Environmental Pollution 357 (2024) 124430

Contents lists available at ScienceDirect

Environmental Pollution

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

Pesticide residues in boreal arable soils: Countrywide study of occurrence and risks☆

M. Hagner[a,*], S. Rämö[a], H. Soinne[b], V. Nuutinen[a], R. Muilu-Mäkelä[b], J. Heikkinen[a], J. Heikkinen[b], J. Hyvönen[c], K. Ohralahti[a], V. Silva[d], R. Osman[d], V. Geissen[d], C.J. Ritsema[d], R. Keskinen[a]

[a] *Natural Resources Institute Finland, Tietotie 2, 31600, Jokioinen, Finland*
[b] *Natural Resources Institute Finland, Latokartanonkaari 9, 00790, Helsinki, Finland*
[c] *Natural Resources Institute Finland, Ounasjoentie 6, 96200, Rovaniemi, Finland*
[d] *Soil Physics and Land Management Group, Wageningen University and Research, the Netherlands*

ABSTRACT

Large volumes of pesticides are applied every year to support agricultural production. The intensive use of pesticides affects soil quality and health, but soil surveys on pesticide residues are scarce, especially for northern Europe. We investigated the occurrence of 198 pesticide residues, including both banned and currently used substances in 148 field sites in Finland. Results highlight that pesticide residues are common in the agricultural soils of Finland. A least one residue was found in 82% of the soils, and of those 32% contained five or more residues. Maximum total residue concentration among the conventionally farmed soils was 3043 μg/kg, of which AMPA and glyphosate contributed the most. Pesticide residues were also found from organically farmed soils, although at 75–90% lower concentrations than in the conventionally farmed fields. Thus, despite the application rates of pesticides in Finland being generally much lower than in most parts of central and southern Europe, the total residue concentrations in the soils occurred at similar or at higher levels. We also established that AMPA and glyphosate residues in soil are significantly higher in fields with cereal dominated rotations than in grass dominated or cereal–grass rotations. However, risk analyses for individual substances indicated low ecological risk for most of the fields. Furthermore, the total ecological risk associated with the mixtures of residues was mostly low except for 21% of cereal dominated fields with medium risk. The results showed that the presence of mixtures of pesticide residues in soils is a rule rather than an exception also in boreal soils. In highly chemicalized modern agriculture, the follow-up of the residues of currently used pesticides in national and international soil monitoring programs is imperative to maintain soil quality and support sustainable environment policies.

1. Introduction

The global use of pesticides increased by 80% between 1990 and 2020, from 2 285 881 to 4 113 591 tonnes of active ingredients (FAOSTAT, 2024.). In the EU the increase has levelