1		0.029
PL51	1		0.120	1		0.372
PL52	1		0.010	1		0.047
PL61	1		0.013	1		0.023
NL11	4	0.320	1.114	4	0.123	0.431
NL13	2	0.012	0.022	4	0.035	0.076
NL21	0		-	2	0.013	0.021
NL23	1		0.322	1		0.014
NL34	1		0.732	1		0.029
FR22	0		-	1		0.355
FR25	0		-	0		-
FR51	0		-	1		0.152
FR52	1		0.001	4	0.498	1.263
FR53	0		-	2	0.118	0.217
FR61	0		-	1		1.093
FR81	0		-	5	1.060	3.529
FR82	0		-	1		0.054
DE11	0		-	1		0.147
DE91	1		0.065	1		0.107
DE92	1		0.045	1		0.142
DE93	1		0.003	1		0.513
DE94	1		0.006	2	0.061	0.115
DEA3	2	0.004	0.009	2	0.085	0.136
DEA4	1		0.031	1		0.271
DEA5	1		0.004	1		3.966
DEB1	1		~0	1		1.519
DEB2	0		-	1		0.002
DEB3	2	~0	~0	2	0.505	0.600

Supplementary material – Chapter 4

Table S4.1 - Compounds applied in conventional farming systems and respective application rates in the sampled fields (total amount applied per field, kg or L compound/ha/year) – P-G-C=conventional grape production in Portugal; N-P-C=conventional potato production in the Netherlands; S-V-C=conventional vegetable production in Southeast-Spain, S-O-C=conventional orange production in Spain. F-fungicide, H-herbicide, I-insecticide; O-other; NA-not available. Typical DT_{50} values and respective interpretations were extracted from the PPDB database (*PPDB. 2020*). DT_{50} values above 100 days were rounded to the unit. An empty box (-) indicates that the compound was not reported to be applied by any of the farmers interviewed in that Case Study Site, CSS. When only some farmers in a CSS applied a compound, the range of applications of that CSS starts with zero. Application rates were rounded to two decimal cases. Mod.=moderately.

Compound	DT_{50} soil (days)	DT_{50} Interpretation	N-P-C	P-G-C	S-V-C	S-O-C
Abamectin (I)	25.3	Non-persistent		-	amount NA	amount NA
Acetamiprid (I)	1.6	Non persistent	-	-	0 - 0.60	-
Aclonifen (H)	117	Persistent	-	-	0 - 1.20	-
Alpha-cypermethrin (I)	23.0	Non-persistent	-	0.01-0.02	0-0.5	-
Ametoctradin (F)	1.8	Non-persistent	-	-	0 - 0.96	-
Azadirachtin (I)	8.0	Non-persistent	-	-	amount NA	-
Azoxystrobin (F)	78.0	Mod. persistent	1.01-1.9	-	amount NA	-
Bentazone (H)	26.4	Non- persistent	0-0.05	-	-	-
Benthiavalicarb (F)	19.1	Non- persistent	<0.01-<0.01	-	-	-
Bifaxen (F)	1235	Very Persistent	0.04-0.29	-	-	-
Boscalid (F)	484	Very persistent	0-<0.01	0-0.08	0 - 8.01	-
Carfentraozone-ethyl (H)	77.1	Mod. Persistent	0.16-1.44	-	-	-
Chlorantraniliprole (I)	246	Persistent	-	-	0 – 0.	-
Chloridazon (H)	144	Persistent	0-0.47	-	-	-
Chlorimuron-ethyl (H)	40.0	Mod. persistent	-	-	amount NA	-
Chlormequat (I)	122	Persistent	0-18.0	-	-	-
Chlorothalonil(F)	3.5	Non persistent	-	-	0 - 12.50	-
Chlorpropham (H)	42.8	Mod. persistent	0-0.26	-	-	-
Chlorpyrifos (I)	386	Very persistent	-	0.72-0.96	0 - 0.50	amount NA
Clethodim (H)	3.0	Non-persistent	0-0.19	-	-	-
Clopyralid (H)	23.7	Non- persistent	0-0.01	-	-	-
Cyazofamid (F)	10.0	Non-persistent	0-1.11	-	-	-
Cyflufenamid (F)	210	Persistent	-	-	0 - <0.01	-
Beta-cyfluthrin (I)	51.0	Mod. persistent	-	-	0 - 0.30	-
Cyhalothrin (I)	175	Persistent	-	-	0-0.04	-
Cymoxanil (F)	<1	Non-persistent	0.06-0.40	0-0.34	amount NA	-
Cypermethrin (I)	70.0	Mod. persistent	-	-	0-0.50	-
Cyromazine (I)	51.5	Mod. persistent	0-0.04	-	-	-
Deltamethrin(I)	26.0	Non-persistent	-	-	0 - 0.03	-
Desmedipham (H)	185	Persistent	0-<0.01	-	-	-
Difenoconazole (F)	130	Persistent	0-0.60	-	0 - 0.40	-
Dimethenamid-P (H)	35.1	Mod. persistent	0-0.18	-	-	-
Dimethomorph (F)	72.7	Mod. persistent	-	0.34-0.45	0 - 1.08	-
Diquat (H)	>1000	Very Persistent	0-0.52	-	-	-
Emamectin (I)	46.0	Mod. persistent	-	-	0 - 0.13	-
Epoxiconazole (F)	248	Persistent	-	0-0.03	-	-
Esfenvalerate (I)	249	Persistent	-	0.06-0.30	-	-

Table S4.1 (cont.) - Compounds applied in conventional farming systems and respective application rates in the sampled fields (total amount applied per field, kg or L compound/ha/year) – P-G-C=conventional grape production in Portugal; N-P-C=conventional potato production in the Netherlands; S-V-C=conventional vegetable production in Southeast-Spain, S-O-C=conventional orange production in Spain. F-fungicide, H-herbicide, I-insecticide; O-other; NA-not available. Typical DT_{50} values and respective interpretations were extracted from the PPDB database (*PPDB. 2020*). DT_{50} values above 100 days were rounded to the unit. An empty box (-) indicates that the compound was not reported to be applied by any of the farmers interviewed in that Case Study Site, CSS. When only some farmers in a CSS applied a compound, the range of applications of that CSS starts with zero. Application rates were rounded to two decimal cases. Mod.=moderately.

Compound	DT_{50} soil (days)	DT_{50} Interpretation	N-P-C	P-G-C	S-V-C	S-O-C
Ethofumesate (H)	37.8	Mod. persistent	-	<0.01-0.80	-	-
Etoxazole (I)	19.3	Non-persistent	-	-	Amount NA	amount NA
Fenhexamid (F)	<1	Non-persistent	-	-	amount NA	-
Fenoxaprop-P(H)	24.8	Non-persistent	-	<0.01-0.01	-	-
Fenpropimorph (F)	50.6	Mod. persistent	-	0.27-2.20	-	-
Flonicamid (I)	1.1	Non-persistent	-	0-0.10	0 – 5.00	-
Florasulam (H)	8.5	Non-persistent	-	0-<0.01	-	-
Fluazinam (F)	25.9	Non-persistent	-	-	0 - 1.50	-
Fludioxonil(F)	164	Mod. persistent	-	-	0 - 0.15	-
Flufenoxuron (I)	72.5	Mod. persistent	-	-	amount NA	-
Fluopicolide (F)	271	Persistent	-	0-0.11	0 - 0.19	-
Fluoxastrobin (F)	58.8	Mod. persistent	-	0-0.08	-	-
Fluroxypyr (H)	51.0	Mod. persistent	-	0.03-0.70	-	-
Folpet (F)	4.7	Non-persistent	1.25-3.96	-	amount NA	amount NA
Fosetyl (F)	<1	Non-persistent	0-0.50	-	amount NA	amount NA
Glyphosate (H)	15.0	Non-persistent	amount NA	0-0.071	-	amount NA
Glufosinate (H)	7.4	Non-persistent	-	0.03-0.38	-	-
Iodosulforon (H)	6.0	Non-persistent	-	0-<0.01	-	-
Imidacloprid (I)	191	Persistent	-	-	0 - 0.42	-
Indoxacarb (I)	113	Persistent	-	-	0.08 - 0.08	-
Isopyrazam (F)	244	Persistent	-	0-0.08	-	-
Iprodione (F)	36.2	Mod. persistent	0-0.67	-	-	-
kresoxim-methyl (F)	1.0	Non-persistent	-	0-0.22		-
kresoxim-methyl (F)	16.0	Non-persistent	0-0.04	-	amount NA	-
Lambda-Cyhalothrin (I)	175	Persistent	-	0.05-0.60	0 - 0.04	-
Lenacil (H)	49.7	Mod. persistent	-	<0.01-<0.01	-	-
Linuron (H)	57.6	Mod. persistent	-	-	amount NA	amount NA
Maleic_hydrazide (H*)	<1	Non-persistent	-	0-4.89	-	-
Mancozeb (F)	<1	Non-persistent	1.08-3.89	0.22-0.89	amount NA	-

Table S4.1 (cont.) - Compounds applied in conventional farming systems and respective application rates in the sampled fields (total amount applied per field, kg or L compound/ha/year) – P-G-C=conventional grape production in Portugal; N-P-C=conventional potato production in the Netherlands; S-V-C=conventional vegetable production in Southeast-Spain, S-O-C=conventional orange production in Spain. F-fungicide, H-herbicide, I-insecticide; O-other; NA-not available. Typical DT_{50} values and respective interpretations were extracted from the PPDB database (*PPDB. 2020*). DT_{50} values above 100 days were rounded to the unit. An empty box (-) indicates that the compound was not reported to be applied by any of the farmers interviewed in that Case Study Site, CSS. When only some farmers in a CSS applied a compound, the range of applications of that CSS starts with zero. Application rates were rounded to two decimal cases. Mod.=moderately.

Compound	DT_{50} soil (days)	DT_{50} Interpretation	N-P-C	P-G-C	S-V-C	S-O-C
Mandipropamid (F)	49.1	Persistent	-	020-1.90	0 - 0.15	-
MCPA (H)	24.0	Non-persistent	-	0-12.00	-	-
Mefenpyr (H)	17.5	Non-persistent	-	0-<0.01	-	-
Mesosulfuron (H)	43.5	Moderately persistent	-	0-0.09	-	-
Metamitron (H)	30.0	Mod. persistent	-	0.09-2.30	-	-
Metalaxyl (F)	36.0	Mod. persistent	0.20-0.58	-	amount NA	amount NA
Metribuzin (H)	11.5	Non-persistent	-	1.18-2.88	amount NA	-
Oxamyl (I)	5.3	Non-persistent	-	0-1.80	-	-
Metiram (F)	1.3	Non-persistent	0-0.83	-	0 - 5.60	-
Metrafenone (F)	201	Persistent	0.13-0.30	-	amount NA	-
Pendimethalin (H)	182	Persistent	-	0-0.25	0 - 1.37	-
Propamocarb (F)	14.0	Non-persistent	-	7.80-11.60	0 - 1.58	-
Oxyfluorfen (H)	35.0	Mod. persistent	-	-	0 - 0.38	amount NA
Penconazole (F)	117	Persistent	0-0.07	-	-	-
Prosulfocarb (H)	11.9	Non-persistent	-	0-0.01	0 - 3.20	-
Permethrin (I)	42.0	Moderately persistent	-	-	-	amount NA
Pirimicarb (I)	86.0	Mod. persistent	-	-	amount NA	-
Prothioconazole (F)	14.1	Non-persistent	-	0.01-1.10	-	-
Propyzamide (H)	50.0	Moderately persistent	-	-	0 - 1.20	-
Pymetrozine (I)	5.0	Non-persistent	-	0-1.20	-	-
Pyraclostrobin (F)	41.9	Mod. persistent	0-0.08	0-0.07	0.07 - 2.21	-
Pyraflufen-ethyl (H)	<1	Non-persistent	-	0.03-0.20	-	-
Pyroxsulam (H)	3.3	Non-persistent	-	0-<0.01	-	-
S-Metolachlor (H)	51.8	Moderately persistent	-	0-0.42	-	-
Pyrimethanil (F)	50.9	Moderately persistent	0-0.80	-	-	-
Pyriproxyfen (I)	10.0	Non-persistent	-	-	-	amount NA
Spinosad (I)	13.0	Non-persistent	-	-	0 - 0.24	-
Spirotetramat (I)	29.9	Non-persistent	-	-	0 - 0.75	-
Tebuconazole (F)	63.0	Mod. persistent	0-0.10	0.01-0.07	-	-
Tembotrione (H)	14.5	Non persistent	-	-	0 - 0.10	-

Table S4.2 - Tested compounds (i.e. active substances and metabolites) across Case Study Sites, CSS. An empty box (-) indicates that the compound was not tested in that CSS samples. Approval status refers to 27 July 2020 status at the EU pesticides database. P-G=grape production in Portugal; N-P=potato production in the Netherlands; S-V=vegetables production in Southeast-Spain, S-O=orange production in Spain.

Compound	Status	Limit of quantification (mg/kg)			
		P-G	N-P	S-V	S-O
2,4,5-T	Not approved	-	-	-	0.010
2,4-DB	Approved	-	-	-	0.010
Abamectin	Approved	-	-	-	0.010
Acephate	Not approved	-	-	-	0.010
Aldicarb	Not approved	-	-	-	0.010
Aldrin	Not approved	0.010	0.001	-	0.010
Ametoctradin	Approved	-	-	0.011	-
AMPA	Metabolite	0.050	0.050	-	0.050
Atrazine	Not approved	0.010	-	-	0.010
Atrazine, Desethyl	Metabolite	0.010	-	-	-
Atrazine, Desisopropyl	Metabolite	0.010	-	-	-
Azadirachtin	Approved	-	-	0.011	-
Azoxystrobin	Approved	0.010	0.001	0.001	-
Bentazone	Approved	-	0.001	-	-
Benthiavalicarb	Approved	-	0.001	-	-
Bixafen	Approved	-	0.001	-	-
Boscalid	Approved	-	0.001	0.001	0.010
Bromacil	Not approved	-	-	-	0.010
Captan	Approved	-	-	-	0.010
Carbaryl	Not approved	-	-	-	0.010
Carbendazim	Not approved	-	-	-	0.010
Carbofuran	Not approved	0.010	-	-	-
Carbofuran, keto	Metabolite	0.010	-	-	-
Carbofuran, 3-hydroxy	Metabolite	0.010	-	-	-
Clethodim	Approved	-	0.001	-	-
Chlorantraniliprole	Approved	-	-	0.001	-
Chlorbromuron	Not approved	-	-	-	0.010
Chlordane, alpha	Not approved	0.010	-	-	-
Chlordane, trans	Not approved	0.010	-		-
Chlorfenvinphos	Not approved	0.010	-	-	0.010
Chloridazon	Not approved	-	0.001	-	-
Clorimuron-ethyl	Not approved	-	-	0.001	-
Chlorpropham	Not approved	-	0.005	-	-
Chlorpyrifos	Not approved	0.010	-	0.004	0.010
Chlorpyrifos-methyl	Not approved	-	-	-	0.010
Clomazone	Approved	-	-	-	0.010
Cyflufenamid	Approved	-	-	0.001	-
Cyfluthrin	Not approved	-	-	0.011	-
Cyhalothrin	Not approved	-	-	0.011	-
Cymoxanil	Approved	-	0.001	0.004	-
Cypermethrin	Approved	-	-	0.011	-
Cyprodinil	Approved	0.010	-	-	0.010
Cyromazine	Not approved	-	0.005	-	-
DDD op	Metabolite	0.010	0.001	-	0.010
DDD pp	Metabolite	0.010	0.001	-	0.010
DDE op	Metabolite	0.010	0.001	-	0.010
DDE pp	Metabolite	0.010	0.001	-	0.010
DDMU	Metabolite	-	-	-	0.010
DDT op	Not approved	0.010	0.001	-	0.010
DDT pp	Not approved	0.010	0.001	-	0.010

Table S4.2 (cont.) - Tested compounds (i.e. active substances and metabolites) across Case Study Sites, CSS. An empty box (-) indicates that the compound was not tested in that CSS samples. Approval status refers to 27 July 2020 status at the EU pesticides database. P-G=grape production in Portugal; N-P=potato production in the Netherlands; S-V=vegetables production in Southeast-Spain, S-O=orange production in Spain.

Compound	Status	Limit of quantification (mg/kg)			
		P-G	N-P	S-V	S-O
Deltamethrin	Approved	-	-	0.001	-
Desmedipham	Not approved	-	0.001	-	-
Diazinon	Not approved	-	-	-	0.010
Dichlofluanid	Not approved	-	-	-	0.010
Dichlorvos	Not approved	-	-	-	0.010
Dieldrin	Not approved	0.010	-	-	-
Difenoconazole	Approved	-	-	0.001	-
Dimethenamid-P	Approved	-	0.001	-	-
Dimethoate	Not approved	-	-	-	0.010
Dimethomorph	Approved	0.010	-	0.001	-
Dinoterb	Not approved	-	-	-	0.010
Disulfoton	Not approved	-	-	-	0.010
Diuron	Approved	-	-	-	0.010
Emamectin	Approved	-	-	0.001	-
Endosulfan, alpha	Not approved	0.010	-	-	0.010
Endosulfan, beta	Not approved	0.010	-	-	0.010
Endosulfan, sulfate	Metabolite	0.010	-	-	0.010
Endrin	Not approved	0.010	-	-	-
Ethion	Not approved	-	-	-	0.010
Ethoprophos	Not approved	-	-	-	0.010
Etoxazole	Approved	-	-	-	0.010
Fenamiphos	Approved	-	-	-	0.010
Fenhexamid	Approved	-	-	0.002	-
Fenitrothion	Not approved	-	-	-	0.010
Fenoxaprop-P	Approved	-	0.001	-	-
Fenpropimorph	Not approved	-	0.001	-	-
Flonicamid	Approved	-	0.001	0.001	-
Fluazinam	Approved	-	-	0.022	-
Flufenoxuron	Not approved	-	-	0.001	-
Fluopicolide	Approved	-	0.001	0.001	-
Flutolanil	Approved	-	-	-	0.010
Folpet	Approved	0.010	-	-	0.010
Glyphosate	Approved	0.050	0.05	-	0.050
Heptachlor	Not approved	0.010	-	-	-
Hexachlorobenzene	Not approved	0.010	-	-	-
Hexachlorocyclohexane, alpha	Not approved	0.010	-	-	-
Hexachlorocyclohexane, beta	Not approved	0.010	-	-	-
Imidacloprid	Approved	-	-	0.001	-
Indoxacarb	Approved	-	-	0.001	-
Isoproturon	Not approved	-	-	-	0.010
Kresoxim-methyl	Approved	-	-	0.022	-
Lenacil	Approved	-	0.001	-	0.010
Lindane	Not approved	0.010	-	-	-
Linuron	Not approved	-	0.001	0.011	0.010
MCPA	Approved	-	-	-	0.010
Malathion	Approved	-	-	-	0.010
Metalaxyl	Approved	0.010	-	0.011	0.010
Metamitron	Approved	-	0.001	-	-
Methabenzthiazuron	Not approved	-	-	-	0.010
Methidathion	Not approved	-	-	-	0.010

Table S4.2 (cont.) - Tested compounds (i.e. active substances and metabolites) across Case Study Sites, CSS. An empty box (-) indicates that the compound was not tested in that CSS samples. Approval status refers to 27 July 2020 status at the EU pesticides database. P-G=grape production in Portugal; N-P=potato production in the Netherlands; S-V=vegetables production in Southeast-Spain, S-O=orange production in Spain.

Compound	Status	Limit of quantification (mg/kg)			
		P-G	N-P	S-V	S-O
Methomyl	Not approved	-	-	-	0.010
Metrafenone	Approved	-	-	0.001	-
Metribuzin	Approved	-	0.001	0.011	-
Metolachlor	Not approved	-	0.001	-	-
Metoxuron	Not approved	-	-	-	0.010
Mevinphos	Not approved	-	-	-	0.010
Myclobutanil	Approved	0.010	-	-	-
Omethoate	Not approved	-	-	-	0.010
Oxamyl	Approved	-	-	-	0.010
Oxydemeton-methyl	Not approved	-	-	-	0.010
Oxyfluorfen	Approved	-	-	0.001	0.010
Parathion	Not approved	-	-	-	0.010
Parathion-methyl	Not approved	-	-	-	0.010
Penconazole	Approved	0.010	-	-	-
Pendimethalin	Approved	-	0.001	0.004	-
Pentachlorobenzene	Not approved	0.010	-	-	-
Permethrin	Not approved	-	-	-	0.010
Phorate	Not approved	-	-	-	0.010
Phthalimide (PTI)	Metabolite	-	-	-	0.010
Pirimicarb	Approved	-	-	0.001	-
Pirimiphos-methyl	Approved	-	-	-	0.010
Prochloraz	Approved	-	-	-	0.010
Procymidone	Not approved	0.010	-	-	-
Profenofos	Not approved	-	-	-	0.010
Propamocarb	Approved	-	0.001	0.001	-
Propiconazole	Not approved	0.010	-	-	-
Propyzamide	Approved	-	-	0.011	-
Prosulfocarb	Approved	-	0.001	-	-
Prothioconazole	Approved	-	0.005	-	-
Prothioconazole, dethio	Metabolite	-	0.001	-	-
Pyraclostrobin	Approved	0.010	-	0.001	-
Pyrazophos	Not approved	-	-	-	0.010
Pyrimethanil	Approved	0.010	-	-	-
Pyriproxyfen	Approved	-	-	-	0.010
Quinoclamine	Not approved	-	-	-	0.010
Quinoxyfen	Not approved	0.010	-	-	-
Simazine	Not approved	-	-	-	0.010
Spinosyn-A	Approved	-	-	0.001	-
Spinosyn-D	Approved	-	-	0.001	-
Spirotetramat	Approved	-	-	0.001	-
Tebuconazole	Approved	0.010	0.001	-	-
Terbuthylazine	Approved	0.010	-	-	-
Terbuthylazine, Desethyl	Metabolite	0.010	-	-	-
Tetradifon	Not approved	-	-	-	0.010
Tetrahydrophthalimide (THPI)	Metabolite	-	-	-	0.010
Thiabendazole	Approved	-	-	-	0.010
Thiacloprid	Not approved	-	-	0.001	-
Tolylfluanid	Not approved	-	-	-	0.010
Trifloxystrobin	Approved	0.010	-	-	-
Vinclozolin	Not approved	0.010	-	-	-

Table S4.3 - Frequency and range of concentrations of detected compounds across Case Study Sites, CSS. An empty box ( ) indicates that the compound was not tested in that CSS samples. An - indicates that the compound was tested but not found (i.e. below the respective limit of quantification).

	P-G (conv)				N-P (conv/org)				SV (conv/org)				S-O (conv/org)			
	% freq	Q1	Max	Median	% freq	Q1	Max	Median	% freq	Q1	Max	Median	% freq	Q1	Max	Median
2,4,5-T													0/0	-	-	-
2,4-D													0/0	-	-	-
Abamectin													0/0	-	-	-
Acephate													0/0	-	-	-
Aldicarb													0/0	-	-	-
Aldrin	0	-	-	-	0/0	-	-	-					0/0	-	-	-
Ametoctradin									0/ 0	-	-	-				
AMPA	83.3	0.260	4.294	0.505	96.4/ 83.3	0.027 / 0.012	0.528/ 0.015	0.038 / 0.014					87.0/ 16.6	0.102/ 0.069	1.626/ 0.593	0.261/ 0.070
Atrazine	0	-	-	-									0/0	-	-	-
Atrazine, Desethyl	0	-	-	-												
Atrazine, Desisopropyl	0	-	-	-												
Azadirachtin									0/ 0	-	-	-				
Azoxystrobin	3.7	0.014	0.022	0.019	85.7/0	0.002/ -	0.044/-	0.005/-	72/ 0	0.005/ -	0.153/ -	0.009/ -				
Bentazone					0/0	-	-	-								
Benthiavalicarb					0/0	-	-	-								
Bixafen					71.4/ 83.3	0.008/ 0.001	0.050/ 0.003	0.011/ 0.001								
Boscalid					60.7/ 66.7	0.008/ 0.001	0.270/ 0.002	0.015/ 0.001	85/ 0	0.011/ -	0.33/ -	0.055/ -	0/0	-	-	-
Bromacil													0/0	-	-	-
Captan													0/0	-	-	-
Carbaryl													0/0	-	-	-
Carbendazim													0/0	-	-	-
Carbofuran	0	-	-	-												
Carbofuran, - keto	0	-	-	-												
Carbofuran, 3-hydroxy	0	-	-	-												
Clethodim					0/0	-	-	-								
Chlorantraniliprole									100/ 7	0.01/ 0.001	0.101/ 0.001	0.017/ 0.001				
Chlorbromuron													0/0	-	-	-
Chlordane- alpha	0	-	-	-												
Chlordane-trans	0	-	-	-												
Chlorfenvinphos	0	-	-	-									0/0	-	-	-
Chloridazon					29.0/0	0.002/-	1.529/0	0.002/0								

Table S4.3 (cont.) - Frequency and range of concentrations of detected compounds across Case Study Sites, CSS. An empty box ( ) indicates that the compound was not tested in that CSS samples. An - indicates that the compound was tested but not found (i.e. below the respective limit of quantification).

	P-G (conv)				N-P (conv/org)				SV (conv/org)				S-O (conv/org)			
	% freq	Q1	Max	Median	% freq	Q1	Max	Median	% freq	Q1	Max	Median	% freq	Q1	Max	Median
Clorimuron-ethyl									6/0	0.002/ -	0.002/ -	0.002/ -				
Chlorpropham					0/0	-	-	-								
Chlorpyrifos	0	-	-	-	0/0	-	-	-					0/0	-	-	-
Chlorpyrifos-methyl													7.4/0	0.013/ -	0.023/ -	0.016/ -
Clomazone													0/0	-	-	-
Cyflufenamid									4/0	0.001/ -	0.001/ -	0.001/ -				
Cyfluthrin									2/0	0.004/ -	0.004/ -	0.004/ -				
Cyhalothrin									0/ 2	-/ 0.012	-/ 0.012	-/ 0.012				
Cymoxanil					0/0	-	-	-	0/0							
Cypermethrin									22/ 0	0.003/ -	0.077/ -	0.012/ -				
Cyprodinil	0	-	-	-									0/0	-	-	-
Cyromazine		-	-	-	0/0	-	-	-								
DDD op	0	-	-	-	0/0	-	-	-					0/2.8	-/0.012	-/0.012	-/0.012
DDD pp	0	-	-	-	32.1/ 16.7	0.001/ 0.002	0.005/ 0.002	0.002/ 0.002					12.9/ 44.4	0.011/ 0.014	0.032/ 0.071	0.017/ 0.017
DDE op	0	-	-	-	0/ 0	-	-	-					0/ 0	-	-	-
DDE pp	0	-	-	-	67.9/ 83.3	0.002/ 0.002	0.030/ 0.004	0.003/ 0.002					77.8 /88.9	0.016 /0.045	0.161 /0.80	0.031 /0.57
DDMU													0/ 0			
DDT o,p	0	-	-	-	0/0	-	-	-					0/8.3	- /0.014	- /0.022	- /0.021
DDT p,p	0	-	-	-	14.3/0	0.011/-	0.022/-	0.012/-					18.5/ 55.6	0.013/ 0.014	0.026/ 0.089	0.016/ 0.021
Deltamethrin									4/2	0.001/ 0.001	0.001/ 0.001	0.001/ 0.001				
Desmedipham					0/0	-	-	-								
Diazonin													0/0	-	-	-
Dichlofluanid													0/0	-	-	-
Dichlorvos													0/0	-	-	-
Dieldrin	11.1	0.025	0.092	0.041												
Difenoconazole									65/ 17	0.006/ 0.001	0.062/ 0.001	0.019/ 0.001				
Dimethenamid-P					0/0	-	-	-								
Dimethoate													0/0	-	-	--
Dimethomorph	100	0.029	0.301	0.056					24/ 0	0.001/ -	0.011/ -	0.003/ -				
Dinoterb													0/0	-	-	-
Disulfoton													0/0	-	-	-
Diuron													0/0	-	-	-
Emamectin									7/0	0.001/ -	0.001/ -	0.001/ -				

Table S4.3 (cont.) - Frequency and range of concentrations of detected compounds across Case Study Sites, CSS. An empty box ( ) indicates that the compound was not tested in that CSS samples. An - indicates that the compound was tested but not found (i.e. below the respective limit of quantification).

	P-G (conv)				N-P (conv/org)				SV (conv/org)				S-O (conv/org)			
	% freq	Q1	Max	Median	% freq	Q1	Max	Median	% freq	Q1	Max	Median	% freq	Q1	Max	Median
Endosulfan alpha	0	-	-	-									0/0	-	-	-
Endosulfan beta	0	-	-	-									0/0	-	-	-
Endosulfan sulfate	0	-	-	-									0/0	-	-	-
Endrin	0	-	-	-												
Ethion													3.7/0	0.011/-	0.014/-	0.012/-
Ethoprophos													0/0	-	-	-
Etoxazole													0/0	-	-	-
Fenamiphos													0/0	-	-	-
Fenhexamid									0/0	-	-	-				
Fenitrothion													0/0	-	-	-
Fenoxaprop-ethyl					0/0	-	-	-								
Fenpropimorph					6.0/0	0.014/-	0.014/-	0.014/-								
Flonicamid					0/0				0/0	-	-	-				
Fluazinam									0/0	-	-	-				
Flufenoxuron									0/0	-	-	-				
Fluopicolide					78.6/0	0.012/-	0.061/-	0.017/-	48/ 0	0.009/-	0.096/ -	0.024/ -				
Flutolanil													0/0	-	-	-
Folpet	3.7	0.021	0.129	0.039									0/0	-	-	-
Glyphosate	77.8	0.179	7.843	0.452	92.9/0	0.019/-	1.306/-	0.030/-					22.2/ 5.6	0.070/ 0.076	0.18/ 0.105	0.090/ 0.090
Heptachlor	0	-	-	-												
HCH	0	-	-	-												
HCH beta	0	-	-	-												
HCH alpha	0	-	-	-												
Imidacloprid									93/ 30	0.002/ 0.001	0.163/ 0.002	0.004/ 0.001				
Indoxacarb									33/ 0	0.001/-	0.022/ -	0.001/-				
Isoproturon													0/0	-	-	-
Kresoxim-methyl									7/0	0.033/ -	0.042/-	0.041/ -				
Lenacil					0/0	-	-	-					0/0	-	-	-
Lindane	0	-	-	-												
Linuron					60.7/0	0.012/-	0.012/-	0.012/-	4/0	0.005/-	0.007/ -	0.005/ -	0/0	-	-	-
MCPA													0/0	-	-	-

Table S4.3 (cont.) - Frequency and range of concentrations of detected compounds across Case Study Sites, CSS. An empty box ( ) indicates that the compound was not tested in that CSS samples. An - indicates that the compound was tested but not found (i.e. below the respective limit of quantification).

	P-G (conv)				N-P (conv/org)				SV (conv/org)				S-O (conv/org)			
	% freq	Q1	Max	Median	% freq	Q1	Max	Median	% freq	Q1	Max	Median	% freq	Q1	Max	Median
Melathion													0/0	-	-	-
Metalaxyl	50.9	0.017	0.173	0.034					0/0	-	-	-	0/0	-	-	-
Metamitron					46.4/0	0.001/-	0.005/-	0.002/-								
Methabenzthiazuron													0/0	-	-	-
Methidathion													0/0	-	-	-
Methomyl													0/0	-	-	-
Metrafenone									56/0	0.006/-	0.021/-	0.009/-				
Metribuzin					0/0	-	-	-	0/0	-	-	-				
Metolachlor					0/0	-	-	-								
Metoxuron													0/0	-	-	-
Mevinphos													0/0	-	-	-
Myclobutanil	0	-	-	-												
Omethoate													0/0	-	-	-
Oxamyl													0/0	-	-	-
Oxydemeton-methyl													0/0	-	-	-
Oxyfluorfen									70/ 0	0.009/ -	0.605/ -	0.051/ -	37.0/0	0.016/-	0.085/-	0.023/-
Parathion													0/0	-	-	-
Parathion-methyl													0/0	-	-	-
Penconazole	16.7	0.012	0.049	0.021												
Pendimethalin					42.9/0	0.002/-	0.024/-	0.004/-	63/ 0	0.007/ -	0.234/ -	0.01/ -				
Pentachlorobenzene	0	-	-	-												
Permethrin													0/0	-	-	-
Phorate													0/0	-	-	-
Phthalimide (PTI)													0/0	-	-	-
Pirimicarb									2/0	0.001/ -	0.001/-	0.001/-				
Pirimiphos-methyl													0/0	-	-	-
Prochloraz													33.3/ 16.7	0.012/ 0.028	0.054/ 0.083	0.013/ 0.033
Procymidone	0	-	-	-												
Profenofos													0/0	-	-	-
Propamocarb					0/0	-	-	-	2/0	0.001/ -	0.001/ -	0.001/ -				
Propiconazole	0	-	-	-												

Table S4.3 (cont.) - Frequency and range of concentrations of detected compounds across Case Study Sites, CSS. An empty box ( ) indicates that the compound was not tested in that CSS samples. An - indicates that the compound was tested but not found (i.e. below the respective limit of quantification).

	P-G (conv)				N-P (conv/org)				SV (conv/org)				S-O (conv/org)			
	% freq	Q1	Max	Median	% freq	Q1	Max	Median	% freq	Q1	Max	Median	% freq	Q1	Max	Median
Propyzamide									6/0	0.002/ -	0.004/ -	0.002/ -				
Prosulfocarb					100/ 100	0.004/ 0.004	0.006/ 0.004	0.004/ 0.004								
Prothioconazole					0/0	-	-	-								
Prothioconazole >dethio					3.6/0	0.010/-	0.010/-	0.010/-								
Pyraclostrobin	31.5	0.018	0.058	0.029					56/ 0	0.002/-	0.034/ -	0.003/ -				
Pyrazophos													0/0	-	-	-
Pyrimethanil	3.7	0.012	0.022	0.015												
Pyriproxyfen													0/0	-	-	-
Quinoclamine													0/0	-	-	-
Quinoxyfen	0	-	-	-												
Simazine													0/0	-	-	-
Spinosyn-A									0/ 20	-/ 0.001	-/ 0.008	-/ 0.001				
Spinosyn-D									0/ 19	-/ 0.001	-/ 0.008	-/ 0.002				
Spirotetramat									0/0	-	-	-				
Tebuconazole	15.7	0.010	0.096	0.011	32.1/ 16.7	0.001/ 0.002	0.013/ 0.002	0.002/ 0.002								
Terbuthylazine	0	-	-	-												
Terbuthylazine, Desethyl	0	-	-	-												
Tetradifon													9/0	0.013/-	0.039/-	0.014/-
THPI													0/0	-	-	-
Thiabendazole													0/0	-	-	-
Thiacloprid									0/0	-	-	-				
Tolylfluanid													0/0	-	-	-
Trifloxystrobin	0	-	-	-												
Vinclozolin	0	-	-	-												

Supplementary material – Chapter 5

Table S5.1 – List of the EU-approved active substances excluded per exclusion criterion.

CRITERION 1: No fungicide, herbicide or insecticide properties (classification PPDB database)	
119	Acaricides: Acequinocyl, Acrinathrin, Bifenazate, Clofentezine, Cyflumetofen, Fenazaquin, Fenpyroximate, Tebufenpyrad; Attractants: (E)-11-Tetradecen-1-yl acetate, (E)-5-Decen-1-ol, (E)-5-Decen-1-yl acetate, (E)-8-Dodecen-1-yl acetate, (E,E)-7,9-Dodecadien-1-yl acetate, (E,E)-8,10-Dodecadien-1-ol, (E,Z)-2,13-Octadecadien-1-yl acetate, (E,Z)-3,8-Tetradecadien-1-yl acetate, (E,Z)-7,9-Dodecadien-1-yl acetate, (E,Z)-8-Dodecen-1-yl acetate, (E,Z)-9-Dodecen-1-yl acetate, (E,Z,Z)-3,8,11-Tetradecatrien-1-yl acetate, (Z)-11-Hexadecen-1-ol, (Z)-11-Hexadecen-1-yl acetate, (Z)-11-Hexadecenal, (Z)-11-Tetradecen-1-yl acetate, (Z)-13-Octadecenal, (Z)-7-Tetradecenal, (Z)-8-Dodecen-1-ol, (Z)-8-Dodecen-1-yl acetate, (Z)-9-Dodecen-1-yl acetate, (Z)-9-Hexadecenal, (Z)-9-Tetradecen-1-yl acetate, (Z,E)-7,11-Hexadecadien-1-yl acetate, (Z,E)-9,11-tetradecadien-1-yl-acetate, (Z,E)-9,12-Tetradecadien-1-yl acetate, (Z,Z)-7,11-Hexadecadien-1-yl acetate, Ammonium acetate, Diammonium phosphate, Dodecan-1-ol, Dodecyl acetate, E,Z-3,13-Octadecadienyl Acetate, n-hexadecanyl acetate, n-Tetradecylacetate, Putrescine (1,4-Diaminobutane), Straight Chain Lepidopteran Pheromones, Tetradecan-1-ol, Trimethylamine hydrochloride, Z,Z-3,13-Octadecadienyl Acetate; Bactericides: Aluminium sulphate, Sodium hypochlorite; Elicitors: Chitosan hydrochloride, Fructose, Heptamaloxyloglucan, Laminarin, Mild Pepino Mosaic Virus isolate VC 1, Mild Pepino Mosaic Virus isolate VX 1, Sucrose, Zucchini Yellow Mosaik Virus weak strain; Elicitor & Virus inoculation: Pepino mosaic virus strain CH2 isolate 1906; Molluscicides: Beer, Ferric phosphate, Metaldehyde; Nematicides: *Bacillus firmus* I-1582, Fenamiphos (aka phenamiphos), Fosthiazate, *Paecilomyces lilacinus* strain 251, *Pasteuria nishizawae* Pn1; Plant activator: Acibenzolar-S-methyl (benzothiadiazole), Cerevisane; Plant growth regulators: 1,4-Dimethylnaphthalene, 1-Decanol; 1-Methyl-cyclopropene, 1-Naphthylacetamide (1-NAD), 1-Naphthylacetic acid (1-NAA), 6-Benzyladenine, Carvone, Chlormequat, Daminozide, Ethephon, Ethylene, Flumetralin, Forchlorfenuron, Gibberellic acid, Gibberellin, Indolylbutyric acid, Maleic hydrazide, Mepiquat, Paclobutrazol, Prohexadione, S-Abscisic acid, Sea-algae extract (formerly sea-algae extract and seaweeds), Sintofen (aka Cintofen), Sodium 5-nitroguaiacolate, Sodium o-nitrophenolate, Sodium p-nitrophenolate, Sodium silver thiosulphate, Trinexapac (aka cimetacarb ethyl); Repellants: Aluminium ammonium sulphate, Aluminium silicate (aka kaolin), Blood meal, Calcium carbide, Calcium carbonate, Denathonium benzoate, Fat distilation residues, Garlic extract, Limestone, Pepper dust extraction residue (PDER), Plant oils / Clove oil, Quartz sand, Repellents by smell of animal or plant origin/ fish oil, Repellents by smell of animal or plant origin/ sheep fat, Sodium aluminium silicate; Rodenticides: Bromadiolone, Calcium phosphide, Difenacoum, Zinc phosphide;unspecified: Clayed charcoal, Onion oil, Plant oils / Spear mint oil, Talc E553B.

Table S5.1 (cont.)– List of the EU-approved active substances excluded per exclusion criterion.

CRITERION 2: No data on degradation rates in soil and on predicted environmental concentration in soil (PECs; data from EU dossiers)	
116	2,5-Dichlorobenzoic acid methylester, 2-Phenylphenol, Acetic acid, *Adoxophyes orana* GV strain BV-000, Aluminium phosphide, *Ampelomyces quisqualis*, *Aureobasidium pullulans*, *Bacillus amyloliquefaciens* MBI 600, *Bacillus amyloliquefaciens* strain FZB24, *Bacillus amyloliquefaciens* strain QST 713, *Bacillus amyloliquefaciens subsp. plantarum* D747, *Bacillus pumilus* QST 2808, *Bacillus thuringiensis subsp. Aizawai* strains ABTS-1857 and GC-91, *Bacillus thuringiensis subsp. Israeliensis* strain AM65-52, *Bacillus thuringiensis subsp. Kurstaki* strains ABTS 351, PB 54, SA 11, SA12 and EG 2348, *Bacillus thuringiensis subsp. Tenebrionis* strain NB 176, *Beauveria bassiana* IMI389521, PPRI 5339, strain 147, strain NPP111B005, strains ATCC 74040 and GHA, Beflubutamid, Benalaxyl, Benfluralin, Bensulfuron methyl, Benzoic acid, Bordeaux mixture, Buprofezin, Calcium hydroxide, *Candida oleophila* strain O, Capric acid, Caprylic acid, Carbon dioxide, Chlorotoluron, Chlorpyrifos-methyl, *Clonostachys rosea* strain J1446, *Coniothyrium minitans* Strain CON/M/91-08 (DSM 9660), Copper hydroxide, Copper oxide, Copper oxychloride, COS-OGA, *Cydia pomonella Granulovirus* (CpGV), Deltamethrin, Diflubenzuron, *Equisetum arvense* L., Etridiazole, Fatty acids C7 to C20, Fatty acids C7-C18 and C18 unsaturated potassium salts, Fatty acids C8-C10 methyl esters (CAS 85566-26-3), Fluquinconazole, Helicoverpa armigera nucleopolyhedrovirus (HearNPV), Hydrogen peroxide, Hydrolysed proteins, I*saria fumosorosea Apopka* strain 97, *Kieselgur*, Lauric acid, *Lecanicillium muscarium* strain Ve6, Lecithins, Lime Sulphur, Magnesium phosphide, Mancozeb, Maltodextrin, MCPA, MCPB, Metalaxyl, *Metarhizium anisopliae* var. anisopliae strain BIPESCO 5/F52, Methyl decanoate, Methyl octanoate, Metiram, *Metschnikowia fructicola*, Milbemectin, Mustard seeds powder, Oleic acid, *Paecilomyces fumosoroseus* strain Fe9901, Paraffin oil/(CAS 72623-86-0), Paraffin oil/(CAS 97862-82-3), Pelargonic acid, *Phlebiopsis gigantea* (several strains), Phosphane, Pirimiphos-methyl, Plant oils / Citronella oil, Potassium hydrogen carbonate, Profoxydim, *Pseudomonas chlororaphis* strain MA342, *Pseudomonas* sp. Strain DSMZ 13134, Pythium oligandrum M1, Quizalofop-P, Rescalure, Salix spp. Cortex, *Saccharomyces cerevisiae* strain LAS02, S-Metolachlor, Sodium chloride, Sodium hydrogen carbonate, *Spodoptera littoralis nucleopolyhedrovirus*, Streptomyces K61, *Streptomyces lydicus* WYEC 108, Sulfuryl fluoride, Sunflower oil, Thiacloprid, Thiamethoxam, Thiencarbazone, Tribasic copper sulfate, *Trichoderma asperellum* strains ICC012, T25 and TV1, *Trichoderma asperellum* (strain T34), *Trichoderma atroviride* strains IMI 206040 and T11, *Trichoderma atroviride* strain I-1237, *Trichoderma atroviride* strain SC1, *Trichoderma gamsii* strain ICC080, *Trichoderma harzianum* strains T-22 and ITEM 908, *Trichoderma polysporum* strain IMI 206039, Triflumizole, Urea, Urtica spp., *Verticillium albo-atrum* strain WCS850, Vinegar, Whey.
CRITERION 3: Not synthetic pesticides (classification from PPDB)	
19	Natural compounds: Abamectin, Azadirachtin (Margosa extract), Emamectin, Eugenol, FEN 560 (Fenugreek seed powder), Geraniol, L-Ascorbic acid, Orange oil, Plant oils/ Rapeseed oil, Pyrethrins, Spinosad, tea tree oil/timorex, Terpenoid blend QRD-460, Thymol; Inorganic compounds: Copper compounds, Disodium phosphonate, Iron sulfate, Potassium phosphonates, Sulphur.

Table S5.2 - Correspondence between PPDB - Pesticide Properties DataBase and EC (eco)toxicological endpoints. All PPDB and EC (eco)toxicological endpoints were used in the comparison however, not all endpoints were considered in this study (in grey cells). A few endpoints were discarded due to major data gaps, i.e. there was no (eco)toxicological data available for at least two-thirds of the 230 selected a.s. Although "other soil macro-organisms" had also major gaps, these endpoints were not discarded, due to the overall limited data available to characterize the soil compartment. The complete directory of EC endpoints was included to guarantee correct identification in EU dossiers. LD_{50}/LC_{50} =Lethal Dose/Lethal Concentration 50% exposed organisms, NOAEL=No Observed Adverse Effect Level, NOEL =No Observable Effect Level. *at last access to PPDB in May 2021 mutagen category was replaced by genotoxicity.

Source PPDB, 2019	Source EC, 2015
Human Endpoints	
1. Carcinogen	Mammalian Toxicity – Impact on Human and Animal Health – Long-term toxicity and carcinogenicity – Relevant long-term NOAEL Mammalian Toxicity – Impact on Human and Animal Health – Long-term toxicity and carcinogenicity – Carcinogenicity Mammalian Toxicity – Impact on Human and Animal Health – Long-term toxicity and carcinogenicity – Relevant NOAEL for carcinogenicity
2. Mutagen* -*	Mammalian Toxicity – Impact on Human and Animal Health – Genotoxicity – Photomutagenicity Mammalian Toxicity – Impact on Human and Animal Health – Genotoxicity – Potential for genotoxicity
3. Endocrine disruptor	Mammalian Toxicity – Impact on Human and Animal Health – Other toxicological studies – Endocrine disrupting properties
4. Reproduction/ development effects	Mammalian Toxicity – Impact on Human and Animal Health – Reproductive toxicity – Reproduction toxicity Relevant parental NOAEL Mammalian Toxicity – Impact on Human and Animal Health – Reproductive toxicity – Reproduction toxicity Relevant reproductive NOAEL Mammalian Toxicity – Impact on Human and Animal Health – Reproductive toxicity – Reproduction toxicity Relevant offspring NOAEL Mammalian Toxicity – Impact on Human and Animal Health – Reproductive toxicity – Developmental toxicity Relevant maternal NOAEL Mammalian Toxicity – Impact on Human and Animal Health – Reproductive toxicity – Developmental toxicity Relevant developmental NOAEL
5. Acetylcholinesterase inhibitor	-
6. Neurotoxicant	Mammalian Toxicity – Impact on Human and Animal Health – Neurotoxicity – Acute neurotoxicity Mammalian Toxicity – Impact on Human and Animal Health – Neurotoxicity – Repeated neurotoxicity
7. Respiratory tract irritant	-
8. Skin irritant	Mammalian Toxicity – Impact on Human and Animal Health – Acute toxicity – Skin irritation
9. Skin sensitiser	Mammalian Toxicity – Impact on Human and Animal Health – Acute toxicity – Skin sensitisation
10. Eye irritant	Mammalian Toxicity – Impact on Human and Animal Health – Acute toxicity – Eye irritation
11. Phototoxicant	Mammalian Toxicity – Impact on Human and Animal Health – Acute toxicity – Phototoxicity
Ecotoxicological endpoints	
Mammals – acute, oral – LD_{50}	Ecotoxicology – Effects on birds and other terrestrial vertebrates – Mammals – acute – LD_{50}
Mammals – short-term, dietary – NOEL	Ecotoxicology – Effects on birds and other terrestrial vertebrates – Mammals – long-term – NOAEL
Birds – acute – LD_{50}	Ecotoxicology – Effects on birds and other terrestrial vertebrates – Birds – acute – LD_{50}
Birds – short-term, dietary – LC_{50}/LD_{50}	Ecotoxicology – Effects on birds and other terrestrial vertebrates – Birds – long-term – LD_{50}

Table S5.2 (cont.) - Correspondence between PPDB - Pesticide Properties DataBase and EC (eco)toxicological endpoints. All PPDB and EC (eco)toxicological endpoints were used in the comparison however, not all endpoints were considered in this study (in grey cells). A few endpoints were discarded due to major data gaps, i.e. there was no (eco)toxicological data available for at least two-thirds of the 230 selected a.s. Although "other soil macro-organisms" had also major gaps, these endpoints were not discarded, due to the overall limited data available to characterize the soil compartment. The complete directory of EC endpoints was included to guarantee correct identification in EU dossiers. LD_{50}/LC_{50} =Lethal Dose/Lethal Concentration 50% exposed organisms, NOAEL=No Observed Adverse Effect Level, NOEL =No Observable Effect Level.

Source PPDB, 2019	Source EC, 2015
Ecotoxicological endpoints (cont.)	
Fish – acute 96 hour – LC_{50} Fish – chronic 21 day – NOEC	Ecotoxicology – Aquatic species – Fish – acute 96 hour – LC_{50}, mortality Ecotoxicology – Aquatic species – Fish – chronic – growth, or development, or behaviour, or reproduction NOEC
Aquatic invertebrates – acute 48 hour – EC_{50} Aquatic invertebrates – chronic 21 day – NOEC	Ecotoxicology – Aquatic species – Aquatic invertebrates – 48 hour – EC_{50}, mortality Ecotoxicology – Aquatic species – Aquatic invertebrates – 21 day – EC_{50}, mortality
Aquatic crustaceans – Acute 96 hour – LC_{50}	-
Aquatic plants – acute 7 day – EC_{50}	Ecotoxicology – Aquatic species – Higher plant – EC_{50}, growth
Algae – acute 72 hour – EC_{50}, growth	Ecotoxicology – Aquatic species – Algae – 72 hour – EC_{50}, growth
Algae – acute 96 hour – NOEC, growth	-
Sediment dwelling organisms – Acute 96 hour – LC_{50}	-
Sediment dwelling organisms - Chronic 28 day – NOEC static, water	Ecotoxicology – Aquatic species – Sediment-dwelling organisms – 28 day – EC_{50}, NOEC static, or semi-static or flow-through
Sediment dwelling organisms – Chronic 28 day – NOEC sediment	-
Honeybees – contact acute 48 hour – LD_{50} Honeybees – oral acute 48 hour – LD_{50}	Ecotoxicology – Bees – acute – contact toxicity, LD_{50} Ecotoxicology – Bees – acute – oral toxicity, LD_{50}
Honeybees – Unknown mode acute 48 hour –LD_{50} -	- Ecotoxicology – Bees – chronic 10 day – LC_{50} Ecotoxicology – Bees – bee brood development – NOEC larvae Ecotoxicology – Bees – sub-lethal effects (behavioural and reproductive) – NOEC
Earthworms – acute 14 day – LC_{50} Earthworms – chronic – NOEC, reproduction	- Ecotoxicology – Non-target soil meso- and macro fauna – Earthworms – chronic – NOEC growth, reproduction, behaviour
Other soil macro-organisms – acute – LC_{50}/% effect Other soil macro-organisms – chronic – NOEC	Ecotoxicology – Non-target soil meso- and macro fauna – Other soil macroorganisms – NOEC
Other arthropod 1 – % effect	Ecotoxicology – Other arthropod species – mortality, LC_{50}
Soil micro-organisms – Nitrogen mineralisation Soil micro-organisms – Carbon mineralisation	Ecotoxicology – Nitrogen transformation, % effect -

Table S5.3 – List of the active substances covered in each pesticide scenario. BAU = Business As Usual, NH = No Herbicides, FDP = Fast Degradable Pesticides, TPB = Total Pesticide Ban, CFSE = Candidates For Substitution Excluded, LHP = Low Hazard Pesticides, SHH = Safe Human Health, LET = Low Ecosystem Toxicity, FU = fungicide; HB = herbicide; IN = insecticide.

Goal	-	Use Reduction				Hazard reduction		
active substance	**BAU**	**NH**	**FDP**	**TPB**	**CFSE**	**LHP**	**SHH**	**LET**
2,4-D (HB)	✓		✓		✓			✓
2,4-DB (HB)	✓		✓		✓	✓		
8-Hydroxyquinoline (FU)	✓	✓	✓					
Acetamiprid (IN)	✓	✓	✓		✓		✓	
Aclonifen (HB)	✓							
Alpha-Cypermethrin (IN)	✓	✓			✓			
Ametoctradin (FU)	✓	✓	✓		✓	✓	✓	
Amidosulfuron (HB)	✓		✓		✓	✓		
Aminopyralid (HB)	✓				✓	✓	✓	
Amisulbrom (FU)	✓	✓		✓	✓	✓		
Azimsulfuron (HB)	✓				✓	✓	✓	
Azoxystrobin (FU)	✓	✓		✓	✓	✓		✓
Benalaxyl-M (FU)	✓	✓			✓	✓		
Bentazone (HB)	✓		✓		✓	✓		
Benthiavalicarb (FU)	✓	✓	✓		✓	✓		
Benzovindiflupyr (FU)	✓	✓		✓		✓		
Beta-Cyfluthrin (IN)	✓	✓	✓	✓	✓			
Bifenox (HB)	✓		✓		✓	✓		
Bifenthrin (IN)	✓	✓		✓				
Bispyribac-sodium (HB)	✓		✓		✓	✓		✓
Bixafen (FU)	✓	✓		✓	✓			
Boscalid (FU)	✓	✓		✓	✓	✓		
Bromoxynil (HB)	✓		✓		✓	✓		✓
Bromuconazole (FU)	✓	✓		✓		✓		✓
Bupirimate (FU)	✓	✓			✓	✓		
Captan (FU)	✓	✓	✓		✓			✓
Carbetamide (HB)	✓		✓		✓	✓		
Carboxin (FU)	✓	✓	✓		✓	✓	✓	✓
Carfentrazone-ethyl (HB)	✓		✓		✓	✓		
Chlorantraniliprole (IN)	✓	✓		✓	✓	✓	✓	
Chlorothalonil (FU)	✓	✓	✓		✓			
Chlorpropham (HB)	✓		✓		✓	✓		✓
Chlorpyrifos (IN)	✓	✓			✓			
Chlorsulfuron (HB)	✓				✓	✓	✓	
Chromafenozide (IN)	✓	✓		✓	✓	✓		
Clethodim (HB)	✓		✓		✓	✓	✓	✓
Clodinafop (HB)	✓		✓		✓	✓		
Clomazone (HB)	✓		✓		✓	✓		✓
Clopyralid (HB)	✓		✓		✓	✓	✓	✓
Cyantraniliprole (IN)	✓	✓			✓	✓	✓	
Cyazofamid (FU)	✓	✓	✓		✓	✓	✓	✓
Cycloxydim (HB)	✓		✓		✓	✓		✓
Cyflufenamid (FU)	✓	✓			✓			
Cyhalofop-butyl (HB)	✓		✓		✓	✓	✓	✓
Cymoxanil (FU)	✓	✓	✓		✓	✓		
Cypermethrin (IN)	✓	✓	✓		✓			
Cyproconazole (FU)	✓	✓		✓				
Cyprodinil (FU)	✓	✓					✓	
Cyromazine (IN)	✓	✓			✓	✓		

Table S5.3 (Cont.) – List of the active substances covered in each pesticide scenario. BAU = Business As Usual, NH = No Herbicides, FDP = Fast Degradable Pesticides, TPB = Total Pesticide Ban, CFSE = Candidates For Substitution Excluded, LHP = Low Hazard Pesticides, SHH = Safe Human Health, LET = Low Ecosystem Toxicity, FU = fungicide; HB = herbicide; IN = insecticide.

Goal	-	Use Reduction				Hazard reduction		
active substance	**BAU**	**NH**	**FDP**	**TPB**	**CFSE**	**LHP**	**SHH**	**LET**
Dazomet (FU, HB)	✓	✓	✓		✓			
Desmedipham (HB)	✓				✓			✓
Dicamba (HB)	✓		✓		✓	✓	✓	✓
Dichlorprop-P (HB)	✓		✓		✓	✓		
Diclofop (HB)	✓					✓		
Diethofencarb (FU)	✓	✓	✓		✓			
Difenoconazole (FU)	✓	✓		✓		✓		
Diflufenican (HB)	✓			✓		✓	✓	
Dimethachlor (HB)	✓		✓		✓			
Dimethenamid-P (HB)	✓		✓		✓			
Dimethoate (IN)	✓	✓	✓					
Dimethomorph (FU)	✓	✓		✓	✓	✓	✓	✓
Dimoxystrobin (FU)	✓	✓		✓				
Dithianon (FU)	✓	✓			✓			
Diuron (HB)	✓			✓	✓	✓		
Dodemorph (FU)	✓	✓			✓			
Dodine (FU)	✓	✓	✓		✓	✓	✓	
Epoxiconazole (FU)	✓	✓		✓				✓
Esfenvalerate (IN)	✓	✓						
Ethofumesate (HB)	✓				✓	✓	✓	✓
Ethoprophos (IN)	✓	✓	✓					
Etofenprox (IN)	✓	✓	✓					
Etoxazole (IN)	✓	✓	✓			✓	✓	
Famoxadone (FU)	✓	✓						
Fenbuconazole (FU)	✓	✓		✓	✓	✓		
Fenhexamid (FU)	✓	✓	✓		✓	✓	✓	
Fenoxaprop-P (HB)	✓		✓		✓	✓		
Fenoxycarb (IN)	✓	✓	✓		✓			
Fenpicoxamid (FU)	✓	✓	✓		✓	✓	✓	
Fenpropidin (FU)	✓	✓			✓			
Fenpropimorph (FU)	✓	✓			✓			
Fenpyrazamine (FU)	✓	✓			✓		✓	
Flazasulfuron (HB)	✓				✓	✓		
Flonicamid (IN)	✓	✓	✓		✓	✓		✓
Florasulam (HB)	✓		✓		✓	✓	✓	
Fluazifop-P (HB)	✓		✓		✓	✓		
Fluazinam (FU)	✓	✓		✓	✓			
Flubendiamide (IN)	✓	✓		✓	✓	✓		
Fludioxonil (FU)	✓	✓						
Flufenacet (HB)	✓						✓	
Flumioxazin (HB)	✓		✓			✓		
Fluometuron (HB)	✓					✓		✓
Fluopicolide (FU)	✓	✓		✓		✓		✓
Fluopyram (FU)	✓	✓		✓	✓	✓		
Fluoxastrobin (FU)	✓	✓			✓	✓	✓	✓
Flupyradifurone (IN)	✓	✓		✓	✓	✓	✓	
Flurochloridone (HB)	✓				✓	✓		
Fluroxypyr (HB)	✓				✓	✓		✓
Flutolanil (FU)	✓	✓		✓	✓	✓	✓	✓
Flutriafol (FU)	✓	✓		✓	✓			✓

Table S5.3 (Cont.) – List of the active substances covered in each pesticide scenario. BAU = Business As Usual, NH = No Herbicides, FDP = Fast Degradable Pesticides, TPB = Total Pesticide Ban, CFSE = Candidates For Substitution Excluded, LHP = Low Hazard Pesticides, SHH = Safe Human Health, LET = Low Ecosystem Toxicity, FU = fungicide; HB = herbicide; IN = insecticide.

Goal	-	Use Reduction				Hazard reduction		
active substance	**BAU**	**NH**	**FDP**	**TPB**	**CFSE**	**LHP**	**SHH**	**LET**
Fluxapyroxad (FU)	✓	✓		✓	✓	✓		✓
Folpet (FU)	✓	✓	✓		✓			
Foramsulfuron (HB)	✓		✓		✓	✓	✓	
Formetanate (IN)	✓	✓	✓		✓			
Fosetyl (FU)	✓	✓	✓		✓			
Fuberidazole (FU)	✓	✓	✓		✓	✓		
Gamma-cyhalothrin (IN)	✓	✓	✓		✓			
Glyphosate (HB)	✓		✓		✓	✓		✓
Halauxifen-methyl (HB)	✓				✓	✓		
Halosulfuron methyl (HB)	✓			✓	✓	✓		
Haloxyfop-P (HB)	✓					✓		✓
Hexythiazox (IN)	✓	✓	✓		✓			
Hymexazol (FU)	✓	✓	✓		✓	✓		
Imazalil (FU)	✓	✓		✓	✓			
Imazamox (HB)	✓					✓		✓
Imidacloprid (IN)	✓	✓		✓	✓			
Indoxacarb (IN)	✓	✓			✓			
Iodosulfuron (HB)	✓		✓		✓			
Ipconazole (FU)	✓	✓		✓	✓	✓		
Iprovalicarb (FU)	✓	✓	✓		✓	✓		
Isofetamid (FU)	✓	✓			✓			
Isopyrazam (FU)	✓	✓		✓		✓		
Isoxaben (HB)	✓			✓	✓			✓
Isoxaflutole (HB)	✓		✓		✓	✓		✓
Kresoxim-methyl (FU)	✓	✓	✓		✓			✓
Lambda-Cyhalothrin (IN)	✓	✓		✓			✓	
Lenacil (HB)	✓					✓		
Lufenuron (IN)	✓	✓		✓				
Malathion (IN)	✓	✓	✓		✓			
Mandestrobin (FU)	✓	✓			✓	✓	✓	
Mandipropamid (FU)	✓	✓			✓	✓	✓	✓
Mecoprop-P (HB)	✓		✓		✓	✓		✓
Mepanipyrim (FU)	✓	✓		✓	✓	✓		
Meptyldinocap (FU)	✓	✓	✓		✓	✓		
Mesosulfuron (HB)	✓				✓	✓	✓	
Mesotrione (HB)	✓		✓		✓	✓		✓
Metaflumizone (IN)	✓	✓			✓	✓		
Metalaxyl-M (FU)	✓	✓	✓		✓	✓	✓	✓
Metam (FU, IN, HB)	✓	✓	✓					
Metamitron (HB)	✓		✓		✓	✓		✓
Metazachlor (HB)	✓		✓		✓	✓		
Metconazole (FU)	✓	✓		✓				
Methiocarb (IN)	✓	✓			✓			
Methomyl (IN)	✓	✓	✓				✓	
Methoxyfenozide (IN)	✓	✓		✓	✓	✓		
Metobromuron (HB)	✓				✓	✓		
Metosulam (HB)	✓				✓	✓		
Metrafenone (FU)	✓	✓		✓	✓	✓		
Metribuzin (HB)	✓		✓					
Metsulfuron-methyl (HB)	✓		✓			✓	✓	

Table S5.3 (Cont.) – List of the active substances covered in each pesticide scenario. BAU = Business As Usual, NH = No Herbicides, FDP = Fast Degradable Pesticides, TPB = Total Pesticide Ban, CFSE = Candidates For Substitution Excluded, LHP = Low Hazard Pesticides, SHH = Safe Human Health, LET = Low Ecosystem Toxicity, FU = fungicide; HB = herbicide; IN = insecticide.

Goal	-	Use Reduction				Hazard reduction		
active substance	**BAU**	**NH**	**FDP**	**TPB**	**CFSE**	**LHP**	**SHH**	**LET**
Myclobutanil (FU)	✓	✓		✓		✓	✓	✓
Napropamide (HB)	✓			✓	✓	✓	✓	✓
Nicosulfuron (HB)	✓		✓				✓	
Oryzalin (HB)	✓			✓	✓	✓		✓
Oxamyl (IN)	✓	✓	✓					
Oxathiapiprolin (FU)	✓	✓		✓	✓	✓	✓	✓
Oxyfluorfen (HB)	✓			✓				
Paraffin oil(CAS 64742-46-7) (IN)	✓	✓			✓	✓		
Paraffin oil(CAS 8042-47-5) (IN)	✓	✓			✓	✓		
Penconazole (FU)	✓	✓		✓	✓			✓
Pencycuron (FU)	✓	✓			✓	✓		
Pendimethalin (HB)	✓			✓				
Penflufen (FU)	✓	✓		✓	✓	✓		
Penoxsulam (HB)	✓				✓	✓		
Penthiopyrad (FU)	✓	✓		✓	✓	✓		
Pethoxamid (HB)	✓		✓		✓	✓	✓	✓
Phenmedipham (HB)	✓		✓		✓	✓		
Phosmet (IN)	✓	✓	✓		✓			
Picloram (HB)	✓				✓			
Picolinafen (HB)	✓				✓	✓	✓	
Pinoxaden (HB)	✓		✓		✓	✓		
Pirimicarb (IN)	✓	✓						
Prochloraz (FU)	✓	✓		✓		✓		
Propamocarb (FU)	✓	✓	✓		✓	✓		
Propaquizafop (HB)	✓				✓	✓		✓
Propoxycarbazone (HB)	✓			✓	✓	✓		
Propyzamide (HB)	✓					✓		
Proquinazid (FU)	✓	✓		✓	✓	✓		
Prosulfocarb (HB)	✓		✓		✓			✓
Prosulfuron (HB)	✓			✓		✓	✓	
Prothioconazole (FU)	✓	✓	✓		✓			✓
Pyraclostrobin (FU)	✓	✓			✓			
Pyraflufen-ethyl (HB)	✓		✓		✓	✓		
Pyridaben (IN)	✓	✓		✓	✓			
Pyridalyl (IN)	✓	✓		✓	✓	✓	✓	
Pyridate (HB)	✓		✓		✓			✓
Pyrimethanil (FU)	✓	✓			✓			✓
Pyriofenone (FU)	✓	✓		✓	✓			
Pyriproxyfen (IN)	✓	✓	✓		✓			
Pyroxsulam (HB)	✓		✓		✓			
Quinmerac (HB)	✓		✓		✓	✓		
Quizalofop-P-ethyl (HB)	✓		✓		✓		✓	
Quizalofop-P-tefuryl (HB)	✓		✓					
Rimsulfuron (HB)	✓		✓		✓	✓		
Sedaxane (FU)	✓	✓			✓	✓		
Silthiofam (FU)	✓	✓			✓	✓		
Spinetoram (IN)	✓	✓	✓		✓	✓		
Spirodiclofen (IN)	✓	✓	✓		✓			
Spiromesifen (IN)	✓	✓	✓		✓	✓	✓	

Table S5.3 (Cont.) – List of the active substances covered in each pesticide scenario. BAU = Business As Usual, NH = No Herbicides, FDP = Fast Degradable Pesticides, TPB = Total Pesticide Ban, CFSE = Candidates For Substitution Excluded, LHP = Low Hazard Pesticides, SHH = Safe Human Health, LET = Low Ecosystem Toxicity, FU = fungicide; HB = herbicide; IN = insecticide.

Goal	-	Use Reduction				Hazard reduction		
active substance	**BAU**	**NH**	**FDP**	**TPB**	**CFSE**	**LHP**	**SHH**	**LET**
Spirotetramat (IN)	✓	✓	✓		✓			✓
Spiroxamine (FU)	✓	✓			✓			
Sulcotrione (HB)	✓		✓			✓		✓
Sulfosulfuron (HB)	✓				✓	✓		
Sulfoxaflor (IN)	✓	✓	✓		✓	✓		
tau-Fluvalinate (IN)	✓	✓			✓			
Tebuconazole (FU)	✓	✓				✓		✓
Tebufenozide (IN)	✓	✓		✓	✓	✓		
Teflubenzuron (IN)	✓	✓			✓			
Tefluthrin (IN)	✓	✓			✓			
Tembotrione (HB)	✓		✓		✓			
Terbuthylazine (HB)	✓				✓			✓
Tetraconazole (FU)	✓	✓		✓	✓			
Thiabendazole (FU)	✓	✓		✓	✓	✓		
Thifensulfuron-methyl (HB)	✓		✓		✓	✓		
Thiophanate-methyl (FU)	✓	✓	✓		✓			✓
Tolclofos-methyl (FU)	✓	✓	✓		✓	✓	✓	
Tralkoxydim (HB)	✓		✓		✓			✓
Triadimenol (FU)	✓	✓		✓	✓			
Tri-allate (HB)	✓					✓		
Triazoxide (FU)	✓	✓		✓		✓		
Tribenuron (HB)	✓		✓		✓			
Triclopyr (HB)	✓				✓	✓	✓	
Trifloxystrobin (FU)	✓	✓	✓		✓			
Triflumuron (IN)	✓	✓	✓		✓	✓		
Triflusulfuron (HB)	✓		✓		✓			
Triticonazole (FU)	✓	✓		✓	✓			✓
Tritosulfuron (HB)	✓		✓		✓	✓	✓	✓
Valifenalate (FU)	✓	✓	✓		✓	✓		
Zeta-Cypermethrin (IN)	✓	✓			✓			
Ziram (FU)	✓	✓	✓					
Zoxamide (FU)	✓	✓	✓		✓	✓	✓	

Table S5.4 – Correspondence between crop classes in EU and specific crops in active substances representative uses. Crop attribution to classes was made according to the LUCAS 2018 classification (*E4 LUCAS ESTAT, 2018*).

Crop class	Specific crops – representative uses
Cereals	"cereals"
	Barley
	Oats
	Rice
	Rye
	Triticale
	Wheat
Dry Pulses, Vegetables, Flowers	"other vegetables"
	Beans
	Cabbages
	Cauliflower
	Cucumber
	Eggplant
	Lettuce
	Ornamental plants
	Peas
	Pepper
	Strawberries
	Tomatoes
Grapes	Grapes
	Vineyards
Grassland	Temporary grassland
Maize	Maize
Non-Permanent Industrial crops	Cotton
	Hops
	Rape and turnip rape
	Soya
	Sunflower
Permanent crops	Apple fruit
	Apricots
	Cherry fruit
	Citrus fruit
	Nuts trees
	Peaches
	Pear fruit
	Plums
Root crops	Carrots
	Onion
	Potato
	Sugar beet

Table S5.5 – Active substances (AS) allowed per crop class and their maximum recommended annual application rates per EU region, based on their EU representative use. Annual application rates were calculated as the product of the number of recommended treatments per year and the maximum recommended application rate per treatment, per crop-EU region. In the case of multiple representative uses per AS-crop-EU region, the application scheme leading to the highest annual application rate was selected. When this rate was the same, we selected the scheme leading to the highest pesticide content in the soil immediately after application. In line with most EU dossiers approach, individual active substance applications are presented in kg/ha, with two decimal places. NEU = Northern Europe; CEU = Central Europe; SEU = Southern Europe; FU = fungicide; HB = herbicide; IN = insecticide.

Crop class	AS	AS input (kg/ha/year)		
		NEU	CEU	SEU
Cereals	2,4-D (HB)	0.75	0.75	0.75
	2,4-DB (HB)		1.80	
	Alpha-Cypermethrin (IN)	0.02	0.02	0.02
	Amidosulfuron (HB)	0.03	0.03	0.03
	Azimsulfuron (HB)		0.03	0.03
	Azoxystrobin (FU)	0.50	0.50	0.50
	Benzovindiflupyr (FU)	0.15	0.15	0.15
	Beta-Cyfluthrin (IN)	0.03	0.03	0.03
	Bifenox (HB)	0.75		0.75
	Bifenthrin (IN)	0.02		0.02
	Bispyribac (HB)			0.03
	Bixafen (FU)		0.25	0.25
	Bromoxynil (HB)	0.34	0.34	0.34
	Bromuconazole (FU)	0.40	0.40	0.40
	Carboxin (FU)	0.13		0.13
	Carfentrazone-ethyl (HB)	0.04		0.04
	Chlorothalonil (FU)	1.50	1.50	1.50
	Chlorsulfuron (HB)	0.02	0.02	0.02
	Clodinafop (HB)	0.06	0.06	0.06
	Clopyralid (HB)		0.08	0.08
	Cyflufenamid (FU)	0.05		0.05
	Cyhalofop-butyl (HB)			0.30
	Cypermethrin (IN)	0.03	0.03	0.03
	Cyproconazole (FU)	0.20		0.20
	Cyprodinil (FU)	0.75	0.75	0.75
	Dichlorprop-P (HB)		1.20	
	Diclofop (HB)	0.57		0.61
	Difenoconazole (FU)	0.01		0.01
	Diflufenican (HB)	0.12	0.12	0.12
	Dimethoate (IN)	0.12	0.12	0.12
	Dimoxystrobin (FU)		0.20	0.20
	Epoxiconazole (FU)	0.25		0.25
	Esfenvalerate (IN)	0.03		0.03
	Fenbuconazole (FU)		0.15	0.15
	Fenoxaprop-P (HB)	0.07	0.07	0.07
	Fenpicoxamid (FU)	0.26	0.26	0.26
	Fenpropidin (FU)	1.50		1.50
	Fenpropimorph (FU)	1.50		1.50
	Flonicamid (IN)	0.07	0.07	0.07
	Florasulam (HB)	0.01	0.01	0.01
	Fludioxonil (FU)	0.01		0.01
	Flufenacet (HB)		0.24	0.24
	Flumioxazin (HB)	0.03		

Table S5.5 (cont.) – Active substances (AS) allowed per crop class and their maximum recommended annual application rates per EU region, based on their EU representative use. Annual application rates were calculated as the product of the number of recommended treatments per year and the maximum recommended application rate per treatment, per crop-EU region. In the case of multiple representative uses per AS-crop-EU region, the application scheme leading to the highest annual application rate was selected. When this rate was the same, we selected the scheme leading to the highest pesticide content in the soil immediately after application. In line with most EU dossiers approach, individual active substance applications are presented in kg/ha, with two decimal places. NEU = Northern Europe; CEU = Central Europe; SEU = Southern Europe; FU = fungicide; HB = herbicide; IN = insecticide.

Crop class	AS	AS input (kg/ha/year)		
		NEU	CEU	SEU
Cereals	Fluoxastrobin (FU)	0.42		0.42
	Fluroxypyr (HB)	0.20		0.20
	Flutriafol (FU)	0.13		0.13
	Fluxapyroxad (FU)	0.25	0.25	0.25
	Folpet (FU)	1.50		1.50
	Fuberidazole (FU)	0.01		
	Gamma-cyhalothrin (IN)	0.01		
	Glyphosate (HB)	2.16	2.16	2.16
	Halauxifen-methyl (HB)			0.01
	Halosulfuron methyl (HB)			0.04
	Imazalil (FU)	0.02	0.02	0.02
	Iodosulfuron (HB)	0.01	0.01	0.01
	Ipconazole (FU)		0.01	0.01
	Isopyrazam (FU)	0.25	0.25	0.25
	Isoxaben (HB)	0.13		0.13
	Kresoxim-methyl (FU)	0.25		0.25
	Lambda-Cyhalothrin (IN)	0.02		0.02
	Mecoprop-P (HB)	1.20	1.20	1.20
	Mesosulfuron (HB)	1.50	1.50	1.50
	Metconazole (FU)	0.18		0.18
	Metosulam (HB)		0.02	0.02
	Metrafenone (FU)	0.30		0.30
	Metsulfuron-methyl (HB)	0.01	0.01	0.01
	Pendimethalin (HB)	1.60	1.60	1.60
	Penflufen (FU)		0.01	
	Penoxsulam (HB)			0.04
	Penthiopyrad (FU)	0.60		
	Picolinafen (HB)	0.10	0.10	0.10
	Pinoxaden (HB)	0.06		0.06
	Pirimicarb (IN)	0.30		0.42
	Prochloraz (FU)	0.90		0.90
	Propoxycarbazone (HB)	0.07	0.07	0.04
	Proquinazid (FU)		0.10	
	Prosulfocarb (HB)	4.00		4.00
	Prothioconazole (FU)	0.63		0.63
	Pyriofenone (FU)	0.18		0.18
	Pyroxsulam (HB)	0.02		0.02
	Sedaxane (FU)			0.03
	Silthiofam (FU)	0.05	0.05	0.05
	Spiroxamine (FU)	0.75		0.75
	Sulfosulfuron (HB)	0.02		0.02

Table S5.5 (cont.) – Active substances (AS) allowed per crop class and their maximum recommended annual application rates per EU region, based on their EU representative use. Annual application rates were calculated as the product of the number of recommended treatments per year and the maximum recommended application rate per treatment, per crop-EU region. In the case of multiple representative uses per AS-crop-EU region, the application scheme leading to the highest annual application rate was selected. When this rate was the same, we selected the scheme leading to the highest pesticide content in the soil immediately after application. In line with most EU dossiers approach, individual active substance applications are presented in kg/ha, with two decimal places. NEU = Northern Europe; CEU = Central Europe; SEU = Southern Europe; FU = fungicide; HB = herbicide; IN = insecticide.

Crop class	AS	AS input (kg/ha/year)		
		NEU	CEU	SEU
Cereals	Sulfoxaflor (IN)	0.02	0.02	0.02
	Tau-Fluvalinate (IN)	0.10	0.10	0.10
	Tebuconazole (FU)	0.50		0.50
	Tetraconazole (FU)	0.13		0.13
	Thifensulfuron-methyl (HB)	0.05	0.05	0.05
	Thiophanate-methyl (FU)		0.75	0.75
	Tralkoxydim (HB)			0.45
	Triadimenol (FU)	0.09		0.09
	Tri-allate (HB)	2.25		
	Triazoxide (FU)		0.01	
	Tribenuron (HB)	0.03	0.03	0.03
	Triticonazole (FU)	0.01		0.01
	Tritosulfuron (HB)	0.05	0.05	0.05
	Zeta-Cypermethrin (IN)	0.03	0.03	0.03
Dry pulses, Vegetables Flowers	2,4-DB (HB)		1.80	1.80
	8-Hydroxyquinoline (FU)			2.99
	Acetamiprid (IN)	0.20	0.20	0.20
	Alpha-Cypermethrin (IN)	0.03	0.03	0.03
	Ametoctradin (FU)	0.72		0.72
	Azoxystrobin (FU)	0.50	0.50	0.50
	Bentazone (HB)	1.44	1.44	1.44
	Benthiavalicarb (FU)			0.45
	Beta-Cyfluthrin (IN)	0.04	0.04	0.04
	Bifenthrin (IN)	0.02		0.01
	Boscalid (FU)	1.00		1.00
	Bupirimate (FU)	0.10		0.10
	Captan (FU)			7.20
	Chlorantraniliprole (IN)			0.08
	Chlorothalonil (FU)	1.00	1.00	1.00
	Chlorpropham (HB)	2.40	2.40	2.40
	Cyantraniliprole (IN)	0.48		0.48
	Cyazofamid (FU)			0.48
	Cycloxydim (HB)	0.80	0.80	0.80
	Cymoxanil (FU)			0.96
	Cyromazine (IN)	1.20		1.20
	Dazomet (FU, HB)	500.00		500.00
	Diethofencarb (FU)	0.75		0.75
	Dodemorph (FU)	16.49		16.49
	Dodine (FU)	3.60		3.60
	Etofenprox (IN)			0.30
	Etoxazole (IN)	0.06		0.06
	Fenhexamid (FU)		3.00	3.00

Table S5.5 (cont.) – Active substances (AS) allowed per crop class and their maximum recommended annual application rates per EU region, based on their EU representative use. Annual application rates were calculated as the product of the number of recommended treatments per year and the maximum recommended application rate per treatment, per crop-EU region. In the case of multiple representative uses per AS-crop-EU region, the application scheme leading to the highest annual application rate was selected. When this rate was the same, we selected the scheme leading to the highest pesticide content in the soil immediately after application. In line with most EU dossiers approach, individual active substance applications are presented in kg/ha, with two decimal places. NEU = Northern Europe; CEU = Central Europe; SEU = Southern Europe; FU = fungicide; HB = herbicide; IN = insecticide.

Crop class	AS	AS input (kg/ha/year)		
		NEU	CEU	SEU
Dry pulses, Vegetables Flowers	Fenpyrazamine (FU)	1.80		1.80
	Fluazifop-P (HB)	0.32		0.32
	Flubendiamide (IN)	0.14	0.14	0.14
	Fluopyram (FU)	0.50	0.50	0.50
	Flupyradifurone (IN)	0.13		0.13
	Folpet (FU)			4.80
	Formetanate (IN)	0.50	0.50	0.50
	Glyphosate (HB)	1.08	1.08	1.08
	Haloxyfop-P (Haloxyfop-R) (HB)	0.11		0.11
	Hymexazol (FU)			1.98
	Imidacloprid (IN)			0.20
	Indoxacarb (IN)	0.15	0.15	0.15
	Isofetamid (FU)		0.80	0.80
	Lambda-Cyhalothrin (IN)	0.05		0.05
	Lufenuron (IN)			0.09
	Malathion (IN)			4.80
	Mandipropamid (FU)	0.60		0.60
	Mepanipyrim (FU)			0.80
	Metaflumizone (IN)	0.05		0.05
	Metalaxyl-M (FU)	0.29	0.29	0.29
	Metam (FU, IN, HB)	612.00	612.00	612.00
	Methomyl (IN)			0.90
	Methoxyfenozide (IN)	0.14	0.14	0.24
	Napropamide (HB)	0.77	0.77	0.77
	Oxathiapiprolin (FU)	0.09		0.09
	Paraffin oil/(CAS 8042-47-5) (IN)		26.21	
	Penconazole (FU)	0.20		0.20
	Pendimethalin (HB)		1.60	
	Penthiopyrad (FU)			0.48
	Propamocarb (FU)	4.77		4.77
	Propyzamide (HB)	1.50	1.50	1.50
	Pyridaben (IN)	0.25		0.25
	Pyridalyl (IN)			0.60
	Pyridate (HB)	0.90	0.90	0.90
	Pyrimethanil (FU)	1.20		
	Pyriproxyfen (IN)	0.06		0.23
	Quizalofop-P-tefuryl (HB)	0.10	0.10	0.10
	Rimsulfuron (HB)			0.03
	Spiromesifen (IN)	0.86	0.86	0.86
	Spirotetramat (IN)	0.14		0.14
	Sulfoxaflor (IN)	0.02	0.02	0.02
	Thiophanate-methyl (FU)		4.15	4.40
	Tolclofos-methyl (FU)	50.00	50.00	
	Zeta-Cypermethrin (IN)	0.03	0.03	0.03

Table S5.5 (cont.) – Active substances (AS) allowed per crop class and their maximum recommended annual application rates per EU region, based on their EU representative use. Annual application rates were calculated as the product of the number of recommended treatments per year and the maximum recommended application rate per treatment, per crop-EU region. In the case of multiple representative uses per AS-crop-EU region, the application scheme leading to the highest annual application rate was selected. When this rate was the same, we selected the scheme leading to the highest pesticide content in the soil immediately after application. In line with most EU dossiers approach, individual active substance applications are presented in kg/ha, with two decimal places. NEU = Northern Europe; CEU = Central Europe; SEU = Southern Europe; FU = fungicide; HB = herbicide; IN = insecticide.

Crop class	AS	AS input (kg/ha/year)		
		NEU	CEU	SEU
Grapes	Amisulbrom (FU)	0.30		0.30
	Benalaxyl-M (FU)	0.40		0.40
	Benthiavalicarb (FU)		0.21	0.21
	Boscalid (FU)	0.60		0.60
	Carfentrazone-ethyl (HB)	0.05		0.05
	Chlorantraniliprole (IN)	0.05		0.09
	Diethofencarb (FU)	0.50		0.50
	Dimethomorph (FU)	1.50		1.50
	Dithianon (FU)	4.48		4.48
	Diuron (HB)	2.00		2.00
	Etofenprox (IN)			0.60
	Etoxazole (IN)	0.06		0.06
	Famoxadone (FU)		0.30	0.30
	Fenbuconazole (FU)		0.43	0.43
	Fenhexamid (FU)		1.60	1.60
	Fenpyrazamine (FU)	0.60		0.60
	Flazasulfuron (HB)			0.05
	Fludioxonil (FU)	0.50		0.50
	Fluopicolide (FU)		0.40	0.34
	Fluopyram (FU)	0.50	0.50	0.50
	Folpet (FU)	15.00		15.00
	Fosetyl (FU)	6.00	6.00	10.56
	Glyphosate (HB)	8.64	8.64	8.64
	Hexythiazox (IN)	0.16		0.16
	Iprovalicarb (FU)	0.86	0.86	0.86
	Isofetamid (FU)		1.20	1.20
	Kresoxim-methyl (FU)	0.37		0.37
	Lufenuron (IN)	0.10		0.10
	Mandipropamid (FU)	0.60		0.60
	Mepanipyrim (FU)			0.60
	Meptyldinocap (FU)	0.84		0.84
	Metalaxyl-M (FU)	0.29	0.29	0.29
	Metam (FU, IN, HB)		1020.00	1020.0
	Methomyl (IN)	0.90		0.90
	Methoxyfenozide (IN)		0.10	0.10
	Metrafenone (FU)	0.80		0.80
	Myclobutanil (FU)	0.19		0.19
	Oryzalin (HB)	3.00	3.00	3.00
	Oxathiapiprolin (FU)	0.12	0.12	0.12
	Oxyfluorfen (HB)	1.44		1.44
	Penconazole (FU)	0.12		0.12
	Proquinazid (FU)			0.30
	Pyraflufen-ethyl (HB)	0.04	0.04	0.04

Table S5.5 (cont.) – Active substances (AS) allowed per crop class and their maximum recommended annual application rates per EU region, based on their EU representative use. Annual application rates were calculated as the product of the number of recommended treatments per year and the maximum recommended application rate per treatment, per crop-EU region. In the case of multiple representative uses per AS-crop-EU region, the application scheme leading to the highest annual application rate was selected. When this rate was the same, we selected the scheme leading to the highest pesticide content in the soil immediately after application. In line with most EU dossiers approach, individual active substance applications are presented in kg/ha, with two decimal places. NEU = Northern Europe; CEU = Central Europe; SEU = Southern Europe; FU = fungicide; HB = herbicide; IN = insecticide.

Crop class	AS	AS input (kg/ha/year)		
		NEU	CEU	SEU
Grapes	Pyrimethanil (FU)	1.00		1.00
	Pyriofenone (FU)	0.27		0.27
	Spinetoram (IN)	0.11		0.11
	Spirodiclofen (IN)	0.10		0.10
	Spiroxamine (FU)			0.90
	Tebuconazole (FU)	0.30		0.30
	Tebufenozide (IN)	0.58		0.69
	Tetraconazole (FU)	0.09		0.09
	Thiophanate-methyl (FU)		1.10	1.10
	Triadimenol (FU)	0.32		0.25
	Trifloxystrobin (FU)		0.38	0.38
	Valifenalate (FU)	0.36		0.36
	Zoxamide (FU)		0.90	0.90
Grassland	2,4-DB (HB)		1.80	
	Amidosulfuron (HB)	0.05		
	Aminopyralid (HB)	0.06	0.06	0.06
	Clopyralid (HB)		0.12	0.12
	Dicamba (HB)	0.96		0.96
	Dichlorprop-P (HB)		1.50	
	Florasulam (HB)	0.01	0.01	0.01
	Fluroxypyr (HB)	0.20		0.20
	Glyphosate (HB)	1.08	1.08	1.08
	Haloxyfop-P (Haloxyfop-R) (HB)	0.11		0.11
	Triclopyr (HB)	1.44	1.44	1.44
Maize	2,4-D (HB)	0.75	0.75	0.75
	Bromoxynil (HB)	0.34	0.34	0.34
	Dicamba (HB)	0.36		0.36
	Dimethenamid-P (HB)	0.86	0.86	0.86
	Florasulam (HB)	0.01	0.01	0.01
	Fluroxypyr (HB)	0.20		0.20
	Foramsulfuron (HB)	0.06	0.06	0.06
	Glyphosate (HB)	2.16	2.16	2.16
	Indoxacarb (IN)	0.08	0.08	0.08
	Isoxaflutole (HB)	0.10		0.10
	Mesotrione (HB)	0.15		0.15
	Methiocarb (IN)	0.15	0.15	0.15
	Methoxyfenozide (IN)		0.14	0.14
	Metosulam (HB)		0.03	
	Nicosulfuron (HB)	0.06	0.06	0.06
	Pethoxamid (HB)		1.20	1.20
	Prosulfuron (HB)	0.02	0.02	0.02
	Pyridate (HB)	0.90	0.90	0.90
	Rimsulfuron (HB)	0.02		0.02
	Sulcotrione (HB)	0.45	0.45	0.45

Table S5.5 (cont.) – Active substances (AS) allowed per crop class and their maximum recommended annual application rates per EU region, based on their EU representative use. Annual application rates were calculated as the product of the number of recommended treatments per year and the maximum recommended application rate per treatment, per crop-EU region. In the case of multiple representative uses per AS-crop-EU region, the application scheme leading to the highest annual application rate was selected. When this rate was the same, we selected the scheme leading to the highest pesticide content in the soil immediately after application. In line with most EU dossiers approach, individual active substance applications are presented in kg/ha, with two decimal places. NEU = Northern Europe; CEU = Central Europe; SEU = Southern Europe; FU = fungicide; HB = herbicide; IN = insecticide.

Crop class	AS	AS input (kg/ha/year)		
		NEU	CEU	SEU
Maize	Tembotrione (HB)	0.10	0.10	0.10
	Terbuthylazine (HB)	0.75		0.84
	Tritosulfuron (HB)	0.05	0.05	0.05
	Zeta-Cypermethrin (IN)	0.04	0.04	0.04
Non-Permanent Industrial crops	Aclonifen (HB)	2.40	2.40	2.40
	Amidosulfuron (HB)		0.03	0.03
	Carbetamide (HB)	1.80		1.80
	Chlorpyrifos (IN)			0.19
	Clomazone (HB)	0.12	0.12	0.12
	Cycloxydim (HB)	0.60	0.60	0.60
	Cypermethrin (IN)	0.05	0.05	
	Dimethachlor (HB)	1.50	1.50	1.50
	Dimethenamid-P (HB)	0.86	0.86	0.86
	Dimethomorph (FU)	3.00		
	Esfenvalerate (IN)	0.05		0.03
	Etofenprox (IN)	0.06		
	Etoxazole (IN)			0.04
	Fenpropimorph (FU)			0.60
	Fluazifop-P (HB)	0.32		0.32
	Flumioxazin (HB)	0.05		0.05
	Fluometuron (HB)			2.00
	Flupyradifurone (IN)	0.15		
	Flurochloridone (HB)	0.75		0.75
	Glyphosate (HB)	2.16	2.16	2.16
	Haloxyfop-P (Haloxyfop-R) (HB)	0.11		0.11
	Imazamox (HB)	0.04	0.05	0.05
	Isofetamid (FU)		0.32	0.32
	Mandestrobin (FU)	0.20		0.20
	Metalaxyl-M (FU)	0.01	0.01	0.01
	Metazachlor (HB)	1.00		1.00
	Napropamide (HB)	0.77	0.77	0.77
	Oxyfluorfen (HB)	0.24		0.24
	Pethoxamid (HB)		1.20	1.20
	Picloram (HB)		0.02	
	Propaquizafop (HB)	0.20		0.20
	Propyzamide (HB)	0.50	0.84	0.75
	Prothioconazole (FU)	0.35		
	Pyridalyl (IN)			0.60
	Pyriproxyfen (IN)			0.08
	Quinmerac (HB)	0.25	0.25	
	Quizalofop-P-tefuryl (HB)	0.10	0.10	0.10
	Sulfoxaflor (IN)	0.02	0.02	0.02
	Tebuconazole (FU)			0.25

Table S5.5 (cont.) – Active substances (AS) allowed per crop class and their maximum recommended annual application rates per EU region, based on their EU representative use. Annual application rates were calculated as the product of the number of recommended treatments per year and the maximum recommended application rate per treatment, per crop-EU region. In the case of multiple representative uses per AS-crop-EU region, the application scheme leading to the highest annual application rate was selected. When this rate was the same, we selected the scheme leading to the highest pesticide content in the soil immediately after application. In line with most EU dossiers approach, individual active substance applications are presented in kg/ha, with two decimal places. NEU = Northern Europe; CEU = Central Europe; SEU = Southern Europe; FU = fungicide; HB = herbicide; IN = insecticide.

Crop class	AS	AS input (kg/ha/year)		
		NEU	CEU	SEU
Permanent Crops	Acetamiprid (IN)	0.15	0.15	0.15
	Bupirimate (FU)	0.60		0.84
	Captan (FU)	12.50		10.00
	Chlorantraniliprole (IN)	0.12		0.12
	Chromafenozide (IN)	0.20		0.20
	Cyantraniliprole (IN)			0.30
	Cyprodinil (FU)	0.90	0.90	0.90
	Dichlorprop-P (HB)			0.11
	Difenoconazole (FU)	0.30		0.30
	Dithianon (FU)	6.30		6.30
	Diuron (HB)	2.00		2.00
	Dodine (FU)	3.20		3.20
	Etofenprox (IN)			0.56
	Etoxazole (IN)	0.06		0.06
	Fenbuconazole (FU)		0.70	0.70
	Fenoxycarb (IN)	0.30		0.45
	Flazasulfuron (HB)			0.05
	Flonicamid (IN)	0.07	0.07	0.07
	Fluazifop-P (HB)	0.21		0.21
	Fosetyl (FU)	10.80	10.80	10.80
	Glyphosate (HB)	8.64	8.64	8.64
	Hexythiazox (IN)	0.10		0.24
	Imidacloprid (IN)	0.18		0.18
	Isofetamid (FU)		0.72	0.72
	Kresoxim-methyl (FU)	0.45		0.45
	lambda-Cyhalothrin (IN)	0.05		0.05
	Oxyfluorfen (HB)	1.44		1.44
	Paraffin oil/(CAS 64742-46-7) (IN)			94.80
	Paraffin oil/(CAS 8042-47-5) (IN)		16.38	
	Penthiopyrad (FU)	0.53		0.53
	Phosmet (IN)			0.50
	Pyridaben (IN)			0.30
	Pyrimethanil (FU)	2.60		2.60
	Spirodiclofen (IN)	0.14		0.14
	Spirotetramat (IN)			0.58
	Tebufenozide (IN)	0.36		0.58
	Teflubenzuron (IN)	0.36		0.36
	Tetraconazole (FU)	0.09		0.09
	Triflumuron (IN)	0.36		0.36
	Ziram (FU)	6.84	6.84	6.84
Root crops	Acetamiprid (IN)	0.15	0.15	0.15
	Ametoctradin (FU)	0.96		0.96
	Amisulbrom (FU)	0.60		0.60
	Bentazone (HB)		0.96	0.96

Table S5.5 (cont.) – Active substances (AS) allowed per crop class and their maximum recommended annual application rates per EU region, based on their EU representative use. Annual application rates were calculated as the product of the number of recommended treatments per year and the maximum recommended application rate per treatment, per crop-EU region. In the case of multiple representative uses per AS-crop-EU region, the application scheme leading to the highest annual application rate was selected. When this rate was the same, we selected the scheme leading to the highest pesticide content in the soil immediately after application. In line with most EU dossiers approach, individual active substance applications are presented in kg/ha, with two decimal places. NEU = Northern Europe; CEU = Central Europe; SEU = Southern Europe; FU = fungicide; HB = herbicide; IN = insecticide.

Crop class	**AS**	**AS input (kg/ha/year)**		
		NEU	**CEU**	**SEU**
Root crops	Benthiavalicarb (FU)		0.17	0.17
	Beta-Cyfluthrin (IN)	0.03	0.03	0.03
	Carfentrazone-ethyl (HB)	0.10		0.10
	Chlorantraniliprole (IN)	0.03		0.03
	Chlorothalonil (FU)	0.75	0.75	0.75
	Chlorpropham (HB)	2.40		
	Clethodim (HB)	0.24		0.38
	Clomazone (HB)	0.09	0.09	0.09
	Cyazofamid (FU)	0.48	0.48	0.48
	Cycloxydim (HB)	0.60	0.60	0.60
	Cymoxanil (FU)	1.40		1.40
	Cypermethrin (IN)			0.05
	Desmedipham (HB)	0.48	0.48	0.48
	Difenoconazole (FU)	0.38		0.38
	Dimethenamid-P (HB)	0.86	0.86	0.86
	Dimethoate (IN)	0.20	0.20	0.20
	Dimethomorph (FU)	1.44		1.44
	Epoxiconazole (FU)	0.25		0.25
	Esfenvalerate (IN)	0.05		0.05
	Ethofumesate (HB)	1.00	1.00	1.00
	Ethoprophos (IN)		6.00	6.00
	Fenpropimorph (FU)	0.75		0.75
	Flonicamid (IN)	0.08	0.08	0.08
	Fluazifop-P (HB)	0.32		0.32
	Fluazinam (FU)	2.00	2.00	2.00
	Fluopicolide (FU)		0.40	0.40
	Flurochloridone (HB)	0.75		0.75
	Flutolanil (FU)	0.28		0.28
	Glyphosate (HB)	1.08	1.08	1.08
	Haloxyfop-P (Haloxyfop-R) (HB)	0.11		0.11
	Hymexazol (FU)	0.07		0.07
	Imidacloprid (IN)	0.12		
	lambda-Cyhalothrin (IN)	0.02		0.02
	Lenacil (HB)	0.50		0.50
	Mandipropamid (FU)	0.90		0.90
	Metaflumizone (IN)	0.18		0.18
	Metam (FU, IN, HB)	153.00	153.00	153.00
	Metamitron (HB)		3.50	
	Metobromuron (HB)	2.00	2.00	2.00
	Metribuzin (HB)	1.05		1.05

Table S5.5 (cont.) – Active substances (AS) allowed per crop class and their maximum recommended annual application rates per EU region, based on their EU representative use. Annual application rates were calculated as the product of the number of recommended treatments per year and the maximum recommended application rate per treatment, per crop-EU region. In the case of multiple representative uses per AS-crop-EU region, the application scheme leading to the highest annual application rate was selected. When this rate was the same, we selected the scheme leading to the highest pesticide content in the soil immediately after application. In line with most EU dossiers approach, individual active substance applications are presented in kg/ha, with two decimal places. NEU = Northern Europe; CEU = Central Europe; SEU = Southern Europe; FU = fungicide; HB = herbicide; IN = insecticide.

Crop class	AS	AS input (kg/ha/year)		
		NEU	CEU	SEU
Root crops	Oxamyl (IN)	5.50		5.50
	Oxathiapiprolin (FU)	0.06		0.06
	Paraffin oil/(CAS 64742-46-7) (IN)			75.60
	Pencycuron (FU)	0.70		0.70
	Pendimethalin (HB)	1.60	1.60	1.60
	Penflufen (FU)	0.10		0.10
	Phenmedipham (HB)	0.96		0.96
	Phosmet (IN)			0.50
	Propamocarb (FU)	6.50		6.50
	Propaquizafop (HB)	0.20		0.20
	Prosulfocarb (HB)	4.00		4.00
	Pyraclostrobin (FU)	0.07	0.07	0.07
	Pyraflufen-ethyl (HB)	0.04	0.04	0.04
	Quizalofop-P-ethyl (QPE) (HB)	0.20	0.20	0.20
	Quizalofop-P-tefuryl (HB)	0.10	0.10	0.10

Table S5.6 – List of the mode of action of the 230 selected active substances (AS), per substance type. The mode of action of individual AS were retrieved from the PPDB database. The modes of action were kept as specific as possible, the only changes and aggregation compared to the PPDB mode of action description corresponded to situations where different AS presented the same mode of action but phrased slightly differently.

Substance group	Mode of action	AS
Acylamino acid	Inhibitor of cellulose synthesis.	Valifenalate
Alkanamide	Inhibitor of cell division.	Napropamide
Alkane hydrocarbon	Other - contact action, eggs covered by an oil film are starved of oxygen and so do not hatch.	Paraffin oil/(CAS 64742-46-7)
		Paraffin oil/(CAS 8042-47-5)
Alkylchlorophenoxy	Other - synthetic auxin.	2,4-D
Amide	Inhibitor of Succinate Dehydrogenase (SDH).	Benzovindiflupyr
		Isofetamid
Amidoxine	Inhibitor of appressoria formation.	Cyflufenamid
Anilinopyrimidine	Inhibitor of protein synthesis.	Cyprodinil
		Mepanipyrim
		Pyrimethanil
Anthranilic diamide	Disrupts the Ca^{2+} balance.	Chlorantraniliprole
Antibiotic	Inhibitor of Qi site.	Fenpicoxamid
Aryloxyalkanoic acid	Other - synthetic auxin.	2,4-DB
		Dichlorprop-P
		Mecoprop-P
Aryloxyphenoxypropionate	Inhibitor of Acetyl CoA carboxylase (ACCase).	Clodinafop
		Cyhalofop-butyl
		Diclofop
		Haloxyfop-P (Haloxyfop-R)
		Propaquizafop
		Quizalofop-P-ethyl (QPE)
		Quizalofop-P-tefuryl
	Not applicable.	Fenoxaprop-P
Benzamide	Inhibitor of cell wall synthesis.	Isoxaben
	Inhibitor of mitosis and cell division.	Zoxamide
	Other - novel mode of action as fluopicolide delocalises spectrin-like proteins.	Fluopicolide
	Inhibitor of microtubule assembly.	Propyzamide
Benzamide, pyramide	Inhibitor of Succinate Dehydrogenase (SDH).	Fluopyram
Benzene-dicarboxamide	Disrupts the Ca^{2+} balance.	Flubendiamide
Benzimidazole	Inhibitor of mitosis and cell division.	Fuberidazole
		Thiophanate-methyl
	Other - compromises the cytoskeleton through a selective interaction with ß-tubulin.	Thiabendazole
Benzofuran	Inhibitor of lipid synthesis.	Ethofumesate
Benzoic acid	Other - synthetic auxin.	Dicamba
Benzophenone	Other - interferes with hyphal morphogenesis.	Metrafenone
Benzothiazinone	Inhibitor of photosynthesis.	Bentazone
Benzotriazine	Other - not known.	Triazoxide
Benzoylpyridine	Inhibitor of appressoria formation.	Pyriofenone
Benzoylurea	Inhibitor of chitin synthesis.	Lufenuron
		Teflubenzuron
		Triflumuron
Butenolide	Agonist of acetylcholine receptor (nAChR).	Flupyradifurone
Carbamate	Inhibitor of Acetylcholinesterase (AChE).	Methiocarb
		Oxamyl
		Pirimicarb

Table S5.6 (cont.) – List of the mode of action of the 230 selected active substances (AS), per substance type. The mode of action of individual AS were retrieved from the PPDB database. The modes of action were kept as specific as possible, the only changes and aggregation compared to the PPDB mode of action description corresponded to situations where different AS presented the same mode of action but phrased slightly differently.

Substance group	Mode of action	AS
Carbamate	Inhibitor of mitosis and cell division.	Carbetamide
		Chlorpropham
		Diethofencarb
	Inhibitor of photosynthesis.	Desmedipham
		Phenmedipham
	Inhibitor of phospholipid biosynthesis.	Benthiavalicarb
	Inhibitor of insect maturation process.	Fenoxycarb
	Inhibitor of Cholinesterase (ChE).	Methomyl
	Inhibitor of cellulose synthesis.	Iprovalicarb
	Other - binds to oxygen carrying molecules and prevents tissues from using oxygen.	Metam
	Other - multi-site activity.	Ziram
	Other - releases methyl isothiocyanate.	Dazomet
	Inhibitor of lipid synthesis.	Propamocarb
Carboxamide	Inhibitor of Succinate Dehydrogenase (SDH).	Boscalid
		Penthiopyrad
	Inhibitor of carotenoid biosynthesis.	Diflufenican
	Other - non-systemic with contact and stomach action	Hexythiazox
Chloroacetamide	Inhibitor of ergosterol/sterol biosynthesis.	Dimethenamid-P
		Metazachlor
	Inhibitor of cell division.	Dimethachlor
		Pethoxamid
Chloronitrile	Other - multi-site activity.	Chlorothalonil
Chlorophenyl	Inhibitor of lipid peroxidation.	Tolclofos-methyl
Cyanoacetamide oxime	Other - not known	Cymoxanil
Cyanoimidazole	Inhibitor of mitochondrial respiration.	Cyazofamid
Cyclohexadione	Inhibitor of Acetyl CoA carboxylase (ACCase).	Tralkoxydim
Cyclohexanedione	Inhibitor of Acetyl CoA carboxylase (ACCase).	Clethodim
		Cycloxydim
Diacylhydrazine	Agonist of ecdysone.	Chromafenozide
	Agonist of moulting hormone.	Tebufenozide
	Agonist of 20-hydroxyecdysone hormone.	Methoxyfenozide
Diamide	Disrupts the Ca2+ balance.	Cyantraniliprole
Dinitroaniline	Inhibitor of mitosis and cell division.	Pendimethalin
	Inhibitor of microtubule assembly.	Oryzalin
Dinitrophenol	Inhibitor of spore germination.	Meptyldinocap
Diphenyl ether	Inhibitor of protoporphyrinogen oxidase (PPO).	Oxyfluorfen
	Inhibitor of carotenoid biosynthesis.	Aclonifen
	Inhibitor of lipid synthesis.	Bifenox
Diphenyl oxazoline	Agonist of moulting hormone.	Etoxazole
Formamidine	Inhibitor of Acetylcholinesterase (AChE).	Formetanate
Guanidine	Other - systemic with protectant and eradicant action.	Dodine
Hydroxyanilide	Disrupts membrane function.	Fenhexamid
Hydroxybenzonitrile	Inhibitor of photosynthesis.	Bromoxynil
Imidazole	Disrupts membrane function.	Imazalil
		Prochloraz

Table S5.6 (cont.) – List of the mode of action of the 230 selected active substances (AS), per substance type. The mode of action of individual AS were retrieved from the PPDB database. The modes of action were kept as specific as possible, the only changes and aggregation compared to the PPDB mode of action description corresponded to situations where different AS presented the same mode of action but phrased slightly differently.

Substance group	Mode of action	AS
Imidazolinone	Inhibitor of plant amino acid synthesis (acetohydroxyacid synthase AHAS).	Imazamox
Isoxazolidinone	Inhibitor of lycopene cyclase.	Clomazone
Mandelamide	Inhibitor of cellulose synthesis.	Mandipropamid
Morpholine	Disrupts membrane function.	Fenpropimorph
		Spiroxamine
	Inhibitor of cellulose synthesis.	Dimethomorph
	Inhibitor of ergosterol/sterol biosynthesis.	Dodemorph
Neonicotinoid	Agonist of acetylcholine receptor (nAChR).	Acetamiprid
		Imidacloprid
N-phenylphtalamides	Inhibitor of protoporphyrinogen oxidase (PPO).	Flumioxazin
Organophosphate	Inhibitor of Acetylcholinesterase (AChE).	Chlorpyrifos
		Dimethoate
		Ethoprophos
		Malathion
		Phosmet
	Other - not known.	Fosetyl
Oxadiazine	Other - voltage-dependent sodium channel blocker.	Indoxacarb
Oxathiin	Inhibitor of Succinate Dehydrogenase (SDH).	Carboxin
		Flutolanil
Oxazole	Disrupts fungal nucleic acid synthesis	Hymexazol
	Inhibitor of mitochondrial respiration.	Famoxadone
Oxyacetamide	Inhibitor of cell division.	Flufenacet
	Inhibitor of 4-hydroxyphenyl-pyruvate-dioxygenase (HPPD).	Isoxaflutole
Phenylamide	Disrupts fungal nucleic acid synthesis.	Benalaxyl-M
		Metalaxyl-M
	Inhibitor of photosynthesis.	Diuron
Phenylpyrazole	Inhibitor of protoporphyrinogen oxidase (PPO).	Pyraflufen-ethyl
Phenylpyridazine	Inhibitor of electron transport at the photosystem II.	Pyridate
Phenylpyridinamine	Other - uncoupler of oxidative phosphorylation.	Fluazinam
Phenylpyrrole	Inhibitor of transport-associated phosphorylation of glucose.	Fludioxonil
Phenylurea	Inhibitor of electron transport at the photosystem II.	Fluometuron
	Inhibition of mitosis and cell division.	Pencycuron
Phosphonoglycine	Inhibition of EPSP synthase.	Glyphosate
Phthalimide	Inhibitor of cell division.	Folpet
	Other - multi-site activity.	Captan
Picolinic acid	Other - synthetic auxin.	Halauxifen-methyl
Piperidinyl thiazole isoxazoline	Other acts via an oxysterol binding protein.	Oxathiapiprolin
Pyrazole	Inhibitor of Succinate Dehydrogenase (SDH).	Isopyrazam
		Sedaxane
Pyrazolium	Inhibitor of Succinate Dehydrogenase (SDH).	Bixafen
		Fluxapyroxad
		Penflufen
	Inhibitor of germ tube and mycelium elongation.	Fenpyrazamine

Table S5.6 (cont.) – List of the mode of action of the 230 selected active substances (AS), per substance type. The mode of action of individual AS were retrieved from the PPDB database. The modes of action were kept as specific as possible, the only changes and aggregation compared to the PPDB mode of action description corresponded to situations where different AS presented the same mode of action but phrased slightly differently.

Substance group	Mode of action	AS
Pyrethroid	Other - sodium channel modulator.	Alpha-Cypermethrin
		Beta-Cyfluthrin
		Bifenthrin
		Cypermethrin
		Esfenvalerate
		Etofenprox
		Gamma-cyhalothrin
		lambda-Cyhalothrin
		Tefluthrin
		Zeta-Cypermethrin
Pyridalyl	Inhibitor of insect vigor.	Pyridalyl
Pyridazinone	Inhibitor of mitochondrial electron transport at complex I.	Pyridaben
Pyridine compound	Other - synthetic auxin.	Clopyralid
		Fluroxypyr
		Picloram
		Triclopyr
	Inhibitor of carotenoid biosynthesis.	Picolinafen
	Disrupts insect feeding pattern.	Flonicamid (IKI-220)
	Other - not known	Aminopyralid
Pyrimidinol	Inhibitor of Nucleic acid synthesis - adenosine-deaminase.	Bupirimate
Pyrimidinyl carboxy compound	Inhibitor of plant amino acid synthesis (acetohydroxyacid synthase AHAS).	bispyribac-sodium
Pyrimidinylsulfonylurea	Inhibitor of Acetolactate synthase (ALS).	Foramsulfuron
Quinazolinone	Inhibitor of appressoria formation.	Proquinazid
Quinoline	Other - chelates various metals required by micro-organisms for their metabolism.	8-Hydroxyquinoline
	Other - synthetic auxin.	Quinmerac
Quinone	Other - multi-site activity.	Dithianon
Semicarbazone	Other - attack insect nervous system causing paralysis	Metaflumizone
Spinosym	Other - acts through a novel site in the nicotinic receptor.	Spinetoram
Strobilurin	Inhibitor of mitochondrial respiration.	Azoxystrobin
		Dimoxystrobin
		Fluoxastrobin
		Mandestrobin
		Pyraclostrobin
		Trifloxystrobin
	Other blocking electron transfer and respiration of the fungi.	Kresoxim-methyl
Sulfonamide	Inhibitor of mitochondrial respiration.	Amisulbrom
Sulfonylurea	Inhibitor of plant amino acid synthesis (acetohydroxyacid synthase AHAS).	Amidosulfuron
		Azimsulfuron
		Chlorsulfuron
		Flazasulfuron
		Halosulfuron methyl
		Iodosulfuron

Table S5.6 (cont.) – List of the mode of action of the 230 selected active substances (AS), per substance type. The mode of action of individual AS were retrieved from the PPDB database. The modes of action were kept as specific as possible, the only changes and aggregation compared to the PPDB mode of action description corresponded to situations where different AS presented the same mode of action but phrased slightly differently.

Substance group	Mode of action	AS
Sulfonylurea	Inhibitor of plant amino acid synthesis (acetohydroxyacid synthase AHAS).	Mesosulfuron
		Metsulfuron-methyl
		Nicosulfuron
		Prosulfuron
		Rimsulfuron
		Sulfosulfuron
		Thifensulfuron-methyl
		Tribenuron
		Triflusulfuron
		Tritosulfuron
Sulfoximine	Agonist of n-acetylcholine receptors in insects.	Sulfoxaflor
Synthetic pyrethroid	Other - sodium channel modulator.	Tau-Fluvalinate
Tetramic acid	Inhibitor of protoporphyrinogen oxidase (PPO).	Spirotetramat
Tetronic acid	Inhibitor of lipid synthesis.	Spirodiclofen
		Spiromesifen
Thiocarbamate	Inhibitor of lipid synthesis.	Prosulfocarb
		Tri-allate
Thiophene	Inhibitor of mitochondrial respiration.	Silthiofam
Triazine	Inhibitor of chitin synthesis.	Cyromazine
	Inhibitor of photosynthesis.	Terbuthylazine
Triazinone	Inhibitor of photosynthesis.	Metamitron
		Metribuzin
Triazole Triazole	Inhibitor of ergosterol/sterol biosynthesis.	Bromuconazole
		Cyproconazole
		Epoxiconazole
		Fenbuconazole
		Flutriafol
		Ipconazole
		Metconazole
		Penconazole
		Tetraconazole
		Triticonazole
	Disrupts membrane function.	Difenoconazole
		Myclobutanil
		Tebuconazole
		Triadimenol
Triazolinthione	Inhibitor of ergosterol/sterol biosynthesis.	Prothioconazole
Triazolone	Disrupts membrane function.	Carfentrazone-ethyl
	Inhibitor of plant amino acid synthesis	Propoxycarbazone
Triazolopyrimidine	Inhibitor of plant amino acid synthesis (acetohydroxyacid synthase AHAS).	Florasulam
		Metosulam
	Inhibitor of Acetolactate synthase (ALS)	Pyroxsulam
	Inhibitor of mitochondrial respiration.	Ametoctradin
Triazopyrimidine	Inhibitor of plant amino acid synthesis (acetohydroxyacid synthase AHAS).	Penoxsulam
Triketone	Inhibitor of 4-hydroxyphenyl-pyruvate-dioxygenase	Mesotrione
		Sulcotrione
	Other multi-site activity.	Tembotrione

Table S5.6 (cont.) – List of the mode of action of the 230 selected active substances (AS), per substance type. The mode of action of individual AS were retrieved from the PPDB database. The modes of action were kept as specific as possible, the only changes and aggregation compared to the PPDB mode of action description corresponded to situations where different AS presented the same mode of action but phrased slightly differently.

Substance group	Mode of action	AS
Unclassified	Inhibitor of ergosterol/sterol biosynthesis.	Fenpropidin
	Other not applicable	Fluazifop-P
	Inhibitor of Acetyl CoA carboxylase (ACCase).	Pinoxaden
	Inhibitor of insect maturation process.	Pyriproxyfen
	Inhibitor of carotenoid biosynthesis.	Flurochloridone
Uracil	Inhibitor of photosynthesis.	Lenacil
Urea	Inhibitor of electron transport at the photosystem II.	Metobromuron

Table S5.7 – Number of active substances (AS) allowed under the No Herbicides (NH) scenario, maximum recommended annual application rate among allowed AS, and total AS use per crop-EU region combination. Annual application rates were calculated as the product of the (maximum) number of recommended treatments per year and the (maximum) recommended application rate per treatment in respective EC approved, AS representative use. Total AS use was calculated as the sum of the highest annual application rate of all the AS allowed per crop-EU region combination. The average of total AS use in NEU, CEU and SEU was used in the European characterization (the last column of the table). Maximum annual application rates among allowed AS are presented in kg/ha/year, with zero or two decimal places (if above or below 100 kg/ha/year, respectively). Total AS use is also presented in kg/ha/year, with zero decimal places. NEU = Northern Europe, CEU = Central Europe, SEU = Southern Europe. DPVF = dry pulses, vegetables, flowers; NPIC = non-permanent industrial crops; Perm. = permanent; Max. = maximum. BAU reference figures (in light blue) were added to the table for comparison.

Crop	**Parameter**	**NEU**		**CEU**		**SEU**		**EUROPE**	
		NH	**BAU**	**NH**	**BAU**	**NH**	**BAU**	**NH**	**BAU**
Cereals	Number of AS allowed	47	77	26	51	50	88	56	98
	Max. recom. annual rate	1.50	4.00	1.50	2.16	1.50	4.00	1.50	4.00
	Total AS use	15	31	6	18	16	31	-	-
Dry Pulses, Vegetables, Flowers	Number of AS allowed	39	49	20	30	56	68	59	72
	Max. recom. annual rate	612	612	612	612	612	612	612	612
	Total AS use	1,200	1,210	701	713	1,185	1,196	-	-
Grapes	Number of AS allowed	34	40	16	19	49	56	49	56
	Max. recom. annual rate	15.00	15.00	1,020	1,020	1,020	1,020	1,020	1,020
	Total AS use	39	54	1,034	1,046	1,073	1,088	-	-
Grassland	Number of AS allowed	0	8	0	7	0	8	0	11
	Max. recom. annual rate		1.44		1.80		1.44		1.80
	Total AS use		4		6		4		-
Maize	Number of AS allowed	3	21	4	18	4	23	4	24
	Max. recom. annual rate	0.15	2.16	0.15	2.16	0.15	2.16	0.15	2.16
	Total AS use	<1	8	<1	7	<1	9	-	-
Non-Permanent Industrial crops	Number of AS allowed	9	28	4	18	11	32	16	39
	Max. recom. annual rate	3.00	3.00	0.32	2.40	0.60	2.40	3.00	3.00
	Total AS use	4	18	<1	11	2	19	-	-
Permanent crops	Number of AS allowed	25	29	8	9	33	39	34	40
	Max. recom. annual rate	12.50	12.50	16.38	16.38	94.80	94.80	94.80	94.80
	Total AS use	48	60	37	45	144	157	-	-
Root crops	Number of AS allowed	34	58	16	30	40	64	41	67
	Max. recom. annual rate	153	153	153	153	153	153	153	153
	Total AS use	179	198	165	178	262	280	-	-

Table S5.8 – Number of active substances (AS) allowed under the Fast Degradable Pesticides (FDP) scenario, maximum recommended annual application rate among allowed AS, and total AS use per crop-EU region combination. Annual application rates were calculated as the product of the (maximum) number of recommended treatments per year and the (maximum) recommended application rate per treatment in respective EC approved, AS representative use. Total AS use was calculated as the sum of the highest annual application rate of all the AS allowed per crop-EU region combination. The average of total AS use in NEU, CEU and SEU was used in the European characterization (the last column of the table). Maximum annual application rates among allowed AS are presented in kg/ha/year, with zero or two decimal places (if above or below 100 kg/ha/year, respectively). Total AS use is also presented in kg/ha/year, with zero decimal places. NEU = Northern Europe, CEU = Central Europe, SEU = Southern Europe. DPVF = dry pulses, vegetables, flowers; NPIC = non-permanent industrial crops; Perm. = permanent; Max. = maximum. BAU reference figures (in light blue) were added to the table for comparison.

Crop	Parameter	NEU		CEU		SEU		EUROPE	
		FDP	BAU	FDP	BAU	FDP	BAU	FDP	BAU
Cereals	Number of AS allowed	32	77	24	51	34	88	39	98
	Max. recom. annual rate	4.00	4.00	2.16	2.16	4.00	4.00	4.00	4.00
	Total AS use	14	31	11	18	16	31	-	-
Dry Pulses, Vegetables, Flowers	Number of AS allowed	24	49	18	30	37	68	38	72
	Max. recom. annual rate	612	612	612	612	612	612	612	612
	Total AS use	1,182	1,210	681	713	1,166	1,196	-	-
Grapes	Number of AS allowed	16	40	11	19	23	56	23	56
	Max. recom. annual rate	15.00	15.00	1,020	1,020	1,020	1,020	1,020	1,020
	Total AS use	34	54	1,040	1,046	1,064	1,088	-	-
Grassland	Number of AS allowed	4	8	5	7	4	8	7	11
	Max. recom. annual rate	1.08	1.44	1.80	1.80	1.08	1.44	1.80	1.80
	Total AS use	2	4	5	6	2	4	-	-
Maize	Number of AS allowed	15	21	12	18	16	23	16	24
	Max. recom. annual rate	2.16	2.16	2.16	2.16	2.16	2.16	2.16	2.16
	Total AS use	6	8	7	7	8	9	-	-
Non-Permanent Industrial crops	Number of AS allowed	16	28	12	18	16	32	20	39
	Max. recom. annual rate	2.16	3.00	2.16	2.40	2.16	2.40	2.16	3.00
	Total AS use	9	18	7	11	10	19	-	-
Permanent crops	Number of AS allowed	14	29	5	9	18	39	18	40
	Max. recom. annual rate	12.50	12.50	10.80	16.38	10.80	94.80	12.50	94.80
	Total AS use	44	60	27	45	43	157	-	-
Root crops	Number of AS allowed	30	58	21	30	34	64	36	67
	Max. recom. annual rate	153	153	153	153	153	153	153	153
	Total AS use	183	198	170	178	189	280	-	-

Table S5.9 – Number of active substances (AS) allowed under the Candidates For Substitution Excluded (CFSE) scenario, maximum recommended annual application rate among allowed AS, and total AS use per crop-EU region combination. Annual application rates were calculated as the product of the (maximum) number of recommended treatments per year and the (maximum) recommended application rate per treatment in respective EC approved, AS representative use. Total AS use was calculated as the sum of the highest annual application rate of all the AS allowed per crop-EU region combination. The average of total AS use in NEU, CEU and SEU was used in the European characterization (the last column of the table). Maximum annual application rates among allowed AS are presented in kg/ha/year, with zero or two decimal places (if above or below 100 kg/ha/year, respectively). Total AS use is also presented in kg/ha/year, with zero decimal places. NEU = Northern Europe, CEU = Central Europe, SEU = Southern Europe. DPVF = dry pulses, vegetables, flowers; NPIC = non-permanent industrial crops; Perm. = permanent; Max. = maximum. BAU reference figures (in light blue) were added to the table for comparison.

Crop	Parameter	NEU		CEU		SEU		EUROPE	
		CFSE	BAU	CFSE	BAU	CFSE	BAU	CFSE	BAU
Cereals	Number of AS allowed	55	77	40	51	66	88	73	98
	Max. recom. annual rate	4.00	4.00	2.16	2.16	4.00	4.00	4.00	4.00
	Total AS use	23	31	14	18	24	31	-	-
Dry Pulses, Vegetables, Flowers	Number of AS allowed	42	49	26	30	57	68	60	72
	Max. recom. annual rate	500	612	50.00	612	500	612	500	612
	Total AS use	596	1,210	98	713	578	1,196	-	-
Grapes	Number of AS allowed	33	40	16	19	45	56	45	56
	Max. recom. annual rate	15.00	15.00	8.64	1,020	15.00	1,020	15.00	1,020
	Total AS use	51	54	25	1,046	63	1,088	-	-
Grassland	Number of AS allowed	7	8	7	7	7	8	10	11
	Max. recom. annual rate	1.44	1.44	1.80	1.80	1.44	1.44	1.80	1.80
	Total AS use	4	4	6	6	4	4	-	-
Maize	Number of AS allowed	18	21	15	18	20	23	21	24
	Max. recom. annual rate	2.16	2.16	2.16	2.16	2.16	2.16	2.16	2.16
	Total AS use	7	8	7	7	9	9	-	-
Non-Permanent Industrial crops	Number of AS allowed	19	28	14	18	21	32	27	39
	Max. recom. annual rate	3.00	3.00	2.16	2.40	2.16	2.40	3.00	3.00
	Total AS use	14	18	8	11	13	19	-	-
Permanent crops	Number of AS allowed	23	29	7	9	32	39	33	40
	Max. recom. annual rate	12.50	12.50	16.38	16.38	94.80	94.80	94.80	94.80
	Total AS use	50	60	37	45	147	157	-	-
Root crops	Number of AS allowed	46	58	24	30	50	64	53	67
	Max. recom. annual rate	6.50	153	3.50	153	75.60	153		153
	Total AS use	35	198	17	178	111	280	-	-

Table S5.10 – Number of active substances (AS) allowed under the Low Hazard Pesticides (LHP) scenario, maximum recommended annual application rate among allowed AS, and total AS use per crop-EU region combination. Annual application rates were calculated as the product of the (maximum) number of recommended treatments per year and the (maximum) recommended application rate per treatment in respective EC approved, AS representative use. Total AS use was calculated as the sum of the highest annual application rate of all the AS allowed per crop-EU region combination. The average of total AS use in NEU, CEU and SEU was used in the European characterization (the last column of the table). Maximum annual application rates among allowed AS are presented in kg/ha/year, with zero or two decimal places (if above or below 100 kg/ha/year, respectively). Total AS use is also presented in kg/ha/year, with zero decimal places. NEU = Northern Europe, CEU = Central Europe, SEU = Southern Europe. DPVF = dry pulses, vegetables, flowers; NPIC = non-permanent industrial crops; Perm. = permanent; Max. = maximum. BAU reference figures (in light blue) were added to the table for comparison.

Crop	Parameter	NEU		CEU		SEU		EUROPE	
		LHP	BAU	LHP	BAU	LHP	BAU	LHP	BAU
Cereals	Number of AS allowed	40	77	34	51	47	88	56	98
	Max. recom. annual rate	2.25	4.00	2.16	2.16	2.16	4.00	2.25	4.00
	Total AS use	15	31	11	18	12	31	-	-
Dry Pulses, Vegetables, Flowers	Number of AS allowed	28	49	17	30	38	68	40	72
	Max. recom. annual rate	50.00	612	50.00	612	4.77	612	50.00	612
	Total AS use	74	1,210	91	713	34	1,196	-	-
Grapes	Number of AS allowed	23	40	13	19	32	56	32	56
	Max. recom. annual rate	8.64	15.00	8.64	1,020	8.64	1,020	8.64	1,020
	Total AS use	22	54	17	1,046	27	1,088	-	-
Grassland	Number of AS allowed	8	8	7	7	8	8	11	11
	Max. recom. annual rate	1.44	1.44	1.80	1.80	1.44	1.44	1.80	1.80
	Total AS use	4	4	6	6	4	4	-	-
Maize	Number of AS allowed	12	21	10	18	14	23	15	24
	Max. recom. annual rate	2.16	2.16	2.16	2.16	2.16	2.16	2.16	2.16
	Total AS use	4	8	4	7	5	9	-	-
Non-Permanent Industrial crops	Number of AS allowed	19	28	11	18	22	32	25	39
	Max. recom. annual rate	3.00	3.00	2.16	2.40	2.16	2.40	2.16	3.00
	Total AS use	12	18	6	11	13	19	-	-
Permanent crops	Number of AS allowed	13	29	4	9	18	39	19	40
	Max. recom. annual rate	8.64	12.50	16.38	16.38	94.80	94.80	94.80	94.80
	Total AS use	17	60	26	45	113	157	-	-
Root crops	Number of AS allowed	35	58	15	30	38	64	40	67
	Max. recom. annual rate	6.50	153	3.50	153	75.60	153	75.60	153
	Total AS use	26	198	12	178	102	280	-	-

Table S5.11 – Number of active substances (AS) allowed under the Safe Human Health (SHH) scenario, maximum recommended annual application rate among allowed AS, and total AS use per crop-EU region combination. Annual application rates were calculated as the product of the (maximum) number of recommended treatments per year and the (maximum) recommended application rate per treatment in respective EC approved, AS representative use. Total AS use was calculated as the sum of the highest annual application rate of all the AS allowed per crop-EU region combination. The average of total AS use in NEU, CEU and SEU was used in the European characterization (the last column of the table). Maximum annual application rates among allowed AS are presented in kg/ha/year, with zero or two decimal places (if above or below 100 kg/ha/year, respectively). Total AS use is also presented in kg/ha/year, with zero decimal places. NEU = Northern Europe, CEU = Central Europe, SEU = Southern Europe. DPVF = dry pulses, vegetables, flowers; NPIC = non-permanent industrial crops; Perm. = permanent; Max. = maximum. BAU reference figures (in light blue) were added to the table for comparison.

Crop	Parameter	NEU		CEU		SEU		EUROPE	
		SHH	BAU	SHH	BAU	SHH	BAU	SHH	BAU
Cereals	Number of AS allowed	12	77	12	51	16	88	16	98
	Max. recom. annual rate	1.50	4.00	1.50	2.16	1.50	4.00	1.50	4.00
	Total AS use	3	31	3	18	4	31	-	-
Dry Pulses, Vegetables, Flowers	Number of AS allowed	14	49	6	30	18	68	19	72
	Max. recom. annual rate	50.00	612	50.00	612	3.60	612	50.00	612
	Total AS use	60	1,210	55	713	15	1,196	-	-
Grapes	Number of AS allowed	9	40	4	19	11	56	11	56
	Max. recom. annual rate	1.50	15.00	1.60	1,020	1.60	1,020	1.60	1,020
	Total AS use	4	54	3	1,046	7	1,088	-	-
Grassland	Number of AS allowed	4	8	4	7	5	8	5	11
	Max. recom. annual rate	1.44	1.44	1.44	1.80	1.44	1.44	1.44	1.80
	Total AS use	2	4	2	6	3	4	-	-
Maize	Number of AS allowed	6	21	6	18	7	23	7	24
	Max. recom. annual rate	0.36	2.16	1.20	2.16	1.20	2.16	1.20	2.16
	Total AS use	1	8	1	7	2	9	-	-
Non-Permanent Industrial crops	Number of AS allowed	5	28	3	18	6	32	8	39
	Max. recom. annual rate	3.00	3.00	1.20	2.40	1.20	2.40	3.00	3.00
	Total AS use	4	18	2	11	3	19	-	-
Permanent crops	Number of AS allowed	6	29	2	9	7	39	7	40
	Max. recom. annual rate	3.20	12.50	0.90	16.38	3.20	94.80	3.20	94.80
	Total AS use	4	60	1	45	5	157	-	-
Root crops	Number of AS allowed	14	58	6	30	14	64	14	67
	Max. recom. annual rate	1.44	153	1.00	153	1.44	153	1.44	153
	Total AS use	7	198	3	178	8	280	-	-

Table S5.12 – Number of active substances (AS) allowed under the Low Ecosystem Toxicity (LET) scenario, maximum recommended annual application rate among allowed AS, and total AS use per crop-EU region combination. Annual application rates were calculated as the product of the (maximum) number of recommended treatments per year and the (maximum) recommended application rate per treatment in respective EC approved, AS representative use. Total AS use was calculated as the sum of the highest annual application rate of all the AS allowed per crop-EU region combination. The average of total AS use in NEU, CEU and SEU was used in the European characterization (the last column of the table). Maximum annual application rates among allowed AS are presented in kg/ha/year, with zero or two decimal places (if above or below 100 kg/ha/year, respectively). Total AS use is also presented in kg/ha/year, with zero decimal places. NEU = Northern Europe, CEU = Central Europe, SEU = Southern Europe. DPVF = dry pulses, vegetables, flowers; NPIC = non-permanent industrial crops; Perm. = permanent; Max. = maximum. BAU reference figures (in light blue) were added to the table for comparison.

Crop	Parameter	NEU		CEU		SEU		EUROPE	
		LET	BAU	LET	BAU	LET	BAU	LET	BAU
Cereals	Number of AS allowed	20	77	11	51	25	88	25	98
	Max. recom. annual rate	4.00	4.00	2.16	2.16	4.00	4.00	4.00	4.00
	Total AS use	12	31	7	18	14	31	-	-
Dry Pulses, Vegetables, Flowers	Number of AS allowed	13	49	8	30	15	68	16	72
	Max. recom. annual rate	2.40	612	4.15	612	7.20	612	7.20	612
	Total AS use	9	1,210	11	713	20	1,196	-	-
Grapes	Number of AS allowed	11	40	6	19	13	56	13	56
	Max. recom. annual rate	8.64	15.00	8.64	1,020	8.64	1,020	8.64	1,020
	Total AS use	16	54	14	1,046	18	1,088	-	-
Grassland	Number of AS allowed	4	8	2	7	5	8	5	11
	Max. recom. annual rate	1.08	1.44	1.08	1.80	1.08	1.44	1.08	1.80
	Total AS use	2	4	1	6	2	4	-	-
Maize	Number of AS allowed	11	21	7	18	12	23	12	24
	Max. recom. annual rate	2.16	2.16	2.16	2.16	2.16	2.16	2.16	2.16
	Total AS use	6	8	6	7	8	9	-	-
Non-Permanent Industrial crops	Number of AS allowed	10	28	7	18	11	32	13	39
	Max. recom. annual rate	3.00	3.00	2.16	2.40	2.16	2.40	3.00	3.00
	Total AS use	7	18	5	11	7	19	-	-
Permanent crops	Number of AS allowed	5	29	2	9	6	39	6	40
	Max. recom. annual rate	12.50	12.50	8.64	16.38	10.00	94.80	12.50	94.80
	Total AS use	24	60	9	45	22	157	-	-
Root crops	Number of AS allowed	17	58	9	30	17	64	19	67
	Max. recom. annual rate	4.00	153	3.50	153	4.00	153	4.00	153
	Total AS use	14	198	8	178	12	280	-	-

Table S5.13 – Reductions in the number of active substances (AS) and in total AS use across the different scenarios. Reductions refer to corresponding Business As Usual scenario (BAU) figures. Reductions in pesticide input below 50% are marked in red, reductions ≥ 50% in green. The 50% threshold corresponds to the pesticide use reduction target of the Farm to Fork Strategy. NH = No Herbicides, FDP = Fast Degradable Pesticides, CFSE = Candidates For Substitution Excluded, LHP = Low Hazard Pesticides, SHH = Safe Human Health, LET = Low Ecosystem Toxicity. No Pesticides scenario was not considered as all reduction in the number of pesticides use and pesticide use are 100%. NEU = Northern Europe, CEU = Central Europe, SEU = Southern Europe. DPVF = dry pulses, vegetables, flowers, NPIC = non-permanent industrial crops, Perm. = permanent, n= number of AS covered in the respective reduction scenario.

	NH (n=139)			FDP (n=106)			CFSE (n=181)			LHP (n=136)			SHH (n=49)			LET (n=57)		
	NEU	CEU	SEU	NEU	CEU	SEU	NEU	CEU	SEU	NEU	CEU	SEU	NEU	CEU	SEU	NEU	CEU	SEU
% reduction in the number of pesticides																		
Cereals	39%	49%	43%	58%	53%	61%	29%	22%	25%	48%	33%	47%	84%	76%	82%	74%	78%	72%
DPVF	20%	33%	18%	51%	40%	46%	14%	13%	16%	43%	43%	44%	71%	80%	74%	73%	73%	78%
Grapes	15%	16%	13%	60%	42%	59%	18%	16%	20%	43%	32%	43%	78%	79%	80%	73%	68%	77%
Grassland	100%	100%	100%	50%	29%	50%	13%	0%	13%	0%	0%	0%	50%	43%	38%	50%	71%	38%
Maize	86%	78%	83%	29%	33%	30%	14%	17%	13%	43%	44%	39%	71%	67%	70%	48%	61%	48%
NPIC	68%	78%	66%	43%	33%	50%	32%	22%	34%	32%	39%	31%	82%	83%	81%	64%	61%	66%
Perm. Crops	14%	11%	15%	52%	44%	54%	21%	22%	18%	55%	56%	54%	79%	78%	82%	83%	78%	85%
Root crops	41%	47%	38%	48%	30%	47%	21%	20%	22%	40%	50%	41%	76%	80%	78%	71%	70%	73%
Average reduction	48%	51%	47%	49%	38%	50%	20%	16%	20%	38%	35%	37%	74%	73%	73%	67%	70%	67%
Overall reduction		**40%**			**54%**			**21%**			**41%**			**79%**			**75%**	
% reduction in total AS use																		
Cereals	52%	66%	49%	55%	40%	49%	28%	22%	22%	54%	37%	60%	89%	82%	87%	61%	63%	55%
DPVF	1%	2%	1%	2%	5%	2%	51%	86%	52%	94%	87%	97%	95%	92%	99%	99%	98%	98%
Grapes	28%	1%	1%	37%	1%	2%	6%	98%	94%	59%	98%	98%	92%	~100%	99%	70%	99%	98%
Grassland	100%	100%	100%	46%	25%	45%	3%	0%	3%	0%	0%	0%	37%	73%	35%	40%	80%	38%
Maize	97%	95%	96%	16%	6%	16%	7%	7%	6%	49%	40%	42%	93%	81%	81%	18%	21%	17%
NPIC	78%	96%	88%	48%	39%	49%	20%	30%	31%	32%	47%	33%	77%	83%	85%	58%	57%	61%
Perm. Crops	21%	19%	8%	27%	41%	72%	16%	17%	6%	72%	43%	28%	93%	98%	97%	59%	81%	86%
Root crops	9%	7%	6%	8%	4%	33%	82%	91%	60%	87%	93%	64%	96%	98%	97%	93%	96%	96%
Average reduction	48%	48%	44%	30%	20%	34%	27%	44%	34%	56%	56%	53%	84%	88%	85%	62%	74%	69%
Overall reduction		**47%**			**28%**			**35%**			**55%**			**86%**			**68%**	

Table S5.14– Ecotoxicological profile of the active substances (AS) allowed in the No Herbicides scenario (NH, n=139) according to PPDB: Pesticide Properties Database (*2019*). The numbers in the table indicate the number of AS known to have low, unknown, moderate or high toxicity to a respective organism-endpoint. PPDB toxicity thresholds are defined according to EU guidelines or EU regulatory values. The detailed timescale was provided whenever this information was available. LC = lethal concentration; EC = effect concentration; NOEC = highest no observed effect concentration. Grey highlighted cells show the most represented toxicity class per ecotoxicological endpoint. Blue cells indicate the average number of AS considered per hazard score.

Hazard score	**0**	**1**	**2**	**3**
Organism – Time scale – Endpoint (exposure route)	**Low toxicity**	**No data available**	**Moderate toxicity**	**High toxicity**
Mammals – acute – LC_{50} survival (oral)	55 (40%)	3 (2%)	66 (47%)	15 (11%)
Mammals – long-term – NOEC, survival, reproduction or development (dietary)	0 (0%)	59 (42%)	4 (3%)	76 (55%)
Birds – acute – LC_{50} survival (oral)	41 (29%)	4 (3%)	80 (58%)	14 (10%)
Birds – long-term – LC_{50}, survival (dietary)	45 (32%)	24 (17%)	67 (48%)	3 (2%)
Fish – acute 96 hour – LC_{50} survival	4 (3%)	1 (1%)	101 (73%)	33 (24%)
Fish – long-term 21 day – NOEC, survival, development, growth or behaviour	4 (3%)	24 (17%)	88 (63%)	23 (17%)
Aquatic invertebrates – acute 48 hour – EC_{50} immobilisation	3 (2%)	2 (1%)	94 (68%)	40 (29%)
Aquatic invertebrates – long-term 21 day – NOEC, immobilisation, reproduction or development	1 (1%)	20 (14%)	79 (57%)	39 (28%)
Aquatic plants – acute 7 day – EC_{50} growth	8 (6%)	78 (56%)	51 (37%)	2 (1%)
Algae – acute 72 hour – EC_{50} growth	25 (18%)	2 (1%)	104 (75%)	8 (6%)
Sediment dwelling organisms – Acute 96hour – LC_{50} survival	2 (1%)	61 (44%)	61 (44%)	15 (11%)
Honeybees – acute 48 hour – LC_{50} survival (contact)	34 (24%)	5 (4%)	77 (55%)	23 (17%)
Honeybees – acute 48 hour – LC_{50} survival (oral)	50 (36%)	8 (6%)	60 (43%)	21 (15%)
Terrestrial arthropods other than bees* – not available – LC_{50} survival	23 (17%)	94 (68%)	5 (4%)	17 (12%)
Earthworms – acute 14 day – LC_{50} survival	3 (2%)	5 (4%)	126 (91%)	5 (4%)
Earthworms – long-term 56 day – NOEC, survival or reproduction	10 (7%)	48 (35%)	79 (57%)	2 (1%)
Soil macro-organisms other than earthworms** – acute – LC_{50} survival	0 (0%)	134 (96%)	2 (1%)	3 (2%)
Soil macro-organisms other than earthworms** – long-term – NOEC, survival or reproduction	5 (4%)	123 (88%)	11 (8%)	0 (0%)
Average number of AS per hazard score	17 (13%)	39 (28%)	64 (46%)	19 (14%)
	No significant adverse effect	**No data available**	**EC/NOEC value or chronic effect**	
Soil micro-organisms – long-term 100 days – Nitrogen mineralisation	119 (86%)	18 (13%)	2 (1%)	
Soil micro-organisms – long-term 100 days – Carbon mineralisation	118 (85%)	20 (14%)	1 (1%)	
Average number of AS per hazard score	119 (85%)	19 (14%)	2 (1%)	

*Low-moderate and moderate-high toxicity thresholds were defined as 25 and 50% effect, respectively; **Data in PPDB is very limited; interpretation of available data was done with earthworms' thresholds.

Table S5.15 – Ecotoxicological profile of the active substances (AS) allowed in the Fast Degradable Pesticide scenario (FDP, n=106) according to PPDB: Pesticide Properties Database (*2019*). The numbers in the table indicate the number of AS known to have low, unknown, moderate or high toxicity to a respective organism-endpoint. PPDB toxicity thresholds are defined according to EU guidelines or EU regulatory values. The detailed timescale was provided whenever this information was available. LC = lethal concentration; EC = effect concentration; NOEC = highest no observed effect concentration. Grey highlighted cells show the most represented toxicity class per ecotoxicological endpoint. Blue cells indicate the average number of AS considered per hazard score.

Hazard score	**0**	**1**	**2**	**3**
Organism – Time scale – Endpoint (exposure route)	**Low toxicity**	**No data available**	**Moderate toxicity**	**High toxicity**
Mammals – acute – LC_{50} survival (oral)	48 (45%)	4 (4%)	48 (45%)	6 (6%)
Mammals – long-term – NOEC, survival, reproduction or development (dietary)	0 (0%)	40 (38%)	12 (11%)	54 (51%)
Birds – acute – LC_{50} survival (oral)	32 (30%)	4 (4%)	63 (59%)	7 (7%)
Birds – long-term – LC_{50}, survival (dietary)	46 (43%)	20 (19%)	38 (36%)	2 (2%)
Fish – acute 96 hour – LC_{50} survival	12 (11%)	1 (1%)	80 (75%)	13 (12%)
Fish – long-term 21 day – NOEC, survival, development, growth or behaviour	22 (21%)	16 (15%)	56 (53%)	12 (11%)
Aquatic invertebrates – acute 48 hour – EC_{50} immobilisation	12 (11%)	4 (4%)	73 (69%)	17 (16%)
Aquatic invertebrates – long-term 21 day – NOEC, immobilisation, reproduction or development	22 (21%)	15 (14%)	49 (46%)	20 (19%)
Aquatic plants – acute 7 day – EC_{50} growth	11 (10%)	38 (36%)	41 (39%)	16 (15%)
Algae – acute 72 hour – EC_{50} growth	26 (25%)	4 (4%)	69 (65%)	7 (7%)
Sediment dwelling organisms – Acute 96hour – LC_{50} survival	5 (5%)	74 (70%)	22 (21%)	5 (5%)
Honeybees – acute 48 hour – LC_{50} survival (contact)	26 (25%)	4 (4%)	65 (61%)	11 (10%)
Honeybees – acute 48 hour – LC_{50} survival (oral)	42 (40%)	9 (8%)	44 (42%)	11 (10%)
Terrestrial arthropods other than bees* – not available – LC_{50} survival	25 (24%)	62 (58%)	5 (5%)	14 (13%)
Earthworms – acute 14 day – LC_{50} survival	6 (6%)	5 (5%)	92 (87%)	3 (3%)
Earthworms – long-term 56 day – NOEC, survival or reproduction	4 (4%)	61 (58%)	40 (38%)	1 (1%)
Soil macro-organisms other than earthworms** – acute – LC_{50} survival	0 (0%)	102 (96%)	2 (2%)	2 (2%)
Soil macro-organisms other than earthworms** – long-term – NOEC, survival or reproduction	2 (2%)	102 (96%)	2 (2%)	0 (0%)
Average number of AS per hazard score	19 (18%)	31 (30%)	45 (42%)	11 (11%)
	No significant adverse effect	**No data available**	**EC/NOEC value or chronic effect**	
Soil micro-organisms – long-term 100 days – Nitrogen mineralisation	91 (86%)	14 (13%)	1 (1%)	
Soil micro-organisms – long-term 100 days – Carbon mineralisation	89 (84%)	15 (14%)	2 (2%)	
Average number of AS per hazard score	90 (85%)	15 (14%)	2 (1%)	

*Low-moderate and moderate-high toxicity thresholds were defined as 25 and 50% effect, respectively; **Data in PPDB is very limited; interpretation of available data was done with earthworms' thresholds.

Table S5.16 – Ecotoxicological profile of the active substances (AS) still likely to be found in the environment after the pesticide use stop in the Total Pesticide Ban scenario (TPB, n=60) according to PPDB: Pesticide Properties Database (2019). The numbers in the table indicate the number of AS known to have low, unknown, moderate or high toxicity to a respective organism-endpoint. PPDB toxicity thresholds are defined according to EU guidelines or EU regulatory values. The detailed timescale was provided whenever this information was available. LC = lethal concentration; EC = effect concentration; NOEC = highest no observed effect concentration. Grey highlighted cells show the most represented toxicity class per ecotoxicological endpoint. Blue cells indicate the average number of AS considered per hazard score.

Hazard score	**0**	**1**	**2**	**3**
Organism – Time scale – Endpoint (exposure route)	**Low toxicity**	**No data available**	**Moderate toxicity**	**High toxicity**
Mammals – acute – LC_{50} survival (oral)	27 (45%)	2 (3%)	27 (45%)	4 (7%)
Mammals – long-term – NOEC, survival, reproduction or development (dietary)	0 (0%)	28 (47%)	0 (0%)	32 (53%)
Birds – acute – LC_{50} survival (oral)	19 (32%)	3 (5%)	35 (58%)	3 (5%)
Birds – long-term – LC_{50}, survival (dietary)	16 (27%)	11 (18%)	32 (53%)	1 (2%)
Fish – acute 96 hour – LC_{50} survival	1 (2%)	3 (5%)	44 (73%)	12 (20%)
Fish – long-term 21 day – NOEC, survival, development, growth or behaviour	0 (0%)	9 (15%)	44 (73%)	7 (12%)
Aquatic invertebrates – acute 48 hour – EC_{50} immobilisation	2 (3%)	3 (5%)	42 (70%)	13 (22%)
Aquatic invertebrates – long-term 21 day – NOEC, immobilisation, reproduction or development	1 (2%)	7 (12%)	44 (73%)	8 (13%)
Aquatic plants – acute 7 day – EC_{50} growth	3 (5%)	26 (43%)	29 (48%)	2 (3%)
Algae – acute 72 hour – EC_{50} growth	5 (8%)	2 (3%)	47 (78%)	6 (10%)
Sediment dwelling organisms – Acute 96hour – LC_{50} survival	1 (2%)	22 (37%)	31 (52%)	6 (10%)
Honeybees – acute 48 hour – LC_{50} survival (contact)	17 (28%)	3 (5%)	35 (58%)	5 (8%)
Honeybees – acute 48 hour – LC_{50} survival (oral)	22 (37%)	3 (5%)	30 (50%)	5 (8%)
Terrestrial arthropods other than bees* – not available – LC_{50} survival	13 (22%)	41 (68%)	1 (2%)	5 (8%)
Earthworms – acute 14 day – LC_{50} survival	0 (0%)	3 (5%)	56 (93%)	1 (2%)
Earthworms – long-term 56 day – NOEC, survival or reproduction	5 (8%)	18 (30%)	36 (60%)	1 (2%)
Soil macro-organisms other than earthworms** – acute – LC_{50} survival	0 (0%)	60 (100%)	0 (0%)	0 (0%)
Soil macro-organisms other than earthworms** – long-term – NOEC, survival or reproduction	5 (8%)	47 (78%)	8 (13%)	0 (0%)
Average number of AS per hazard score	8 (13%)	16 (27%)	30 (50%)	6 (10%)
	No significant adverse effect	**No data available**	**EC/NOEC value or chronic effect**	
Soil micro-organisms – long-term 100 days – Nitrogen mineralisation	51 (85%)	8 (13%)	1 (2%)	
Soil micro-organisms – long-term 100 days – Carbon mineralisation	52 (87%)	8 (13%)	0 (0%)	
Average number of AS per hazard score	52 (86%)	8 (13%)	1 (3%)	

*Low-moderate and moderate-high toxicity thresholds were defined as 25 and 50% effect, respectively; **Data in PPDB is very limited; interpretation of available data was done with earthworms' thresholds.

Table S5.17 – Ecotoxicological profile of the active substances (AS) allowed in the Candidates For Substitution Excluded scenario (CFSE, n=181) according to PPDB: Pesticide Properties Database (2019). The numbers in the table indicate the number of AS known to have low, unknown, moderate or high toxicity to a respective organism-endpoint. PPDB toxicity thresholds are defined according to EU guidelines or EU regulatory values. The detailed timescale was provided whenever this information was available. LC = lethal concentration; EC = effect concentration; NOEC = highest no observed effect concentration. Grey highlighted cells show the most represented toxicity class per ecotoxicological endpoint. Blue cells indicate the average number of AS considered per hazard score.

Hazard score	**0**	**1**	**2**	**3**
Organism – Time scale – Endpoint (exposure route)	**Low toxicity**	**No data available**	**Moderate toxicity**	**High toxicity**
Mammals – acute – LC_{50} survival (oral)	90 (50%)	7 (4%)	76 (42%)	8 (4%)
Mammals – long-term – NOEC, survival, reproduction or development (dietary)	0 (0%)	81 (45%)	14 (8%)	86 (48%)
Birds – acute – LC_{50} survival (oral)	61 (34%)	8 (4%)	106 (59%)	6 (3%)
Birds – long-term – LC_{50}, survival (dietary)	65 (36%)	41 (23%)	74 (41%)	1 (1%)
Fish – acute 96 hour – LC_{50} survival	13 (7%)	3 (2%)	140 (77%)	25 (14%)
Fish – long-term 21 day – NOEC, survival, development, growth or behaviour	27 (15%)	34 (19%)	102 (56%)	18 (10%)
Aquatic invertebrates – acute 48 hour – EC_{50} immobilisation	14 (8%)	6 (3%)	132 (73%)	29 (16%)
Aquatic invertebrates – long-term 21 day – NOEC, immobilisation, reproduction or development	25 (14%)	26 (14%)	100 (55%)	30 (17%)
Aquatic plants – acute 7 day – EC_{50} growth	18 (10%)	69 (38%)	75 (41%)	19 (10%)
Algae – acute 72 hour – EC_{50} growth	40 (22%)	7 (4%)	122 (67%)	12 (7%)
Sediment dwelling organisms – Acute 96hour – LC_{50} survival	8 (4%)	101 (56%)	61 (34%)	11 (6%)
Honeybees – acute 48 hour – LC_{50} survival (contact)	42 (23%)	9 (5%)	114 (63%)	16 (9%)
Honeybees – acute 48 hour – LC_{50} survival (oral)	67 (37%)	15 (8%)	85 (47%)	14 (8%)
Terrestrial arthropods other than bees* – not available – LC_{50} survival	41 (23%)	115 (64%)	6 (3%)	19 (10%)
Earthworms – acute 14 day – LC_{50} survival	8 (4%)	8 (4%)	161 (89%)	4 (2%)
Earthworms – long-term 56 day – NOEC, survival or reproduction	12 (7%)	84 (46%)	84 (46%)	1 (1%)
Soil macro-organisms other than earthworms** – acute – LC_{50} survival	0 (0%)	177 (98%)	2 (1%)	2 (1%)
Soil macro-organisms other than earthworms** – long-term – NOEC, survival or reproduction	4 (2%)	167 (92%)	10 (6%)	0 (0%)
Average number of AS per hazard score	30 (16%)	53 (29%)	81 (45%)	17 (9%)
	No significant adverse effect	**No data available**	**EC/NOEC value or chronic effect**	
Soil micro-organisms – long-term 100 days – Nitrogen mineralisation	150 (83%)	30 (16%)	1 (1%)	
Soil micro-organisms – long-term 100 days – Carbon mineralisation	148 (82%)	32 (18%)	1 (1%)	
Average number of AS per hazard score	149 (82%)	31 (17%)	1 (1%)	

*Low-moderate and moderate-high toxicity thresholds were defined as 25 and 50% effect, respectively; **Data in PPDB is very limited; interpretation of available data was done with earthworms' thresholds.

Table S5.18 – Ecotoxicological profile of the active substances (AS) allowed in the Low Hazard Pesticides scenario (LHP, n=136) according to PPDB: Pesticide Properties Database (2019). The numbers in the table indicate the number of AS known to have low, unknown, moderate or high toxicity to a respective organism-endpoint. PPDB toxicity thresholds are defined according to EU guidelines or EU regulatory values. The detailed timescale was provided whenever this information was available. LC = lethal concentration; EC = effect concentration; NOEC = highest no observed effect concentration. Grey highlighted cells show the most represented toxicity class per ecotoxicological endpoint. Blue cells indicate the average number of AS considered per hazard score.

Hazard score	**0**	**1**	**2**	**3**
Organism – Time scale – Endpoint (exposure route)	**Low toxicity**	**No data available**	**Moderate toxicity**	**High toxicity**
Mammals – acute – LC_{50} survival (oral)	78 (57%)	8 (6%)	49 (36%)	1 (1%)
Mammals – long-term – NOEC, survival, reproduction or development (dietary)	0 (0%)	68 (50%)	12 (9%)	56 (41%)
Birds – acute – LC_{50}, survival (oral)	53 (39%)	8 (6%)	74 (54%)	1 (1%)
Birds – long-term – LC_{50}, survival (dietary)	54 (40%)	35 (26%)	47 (35%)	0 (0%)
Fish – acute 96 hour – LC_{50} survival	13 (10%)	4 (3%)	109 (80%)	10 (7%)
Fish – long-term 21 day – NOEC, survival, development, growth or behaviour	26 (19%)	26 (19%)	77 (57%)	7 (5%)
Aquatic invertebrates – acute 48 hour – EC_{50} immobilisation	13 (10%)	5 (4%)	106 (78%)	12 (9%)
Aquatic invertebrates – long-term 21 day – NOEC, immobilisation, reproduction or development	28 (21%)	20 (15%)	77 (57%)	11 (8%)
Aquatic plants – acute 7 day – EC_{50} growth	16 (12%)	44 (32%)	58 (43%)	18 (13%)
Algae – acute 72 hour – EC_{50} growth	35 (26%)	5 (4%)	84 (62%)	12 (9%)
Sediment dwelling organisms – Acute 96hour – LC_{50} survival	7 (5%)	84 (62%)	42 (31%)	3 (2%)
Honeybees – acute 48 hour – LC_{50} survival (contact)	41 (30%)	9 (7%)	83 (61%)	3 (2%)
Honeybees – acute 48 hour – LC_{50} survival (oral)	58 (43%)	15 (11%)	61 (45%)	2 (1%)
Terrestrial arthropods other than bees* – not available – LC_{50} survival	38 (28%)	85 (63%)	2 (1%)	11 (8%)
Earthworms – acute 14 day – LC_{50} survival	5 (4%)	8 (6%)	122 (90%)	1 (1%)
Earthworms – long-term 56 day – NOEC, survival or reproduction	11 (8%)	69 (51%)	55 (40%)	1 (1%)
Soil macro-organisms other than earthworms** – acute – LC_{50}, survival	0 (0%)	134 (99%)	1 (1%)	1 (1%)
Soil macro-organisms other than earthworms** – long-term – NOEC, survival or reproduction	6 (4%)	126 (93%)	4 (3%)	0 (0%)
Average number of AS per hazard score	27 (20%)	42 (31%)	59 (43%)	8 (6%)
	No significant adverse effect	**No data available**	**EC/NOEC value or chronic effect**	
Soil micro-organisms – long-term 100 days – Nitrogen mineralisation	111 (82%)	24 (18%)	1 (<1%)	
Soil micro-organisms – long-term 100 days – Carbon mineralisation	110 (81%)	25 (18%)	1 (<1%)	
Average number of AS per hazard score	111 (82%)	25 (18%)	1 (<1%)	

*Low-moderate and moderate-high toxicity thresholds were defined as 25 and 50% effect, respectively; **Data in PPDB is very limited; interpretation of available data was done with earthworms' thresholds.

Table S5.19 – Ecotoxicological profile of the active substances (AS) allowed in the Safe Human Health scenario (SHH, n=49) according to PPDB: Pesticide Properties Database (*2019*). The numbers in the table indicate the number of AS known to have low, unknown, moderate or high toxicity to a respective organism-endpoint. PPDB toxicity thresholds are defined according to EU guidelines or EU regulatory values. The detailed timescale was provided whenever this information was available. LC = lethal concentration; EC = effect concentration; NOEC = highest no observed effect concentration. Grey highlighted cells show the most represented toxicity class per ecotoxicological endpoint. Blue cells indicate the average number of AS considered per hazard score.

Hazard score	**0**	**1**	**2**	**3**
Organism – Time scale – Endpoint (exposure route)	**Low toxicity**	**No data available**	**Moderate toxicity**	**High toxicity**
Mammals – acute – LC_{50} survival (oral)	26 (53%)	1 (2%)	20 (41%)	2 (4%)
Mammals – long-term – NOEC, survival, reproduction or development (dietary)	0 (0%)	24 (49%)	4 (8%)	21 (43%)
Birds – acute – LC_{50} survival (oral)	16 (33%)	0 (0%)	31 (63%)	2 (4%)
Birds – long-term – LC_{50}, survival (dietary)	22 (45%)	10 (20%)	17 (35%)	0 (0%)
Fish – acute 96 hour – LC_{50} survival	4 (8%)	0 (0%)	40 (82%)	5 (10%)
Fish – long-term 21 day – NOEC, survival, development, growth or behaviour	9 (18%)	6 (12%)	29 (59%)	5 (10%)
Aquatic invertebrates – acute 48 hour – EC_{50} immobilisation	6 (12%)	0 (0%)	34 (69%)	9 (18%)
Aquatic invertebrates – long-term 21 day – NOEC, immobilisation, reproduction or development	12 (24%)	4 (8%)	25 (51%)	8 (16%)
Aquatic plants – acute 7 day – EC_{50} growth	7 (14%)	9 (18%)	25 (51%)	8 (16%)
Algae – acute 72 hour – EC_{50} growth	15 (31%)	1 (2%)	27 (55%)	6 (12%)
Sediment dwelling organisms – Acute 96hour – LC_{50} survival	3 (6%)	28 (57%)	15 (31%)	3 (6%)
Honeybees – acute 48 hour – LC_{50} survival (contact)	14 (29%)	0 (0%)	32 (65%)	3 (6%)
Honeybees – acute 48 hour – LC_{50} survival (oral)	20 (41%)	4 (8%)	23 (47%)	2 (4%)
Terrestrial arthropods other than bees* – not available – LC_{50} survival	11 (22%)	30 (61%)	3 (6%)	5 (10%)
Earthworms – acute 14 day – LC_{50} survival	1 (2%)	2 (4%)	45 (92%)	1 (2%)
Earthworms – long-term 56 day – NOEC, survival or reproduction	5 (10%)	18 (37%)	25 (51%)	1 (2%)
Soil macro-organisms other than earthworms** – acute – LC_{50} survival	0 (0%)	48 (98%)	0 (0%)	1 (2%)
Soil macro-organisms other than earthworms** – long-term – NOEC, survival or reproduction	1 (2%)	47 (96%)	1 (2%)	0 (0%)
Average number of AS per hazard score	10 (20%)	13 (26%)	22 (45%)	5 (9%)
	No significant adverse effect	**No data available**	**EC/NOEC value or chronic effect**	
Soil micro-organisms – long-term 100 days – Nitrogen mineralisation	45 (92%)	4 (8%)	0 (0%)	
Soil micro-organisms – long-term 100 days – Carbon mineralisation	44 (90%)	5 (10%)	0 (0%)	
Average number of AS per hazard score	45 (91%)	5 (9%)	0 (0%)	

*Low-moderate and moderate-high toxicity thresholds were defined as 25 and 50% effect, respectively; **Data in PPDB is very limited; interpretation of available data was done with earthworms' thresholds.

Table S5.20 – Ecotoxicological profile of the active substances (AS) allowed in the Low Ecosystem Toxicity scenario (LET, n=57) according to PPDB: Pesticide Properties Database (2019). The numbers in the table indicate the number of AS known to have low, unknown, moderate or high toxicity to a respective organism-endpoint. PPDB toxicity thresholds are defined according to EU guidelines or EU regulatory values. The detailed timescale was provided whenever this information was available. LC = lethal concentration; EC = effect concentration; NOEC = highest no observed effect concentration. Grey highlighted cells show the most represented toxicity class per ecotoxicological endpoint. Blue cells indicate the average number of AS considered per hazard score.

Hazard score	**0**	**1**	**2**	**3**
Organism – Time scale – Endpoint (exposure route)	**Low toxicity**	**No data available**	**Moderate toxicity**	**High toxicity**
Mammals – acute – LC_{50} survival (oral)	28 (49%)	0 (0%)	29 (51%)	0 (0%)
Mammals – long-term – NOEC, survival, reproduction or development (dietary)	0 (0%)	14 (25%)	4 (7%)	39 (68%)
Birds – acute – LC_{50} survival (oral)	16 (28%)	0 (0%)	41 (72%)	0 (0%)
Birds – long-term – LC_{50}, survival (dietary)	27 (47%)	0 (0%)	30 (53%)	0 (0%)
Fish – acute 96 hour – LC_{50} survival	4 (7%)	0 (0%)	53 (93%)	0 (0%)
Fish – long-term 21 day – NOEC, survival, development, growth or behaviour	10 (18%)	1 (2%)	46 (81%)	0 (0%)
Aquatic invertebrates – acute 48 hour – EC_{50} immobilisation	4 (7%)	0 (0%)	53 (93%)	0 (0%)
Aquatic invertebrates – long-term 21 day – NOEC, immobilisation, reproduction or development	15 (26%)	1 (2%)	41 (72%)	0 (0%)
Aquatic plants – acute 7 day – EC_{50} growth	10 (18%)	1 (2%)	46 (81%)	0 (0%)
Algae – acute 72 hour – EC_{50} growth	16 (28%)	0 (0%)	41 (72%)	0 (0%)
Sediment dwelling organisms – Acute 96hour – LC_{50} survival	4 (7%)	34 (60%)	19 (33%)	0 (0%)
Honeybees – acute 48 hour – LC_{50} survival (contact)	16 (28%)	0 (0%)	41 (72%)	0 (0%)
Honeybees – acute 48 hour – LC_{50} survival (oral)	20 (35%)	1 (2%)	36 (63%)	0 (0%)
Terrestrial arthropods other than bees* – not available – LC_{50} survival	15 (26%)	31 (54%)	2 (4%)	9 (16%)
Earthworms – acute 14 day – LC_{50} survival	3 (5%)	1 (2%)	53 (93%)	0 (0%)
Earthworms – long-term 56 day – NOEC, survival or reproduction	3 (5%)	24 (42%)	29 (51%)	1 (2%)
Soil macro-organisms other than earthworms** – acute – LC_{50} survival	0 (0%)	55 (96%)	1 (2%)	1 (2%)
Soil macro-organisms other than earthworms** – long-term – NOEC, survival or reproduction	0 (0%)	53 (93%)	4 (7%)	0 (0%)
Average number of AS per hazard score	11 (19%)	12 (21%)	32 (55%)	3 (5%)
	No significant adverse effect	**No data available**	**EC/NOEC value or chronic effect**	
Soil micro-organisms – long-term 100 days – Nitrogen mineralisation	56 (98%)	1 (2%)	0 (0%)	
Soil micro-organisms – long-term 100 days – Carbon mineralisation	56 (98%)	1 (2%)	0 (0%)	
Average number of AS per hazard score	56 (98%)	1 (2%)	0 (0%)	

*Low-moderate and moderate-high toxicity thresholds were defined as 25 and 50% effect, respectively; **Data in PPDB is very limited; interpretation of available data was done with earthworms' thresholds.

Table S5.21 – Human health problems associated with the active substances (AS) allowed in the No Herbicides scenario (NH, n=139), according to PPDB (2019). The numbers in the table indicate the number of active substances known to cause the respective problem, known to not cause the problem, with status not identified or no data available. Grey highlighted cells show the most represented class per endpoint. Blue cells indicate the average number of AS considered per hazard score (the 11 human endpoints considered).

Hazard scores	**0**	**1**	**2**	**3**
Effect / **Endpoint**	**No (known to not cause a problem)**	**Unknown (no data found)**	**Possibly (status not identified)**	**Yes (known to cause a problem)**
Carcinogen	78 (56%)	4 (3%)	50 (36%)	7 (5%)
Mutagen	55 (40%)	71 (51%)	10 (7%)	3 (2%)
Endocrine distruptor	36 (26%)	65 (47%)	32 (23%)	6 (4%)
Reproduction/development effects	25 (18%)	11 (8%)	66 (47%)	37 (27%)
Acetyl cholinesterase inhibitor	111 (80%)	14 (10%)	4 (3%)	10 (7%)
Neurotoxicant	88 (63%)	17 (12%)	23 (17%)	11 (8%)
Respiratory tract irritant	48 (35%)	57 (41%)	9 (6%)	25 (18%)
Skin irritant	82 (59%)	5 (4%)	18 (13%)	34 (24%)
Skin sensitiser	17 (12%)	79 (57%)	16 (12%)	27 (19%)
Eye irritant	68 (49%)	5 (4%)	20 (14%)	46 (33%)
Phototoxicant	19 (14%)	117 (84%)	2 (1%)	1 (1%)
Average number of AS per hazard score	57 (41%)	40 (29%)	23 (16%)	19 (14%)

Table S5.22 – Human health problems associated with the active substances (AS) allowed in the Fast Degradable Pesticides (FDP, n=106), according to PPDB. The numbers in the table indicate the number of active substances known to cause the respective problem, known to not cause the problem, with status not identified or no data available. Grey highlighted cells show the most represented class per endpoint. Blue cells indicate the average number of AS considered per hazard score (the 11 human endpoints considered).

Hazard scores	**0**	**1**	**2**	**3**
Effect / **Endpoint**	**No (known to not cause a problem)**	**Unknown (no data found)**	**Possibly (status not identified)**	**Yes (known to cause a problem)**
Carcinogen	61 (58%)	7 (7%)	36 (34%)	2 (2%)
Mutagen	49 (46%)	48 (45%)	6 (6%)	3 (3%)
Endocrine distruptor	28 (26%)	58 (55%)	18 (17%)	2 (2%)
Reproduction/development effects	23 (22%)	15 (14%)	41 (39%)	27 (25%)
Acetyl cholinesterase inhibitor	90 (85%)	4 (4%)	5 (5%)	7 (7%)
Neurotoxicant	64 (60%)	18 (17%)	15 (14%)	9 (8%)
Respiratory tract irritant	33 (31%)	41 (39%)	6 (6%)	26 (25%)
Skin irritant	53 (50%)	6 (6%)	12 (11%)	35 (33%)
Skin sensitiser	17 (16%)	50 (47%)	11 (10%)	28 (26%)
Eye irritant	40 (38%)	6 (6%)	8 (8%)	52 (49%)
Phototoxicant	23 (22%)	81 (76%)	2 (2%)	0 (0%)
Average number of AS per hazard score	44 (41%)	30 (29%)	15 (14%)	17 (16%)

Table S5.23 – Human health problems associated with the active substances (AS) likely to be found in the environment after a possible/planned pesticide use stop in the Total Pesticide Ban scenario (TPB, n=60), according to PPDB. The numbers in the table indicate the number of active substances known to cause the respective problem, known to not cause the problem, with status not identified or no data available. Grey highlighted cells show the most represented class per endpoint. Blue cells indicate the average number of AS considered per hazard score (the 11 human endpoints considered).

Hazard scores	**0**	**1**	**2**	**3**
Effect / Endpoint	**No (known to not cause a problem)**	**Unknown (no data found)**	**Possibly (status not identified)**	**Yes (known to cause a problem)**
Carcinogen	30 (50%)	2 (3%)	24 (40%)	4 (7%)
Mutagen	23 (38%)	31 (52%)	6 (10%)	0 (0%)
Endocrine distruptor	11 (18%)	32 (53%)	13 (22%)	4 (7%)
Reproduction/development effects	5 (8%)	4 (7%)	36 (60%)	15 (25%)
Acetyl cholinesterase inhibitor	49 (82%)	11 (18%)	0 (0%)	0 (0%)
Neurotoxicant	41 (68%)	10 (17%)	7 (12%)	2 (3%)
Respiratory tract irritant	19 (32%)	24 (40%)	5 (8%)	12 (20%)
Skin irritant	43 (72%)	4 (7%)	6 (10%)	7 (12%)
Skin sensitiser	8 (13%)	40 (67%)	4 (7%)	8 (13%)
Eye irritant	35 (58%)	4 (7%)	7 (12%)	14 (23%)
Phototoxicant	4 (7%)	54 (90%)	1 (2%)	1 (2%)
Average number of AS per hazard score	24 (41%)	20 (33%)	10 (17%)	6 (10%)

Table S5.24 – Human health problems associated with the active substances (AS) allowed in the Candidates For Substitution Excluded scenario (CFSE, n=181), according to PPDB. The numbers in the table indicate the number of active substances known to cause the respective problem, known to not cause the problem, with status not identified or no data available. Grey highlighted cells show the most represented class per endpoint. Blue cells indicate the average number of AS considered per hazard score (the 11 human endpoints considered).

Hazard scores	**0**	**1**	**2**	**3**
Effect / Endpoint	**No (known to not cause a problem)**	**Unknown (no data found)**	**Possibly (status not identified)**	**Yes (known to cause a problem)**
Carcinogen	101 (56%)	10 (6%)	62 (34%)	8 (4%)
Mutagen	82 (45%)	89 (49%)	9 (5%)	1 (1%)
Endocrine distruptor	44 (24%)	100 (55%)	31 (17%)	6 (3%)
Reproduction/development effects	43 (24%)	13 (7%)	82 (45%)	43 (24%)
Acetyl cholinesterase inhibitor	152 (84%)	18 (10%)	6 (3%)	5 (3%)
Neurotoxicant	112 (62%)	33 (18%)	23 (13%)	13 (7%)
Respiratory tract irritant	60 (33%)	72 (40%)	12 (7%)	37 (20%)
Skin irritant	110 (61%)	6 (3%)	17 (9%)	48 (27%)
Skin sensitiser	25 (14%)	104 (57%)	17 (9%)	35 (19%)
Eye irritant	89 (49%)	6 (3%)	21 (12%)	65 (36%)
Phototoxicant	29 (16%)	148 (82%)	3 (2%)	1 (1%)
Average number of AS per hazard score	77 (43%)	54 (30%)	26 (14%)	24 (13%)

Table S5.25 – Human health problems associated with the active substances (AS) allowed in the Low Hazard Pesticide scenario (LHP, n=136), according to PPDB (2019). The numbers in the table indicate the number of active substances known to cause the respective problem, known to not cause the problem, with status not identified or no data available. Grey highlighted cells show the most represented class per endpoint. Blue cells indicate the average number of AS considered per hazard score (the 11 human endpoints considered).

Hazard scores	**0**	**1**	**2**	**3**
Effect / **Endpoint**	**No (known to not cause a problem)**	**Unknown (no data found)**	**Possibly (status not identified)**	**Yes (known to cause a problem)**
Carcinogen	82 (60%)	10 (7%)	36 (26%)	8 (6%)
Mutagen	74 (54%)	58 (43%)	4 (3%)	0 (0%)
Endocrine distruptor	43 (32%)	78 (57%)	13 (10%)	2 (1%)
Reproduction/development effects	33 (24%)	9 (7%)	67 (49%)	27 (20%)
Acetyl cholinesterase inhibitor	120 (88%)	13 (10%)	3 (2%)	0 (0%)
Neurotoxicant	101 (74%)	22 (16%)	10 (7%)	3 (2%)
Respiratory tract irritant	53 (39%)	53 (39%)	11 (8%)	19 (14%)
Skin irritant	96 (71%)	7 (5%)	11 (8%)	22 (16%)
Skin sensitiser	24 (18%)	83 (61%)	9 (7%)	20 (15%)
Eye irritant	75 (55%)	7 (5%)	15 (11%)	39 (29%)
Phototoxicant	20 (15%)	112 (82%)	3 (2%)	1 (1%)
Average number of AS per hazard score	66 (48%)	41 (30%)	17 (12%)	13 (9%)

Table S5.26 – Human health problems associated with the active substances (AS) allowed in the Safe Human Health (SHH) scenario (n=49), according to PPDB. The numbers in the table indicate the number of active substances known to cause the respective problem, known to not cause the problem, with status not identified or no data available. Grey highlighted cells show the most represented class per endpoint. Blue cells indicate the average number of AS considered per hazard score (the 11 human endpoints considered).

Hazard scores	**0**	**1**	**2**	**3**
Effect / **Endpoint**	**No (known to not cause a problem)**	**Unknown (no data found)**	**Possibly (status not identified)**	**Yes (known to cause a problem)**
Carcinogen	49 (100%)	0 (0%)	0 (0%)	0 (0%)
Mutagen	49 (100%)	0 (0%)	0 (0%)	0 (0%)
Endocrine distruptor	19 (39%)	26 (53%)	4 (8%)	0 (0%)
Reproduction/development effects	13 (27%)	3 (6%)	33 (67%)	0 (0%)
Acetyl cholinesterase inhibitor	43 (88%)	4 (8%)	1 (2%)	1 (2%)
Neurotoxicant	38 (78%)	6 (12%)	5 (10%)	0 (0%)
Respiratory tract irritant	15 (31%)	17 (35%)	4 (8%)	13 (27%)
Skin irritant	34 (69%)	0 (0%)	4 (8%)	11 (22%)
Skin sensitiser	9 (18%)	27 (55%)	1 (2%)	12 (24%)
Eye irritant	24 (49%)	0 (0%)	7 (14%)	18 (37%)
Phototoxicant	11 (22%)	37 (76%)	1 (2%)	0 (0%)
Average number of AS per hazard score	28 (56%)	11 (22%)	5 (11%)	5 (10%)

Table S5.27 – Human health problems associated with the active substances (AS) allowed in the Low Ecosystem Toxicity (LET) scenario (n=57), according to PPDB. The numbers in the table indicate the number of active substances known to cause the respective problem, known to not cause the problem, with status not identified or no data available. Grey highlighted cells show the most represented class per endpoint. Blue cells indicate the average number of AS considered per hazard score (the 11 human endpoints considered).

Hazard scores	**0**	**1**	**2**	**3**
Endpoint / **Effect**	**No (known to not cause a problem)**	**Unknown (no data found)**	**Possibly (status not identified)**	**Yes (known to cause a problem)**
Carcinogen	36 (63%)	1 (2%)	20 (35%)	0 (0%)
Mutagen	31 (54%)	21 (37%)	4 (7%)	1 (2%)
Endocrine distruptor	16 (28%)	30 (53%)	10 (18%)	1 (2%)
Reproduction/development effects	12 (21%)	3 (5%)	28 (49%)	14 (25%)
Acetyl cholinesterase inhibitor	50 (88%)	4 (7%)	3 (5%)	0 (0%)
Neurotoxicant	40 (70%)	8 (14%)	6 (11%)	3 (5%)
Respiratory tract irritant	25 (44%)	17 (30%)	3 (5%)	12 (21%)
Skin irritant	36 (63%)	0 (0%)	5 (9%)	16 (28%)
Skin sensitiser	12 (21%)	30 (53%)	3 (5%)	12 (21%)
Eye irritant	31 (54%)	0 (0%)	3 (5%)	23 (40%)
Phototoxicant	11 (19%)	45 (79%)	1 (2%)	0 (0%)
Average number of AS per hazard score	27 (48%)	14 (25%)	8 (14%)	7 (13%)

Table S5.28 – Expected reductions in the number (N) of active substances (AS) with high or moderate ecotoxicity, and in the number of AS known to have an effect or possible effect (status not identified) on human toxicity endpoints. Reductions refer to corresponding Business As Usual scenario N values. Hazard reductions below 50% are marked in red, reductions ≥ 50% in green. The 50% threshold corresponds to the pesticide risk reduction target of the Farm to Fork Strategy. NH = No Herbicides, FDP = Fast Degradable Pesticides, TPB = Total Pesticide Ban, CFSE = Candidates For Substitution Excluded, LHP = Low Hazard Pesticides, SHH = Safe Human Health, LET = Low Ecosystem Toxicity. DPVF = dry pulses, vegetables, flowers, NPIC = non-permanent industrial crops, Perm. = permanent, n = number of AS covered in the reduction scenario, Mod. = moderate.

	NH (n=139)		FDP (n=106)		TPB (n=60)		CFSE (n=181)		LHP (n=136)		SHH (n=49)		LET (n=57)	
% reduction in N of AS - ecosystem	**High**	**Mod.**	**High**	**Mod.**	**High**	**Mod.**	**High**	**Mod.**	**High**	**Mod.**	**High**	**Mod.**	**High**	**Mod.**
Mammals – acute	0%	33%	60%	52%	73%	73%	47%	23%	93%	51%	87%	80%	100%	71%
Mammals – short-term	34%	75%	53%	25%	72%	100%	26%	13%	52%	25%	82%	75%	66%	75%
Birds – acute	0%	40%	50%	53%	79%	74%	57%	21%	93%	45%	86%	77%	100%	69%
Birds – short-term	0%	32%	33%	62%	67%	68%	67%	25%	100%	53%	100%	83%	100%	70%
Fish – acute	3%	42%	62%	54%	65%	75%	26%	20%	71%	38%	85%	77%	100%	70%
Fish – chronic	15%	35%	56%	59%	74%	68%	33%	25%	74%	43%	81%	79%	100%	66%
Aquatic invertebrates – acute	2%	43%	59%	56%	68%	75%	29%	20%	71%	36%	78%	79%	100%	68%
Aquatic invertebrates – chronic	5%	38%	51%	62%	80%	66%	27%	22%	73%	40%	80%	80%	100%	68%
Aquatic plants – acute	93%	46%	43%	56%	93%	69%	32%	20%	36%	38%	71%	73%	100%	51%
Algae – acute	62%	32%	67%	55%	71%	69%	43%	21%	43%	45%	71%	82%	100%	73%
Sediment dwelling organisms – acute	0%	26%	67%	73%	60%	62%	27%	26%	80%	49%	80%	82%	100%	77%
Honeybees – acute (contact)	0%	46%	52%	54%	78%	75%	30%	20%	87%	42%	87%	77%	100%	71%
Honeybees – acute (oral)	0%	45%	48%	60%	76%	73%	33%	23%	90%	45%	90%	79%	100%	67%
Other Terrestrial arthropods – not known	37%	50%	48%	50%	81%	90%	30%	40%	59%	80%	81%	70%	67%	80%
Earthworms – acute	0%	39%	40%	56%	80%	73%	20%	22%	80%	41%	80%	78%	100%	74%
Earthworms – chronic	0%	28%	50%	63%	50%	67%	50%	23%	50%	50%	50%	77%	50%	73%
Other Soil macro-organisms – acute	0%	33%	33%	33%	100%	100%	33%	33%	67%	67%	67%	100%	67%	67%
Other Soil macro-organisms – chronic		21%		86%		43%		29%		71%		93%		71%
Average reduction	15%	39%	51%	56%	75%	73%	36%	24%	72%	48%	80%	80%	91%	70%
Overall hazard reduction	**27%**		**54%**		**74%**		**30%**		**59%**		**80%**		**80%**	
% reduction in N of AS - human	**yes**	**maybe**	**yes**	**maybe**	**yes**	**maybe**	**yes**	**maybe**	**yes**	**maybe**	**yes**	**maybe**	**yes**	**maybe**
Carcinogen	42%	38%	83%	56%	67%	70%	33%	23%	33%	56%	100%	100%	100%	75%
Mutagen	0%	23%	0%	54%	100%	54%	67%	31%	100%	69%	100%	100%	67%	69%
Endocrine disrupter	25%	24%	75%	57%	50%	69%	25%	26%	75%	69%	100%	90%	88%	76%
Reproduction/development effects	34%	38%	52%	62%	73%	66%	23%	23%	52%	37%	100%	69%	75%	74%
Acetyl cholinesterase inhibitor	0%	43%	30%	29%	100%	100%	50%	14%	100%	57%	90%	86%	100%	57%
Neurotoxicant	31%	23%	44%	50%	88%	77%	19%	23%	81%	67%	100%	83%	81%	80%
Respiratory tract irritant	51%	47%	49%	65%	76%	71%	27%	29%	63%	35%	75%	76%	76%	82%
Skin irritant	41%	38%	40%	59%	88%	79%	17%	41%	62%	62%	81%	86%	72%	83%
Skin sensitiser	45%	24%	43%	48%	84%	81%	29%	19%	59%	57%	76%	95%	76%	86%
Eye irritant	46%	20%	39%	68%	84%	72%	24%	16%	54%	40%	79%	72%	73%	88%
Phototoxicant	0%	50%	100%	50%	0%	75%	0%	25%	0%	25%	100%	75%	100%	75%
Average reduction	29%	33%	50%	54%	74%	74%	29%	25%	62%	52%	91%	85%	83%	77%
Overall hazard reduction	**31%**		**52%**		**74%**		**27%**		**57%**		**88%**		**80%**	

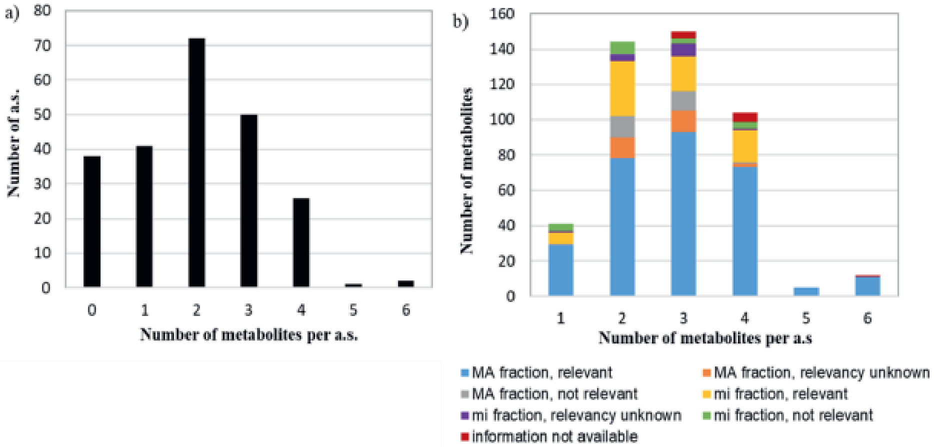


Figure S5.1 – Number of known soil metabolites of 230 selected a.s. (BAU scenario, a) and distribution of those metabolites according to formation fraction and relevancy (b). Metabolite information was extracted from PPDB (2019). a.s. – active substance; MA – major; mi – minor. Major and minor fractions refer to metabolites with maximum formation fractions above or below 10%, respectively. Relevant metabolites are those with target activity comparable to the parent substance, comparable or higher hazard level than the parent substance or severe toxicological properties (EC 1107/2009). Number of selected a.s.=230. Number of soil metabolites=414, of which 243 are of relevance for further study and investigation.

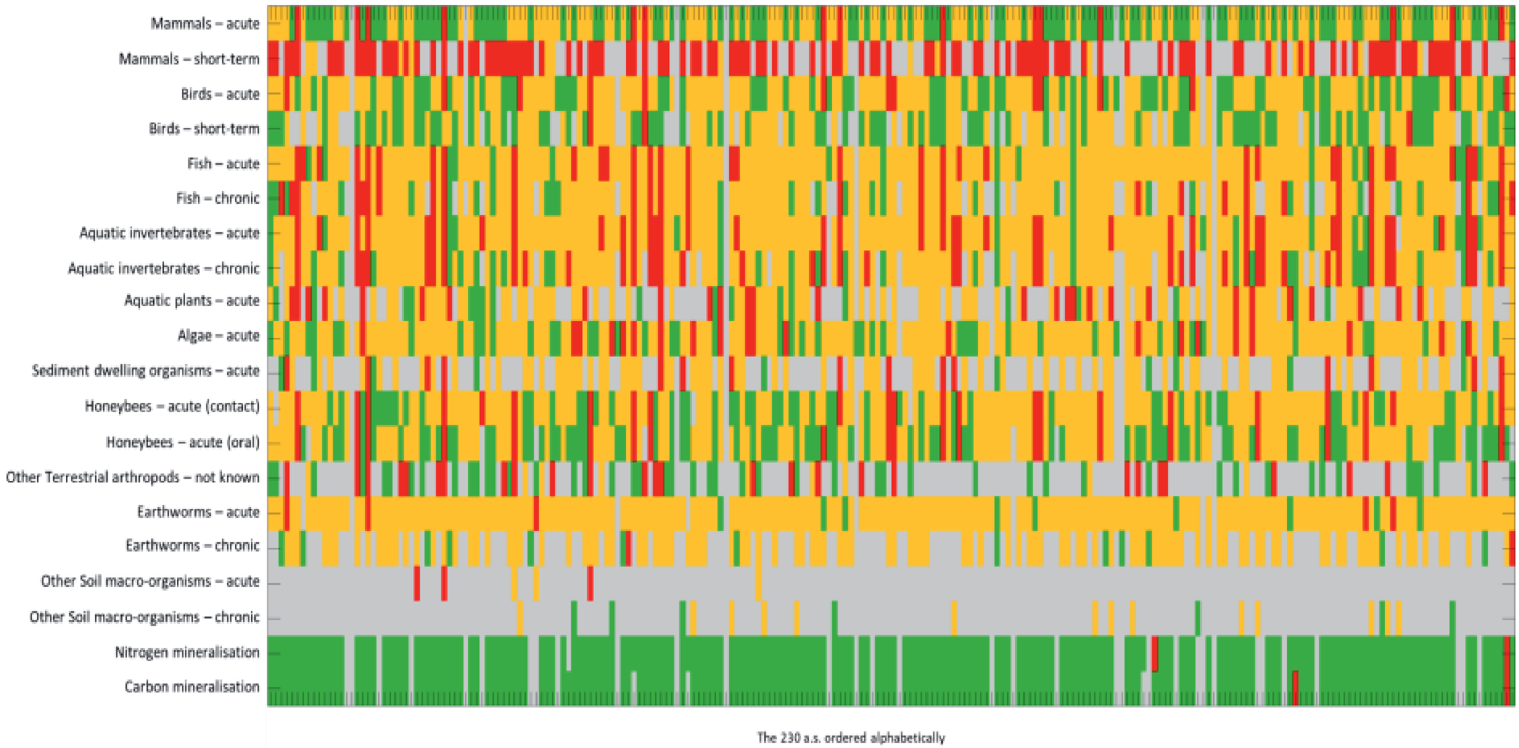


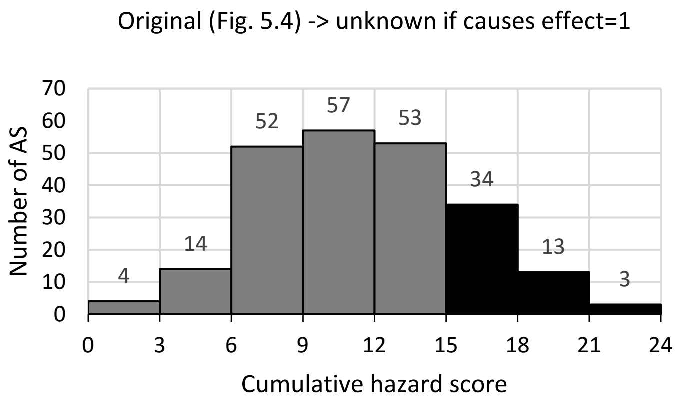
Figure S5.2 – Hazard profile of the 230 selected a.s. (BAU scenario) for the 20 eco-toxicological endpoints considered in this study, according to PPDB database. Different colours indicate different hazard scores, which were attributed to the severity of effect: low toxicity = GREEN, no data found = GREY, moderate toxicity = YELLOW, high toxicity = RED. 23% of the cells in the diagram are coloured green, 27% are coloured grey, 41% are coloured yellow and the remaining 9% are coloured red.

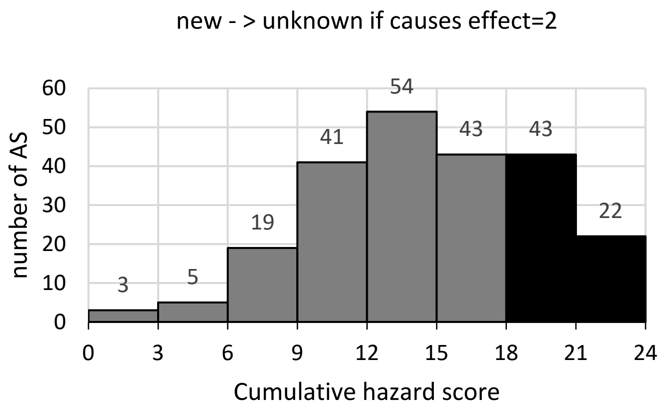
Figure S5.3 – Hazard profile of the 230 selected a.s. (BAU scenario) for the 11 human endpoints considered in this study, according to PPDB database. Different colours indicate different hazard scores, which were attributed to the severity of effect: no effect = GREEN, unknown effect = GREY, possible effect = YELLOW, known adverse effect = RED. 42% of the cells in the diagram are coloured green, 29% are coloured grey, 15% are coloured yellow and the remaining 14% are coloured red.

Sensitivity analyses

Human:

In this sensitivity analysis, a hazard score of 2 was attributed to UNKNOWN IF CAUSES EFFECT. Once the original dataset was corrected, we proceed with histograms and top hazard lists. We considered the same number of bins, the same bin width, and targeted also ~25% AS in right tail of the histogram. In the original histogram (where missing data =1) there were 50 top AS - cumulative hazard score ≥15, marked in black bins in the figure below. In the new histogram (missing data =2) there are 65 top AS - cumulative hazard score ≥18, marked in black bins. There is a 61% match between original and new top risk AS. 21 AS, with several missing data endpoints, appear in the new top list (marked in yellow cells), but mostly at the bottom of the table of the original AS, in the bottom of the table (marked in pink cells), become overtaken by the consequences of the change of hazard score and the new, left skewed histogram.

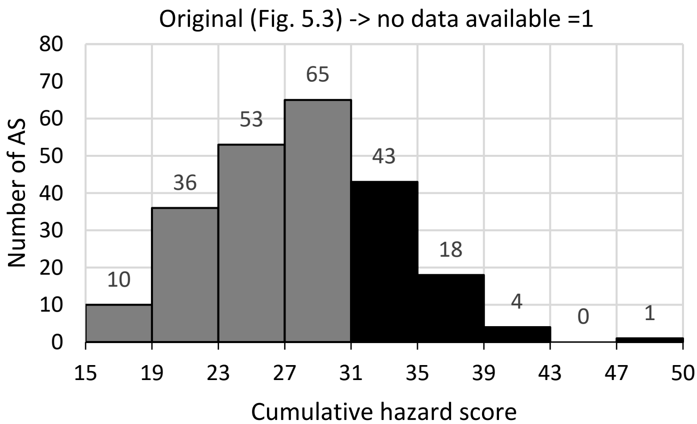


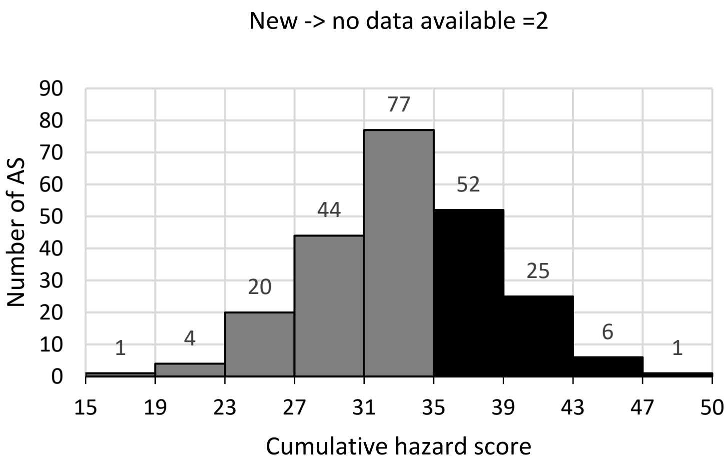


ORIGINAL (Fig. 5.4) missing data=1 Cumulative score	AS	NEW missing data=2 Cumulative score	AS	Cumulative score	AS
22	fenoxycarb	24	fenoxycarb	18	azoxystrobin
21	pendimethalin		iodosulfuron		bifenox
	ziram		prosulfocarb		cyprodinil
20	chlorothalonil		tralkoxydim		dithianon
	gamma-				
	cyhalothrin	23	diethofencarb		ethoprophos
19	bifenthrin		fluazinam		fludioxonil
	fluazinam		gamma-cyhalothrin		fluxapyroxad
	malathion		terbuthylazine		formetanate
	terbuthylazine	22	cyflufenamid		isopyrazam
	triadimenol		fenoxaprop-P		metam
18	2,4-D		fluazifop-P		nicosulfuron
	diethofencarb		tembotrione		phosmet
	flutriafol		triadimenol		pyridate
	iodosulfuron		ziram		sulcotrione
	prosulfocarb	21	bifenthrin		triclopyr
	zeta-cypermethrin		hexythiazox		
17	8-hydroxyq.		pendimethalin		
	dimethachlor		pirimicarb		
	folpet		quizalofop-P-tefuryl		
	phosmet		tefluthrin		
	pirimicarb		triflusulfuron		
	quizalofop-P-				
	tefuryl		zeta-cypermethrin		
	tefluthrin	20	2,4-D		
	tembotrione		captan		
	tralkoxydim		chlorothalonil		
16	captan		clodinafop		
	cyprodinil		dimethachlor		
	dazomet		folpet		
	dimethenamid-P		fosetyl		
	ethoprophos		Fuberidazole		
	fosetyl		halosulfuron		
	hexythiazox		malathion		
	lambda-				
	cyhalothrin		oxamyl		
	methomyl		pyriofenone		
	oxamyl	19	8-hydroxyquinoline		
	picloram		beta-cyfluthrin		
	triflusulfuron		chromafenozide		
	alpha-				
15	cypermethrin		dazomet		
	cyflufenamid		dimoxystrobin		
	desmedipham		dodemorph		
	dodemorph		flutriafol		
	imazalil		kresoxim-methyl		
	kresoxim-methyl		methomyl		
	metam-potassium		picloram		
	nicosulfuron		propamocarb		
	pyridate		proquinazid		
	pyroxsulam		pyroxsulam		
	spirodiclofen		quinmerac		
	thiophanate-				
	methyl		spirodiclofen		
	tribenuron		tribenuron		

Ecosystem:

In this sensitivity analysis, a hazard score of 2 was attributed to NO DATA available. Once the original dataset was corrected, we proceed with histograms and top hazard lists. We considered the same number of bins, the same bin width, and targeted also ~25% AS in right tail of the histogram. In the original histogram (where missing data =1) there were 66 top AS - cumulative hazard score ≥31, marked in black bins in the figure below. In the new histogram (missing data =2) there are 84 top AS - cumulative hazard score ≥35, marked in black bins. There is a 61% match between original and new top risk AS. 27 AS, with several missing data endpoints, appear in the new top list (marked in yellow cells), but mostly at the bottom of the table of the original AS, in the bottom of the table (marked in pink cells), become overtaken by the consequences of the change of hazard score and the new, normal distributed histogram.





ORIGINAL (Fig. 5.3)
missing data=1

Cum. score	AS
47	Chlorpyrifos
42	Bifenthrin
39	Beta-Cyfluthrin
	Dimethoate
	Gamma-cyhalothrin
38	Alpha-Cypermethrin
	Esfenvalerate
37	Cypermethrin
	Famoxadone
36	Imidacloprid
	Indoxacarb
	Methiocarb
	Methomyl
	Phosmet
	Tefluthrin
	Trifloxystrobin
	Zeta-Cypermethrin
35	Acetamiprid
	Cyproconazole
	lambda-Cyhalothrin
	Oxamyl
	Pyriproxyfen
	tau-Fluvalinate
34	Chlorothalonil
	Formetanate
	Malathion
	Metribuzin
	Pyridaben
	Triadimenol
	Ziram
33	Aclonifen
	Dimoxystrobin
	Epoxiconazole
	Ethoprophos
	Etofenprox
	Fenpropidin
	Oxyfluorfen
	Penconazole
	Pyraclostrobin
	Terbuthylazine
32	Dithianon
	Fenpropimorph
	Fludioxonil
	Flufenacet
	Isoxaben
	Lufenuron
	Metconazole
	Spiroxamine
	Tetraconazole
	Triticonazole
31	Bixafen
	Captan
	Cyprodinil
	Desmedipham
	Fenpyrazamine

NEW
missing data=2

Cum. score	AS
48	Chlorpyrifos
45	Bifenthrin
44	Gamma-cyhalothrin
43	Alpha-Cypermethrin
	Beta-Cyfluthrin
	Esfenvalerate
	Tefluthrin
42	Zeta-Cypermethrin
41	Dimethoate
	Imidacloprid
	Methiocarb
	Methomyl
	Oxamyl
	Phosmet
	Pyridaben
	Pyriproxyfen
40	Benzovindiflupyr
	Clodinafop
	Cypermethrin
	Etofenprox
	Fluazifop-P
	Indoxacarb
	lambda-Cyhalothrin
	Malathion
	Mesosulfuron
	Metamitron
	Propoxycarbazone
	Sedaxane
39	Dazomet
	Ethoprophos
	Famoxadone
	Ziram
38	Benthiavalicarb
	Bixafen
	Cyproconazole
	Formetanate
	Metosulam
	Metribuzin
	Pyridalyl
	tau-Fluvalinate
	Trifloxystrobin
37	Acetamiprid
	Aclonifen
	Chlorothalonil
	Dimoxystrobin
	Dithianon
	Fenpicoxamid
	Fenpropimorph
	Quizalofop-P-ethyl (QPE)
	Terbuthylazine
	Triadimenol
36	Amisulbrom
	Epoxiconazole
	Fenoxaprop-P
	Fenpropidin

Cum. score	AS
35	Cyflufenamid
	Dodine
	Flufenacet
	Hymexazol
	Isoxaben
	Lenacil
	Metam
	Metconazole
	Nicosulfuron
	Prochloraz
	Spirotetramat
	Teflubenzuron

Fluazinam	Fenpyrazamine
Isofetamid	Halosulfuron methyl
Metam	Iodosulfuron
Nicosulfuron	Ipconazole
Pirimicarb	Isofetamid
Prothioconazole	Lufenuron
Pyrimethanil	Meptyldinocap
Pyriofenone	Metazachlor
Quizalofop-P-ethyl	Oxyfluorfen
Spirotetramat	Paraffin oil/(64742-46-7)
Teflubenzuron	Paraffin oil/(8042-47-5)
	Penconazole
	Pirimicarb
	Propamocarb
	Pyraclostrobin
	Pyriofenone
	Spiroxamine

English summary

Pesticides have contributed significantly to increases in food production over the last few decades. In the European Union (EU), nearly 500 active substances have been approved for use as pesticides. The EU has one of the highest pesticide use in the world, with 374 000 tons being sold annually. Around 90% of pesticide sales can be linked to the agricultural sector. The pesticides used in agriculture, also known as Plant Protection Products (PPP), are applied to soil to prevent or combat the growth of undesired plants that compete with crops for resources, or to crops to combat organisms that can cause damage and reduce crop yields. There are several benefits associated with pesticides, the main ones relate to increasing yields, improving food security, and positively impacting the regional and national economies. On the other hand, intensive and widespread use of pesticides raises serious environmental and human health concerns. This is because substantial amounts of the pesticides applied in agriculture are released into the environment during or after application, and several pesticides (and/or their degradation products) are toxic to non-target-species, persistent in the environment, and accumulate through food chains. The high frequency of reports, increased diversity, and severity of negative effects of some pesticides raise serious concerns about the protection level of the current pesticide regulatory systems. The EU has the strictest system in the world but even it has shortcomings. The main problems relate to the low representativity of pre-approval risk assessments, the effective applicability of precautionary principles, and the limited post-approval monitoring of pesticide risks.

Chapter 2 focuses on the limited post-approval monitoring data point, more specifically in soil, a compartment where pesticide data is particularly scarce and fragmented. We analysed the occurrence and levels of 76 pesticide residues in 317 agricultural topsoil samples from the EU-LUCAS 2015 survey. The compounds were selected based on the most commonly used active substances in Europe and on the findings of previous EU studies on soil contamination by pesticide residues. The soils originated from 11 EU Member States and 6 main cropping systems where pesticide use is assumed to be the highest. We observed that 83% of the tested soils contained pesticide residues and 58% had mixtures of compounds. Glyphosate, AMPA, DDTs, boscalid, epoxiconazole, and tebuconazole were the most frequent compounds found in soil and the ones with the highest concentrations. Occasionally, the measured levels of glyphosate, epoxiconazole, and tebuconazole exceeded predicted environmental concentrations in soil. Also, measured DDT levels occasionally exceeded the maximum values of the respective countries. Total pesticide content in soil reached values as high as 2.87 mg/kg. This study shed some light on the soil contamination problem and highlighted problems with current risk assessment evaluations.

Chapter 3 starts with a zoom-in of Chapter 2, exploring the distribution of glyphosate and its main metabolite AMPA across the same 317 agricultural topsoil samples and follows with the potential export of these substances by wind and water erosion. We conducted this more targeted study because such results could contribute to the ongoing debate about the approval of glyphosate use in the EU. Glyphosate was present in 21% of the samples and AMPA in 42% of the samples. Both compounds had a maximum concentration of 2 mg/kg. The highest levels of glyphosate and AMPA were found in southern parts of the EU in fields of permanent crops. Glyphosate and/or AMPA contaminated soils occurred often in areas that were highly susceptible to water and wind erosion. Pesticide export can be higher due to water as compared to wind erosion. Maximum export was estimated to be close to 48 g/ha/year for AMPA via water erosion. Our results corroborate the widespread soil contamination by these residues and indicate that particulate transport can contribute to human and environmental exposure to herbicide residues.

Chapter 4 investigates pesticide profiles in soils from conventional and organic farms. This was explored via the analyses of 340 topsoil samples originating from 4 representative EU case study sites: vegetable production in Spain (S-V), orange production in Spain (S-O), grape production in Portugal (P-G), and potato production in the Netherlands (N-P). The organic fields were converted to organic farming more than 5 or 10 years before the soil sampling was conducted. Over 70% of the soils from the conventional fields had mixtures of pesticide residues, with a maximum of 16 residues per sample. The residues with the highest frequency of detection and the highest content in these soils were glyphosate/AMPA (P-G, N-P, S-O) and pendimethalin (S-V). Total pesticide content in soil reached values up to 0.8 mg/kg for S-V, 2 mg/kg for S-O and N-P, and 12 mg/kg for P-G. Soils from the organic fields presented significantly fewer residues, but mixtures of 2 to 5 residues were rather common. Organic soils presented 70-90% lower pesticide content than the corresponding conventional soils. Prosulfocarb, DDTs, AMPA, and bixafen were the most common compounds in organic soils. DDTs and AMPA had the highest levels. Our results stress the need for regular monitoring of pesticide residues and the necessity of establishing pesticide thresholds for both conventional and organic soils, including maximum levels of total pesticide residues. This will provide clarity to farmers and awareness of the time needed to change from a conventional to an organic farming system as thresholds and targets set for organic farm systems will be more strict than for conventional ones.

Chapter 5 establishes an EU pesticide use and risk baseline and explores the potential of seven pesticide reduction scenarios to achieve the envisioned 50% reduction goals of the Farm to Fork Strategy. To establish the use baseline, we compiled the recommended application rates of all 230 EU-approved, synthetic, open-field use active substances used as herbicides, fungicides, and insecticides. For the risk baseline, we compiled their (eco)toxicological risk/hazard information from PPDB. Our compilation revealed very high use levels of a couple of compounds (the soil sterilam metam and the soil fumigant dazomet) and evidence that all the 230 compounds are potentially harmful to humans and ecosystems. These results emphasize the need for a re-evaluation of pre-market requirements for pesticides. The presented pesticide reduction scenarios provide practical cut-off criteria for the EC, e.g., with regard to pesticide type, presence on the candidate for substitution EC list, or posing a hazard to humans or ecosystems. The 7 scenarios represent a decrease from 21 to 100% in the number of substances on the EU market. Only the 4 most restrictive scenarios (complete conversion to organic farming; allowing only low hazard pesticides; no/acceptable human health effects; no/low toxicity to the ecosystem) resulted in the targeted 50% reduction in pesticides use and risk. Our results highlight the need for severe restrictions to achieve the Farm to Fork Strategy reduction goals, which could end up covering a combination of the pesticide reduction scenarios presented.

In Chapter 6, we present and discuss the main pesticide findings for soil, based on pesticide properties, pesticide application information, soil sampling time, and, of course, field management type. Implications of achieved results for soil monitoring programs, environmental risk assessment, pesticide approval procedures, and sustainable plant protection are highlighted in detail. Main thesis shortcomings are identified in this chapter as well, and recommendations for future work are outlined. Overall, this PhD thesis enhances our knowledge and adds to the discussion in three main fields: soil contamination, post-approval pesticide monitoring, and the required measures to achieve the 50% pesticide reduction targets of the EU Farm to Fork Strategy. This thesis corroborates the notion that intensive pesticide use turns soil into sinks and potential sources of pesticide residues. Results show that some pesticides persist in the soil longer than expected from pre-registration studies and that banned compounds may still be found in EU agricultural soils. It is critical to establish better monitoring programs for pesticide residues in soil which should include assessments on the risks of pesticide residue cocktails found in soil systems and elsewhere. Risk assessment procedures must continue to evolve around mixtures, accounting for exposure pulses, chronic pesticide exposure, and indirect effects of pesticides. More sustainable agronomic practices and substantial reductions in the pesticides available on the EU market are urgently needed to meet the envisioned Farm to Fork targets in order to facilitate the transition towards more sustainable food production systems and improve human and environmental health.

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About the author

Vera Silva was born on November 30, 1989 in Leiria, Portugal. She graduated in Biology from the University of Coimbra in 2010 and got a master's degree in Applied Biology, from the University of Aveiro in 2012. During the following three years, she worked in the University of Aveiro, first in a research project on the impacts of agriculture practices in aquatic ecosystems, and then on another project on the impacts of wildfires in aquatic ecosystems. In the beginning of 2015, she started her PhD on soil pollution by pesticide residues at Wageningen University. In 2019 she started working as Project Scientific Manager of the SPRINT project (Sustainable plant protection transition: A global health approach) – a role that she is mostly devoted to nowadays. And in 2020 she got involved in EU and African pesticides monitoring in programs (being part of the analytical and consultancy team dealing with the pesticide data of the LUCAS 2018 survey, and partner of the Soils4Africa project). In the same year she also joined the Wageningen University Soil Science cluster, in which she co-leads the Nutrient cycling and contaminant mitigation research line. Besides work, Vera loves to play ping-pong, play board games and have dinner with friends, spend time with her family, binge-watching series on Netflix, and travel.
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- *Agricultural soils of the European Union contaminated with pesticide residues*. Global Symposium On Soil Pollution, 26-28 September 2018, Rome, Italy.
- *Multiple pesticide residues in agricultural soils – a reason to worry?* 9th ESSC International Congress, 26-28 September 2019, Tirana, Albania
- *Cocktails of pesticide residues in conventional and organic farming systems in Europe – Legacy of the past and turning point for the future*. vEGU, 19 April, 2021

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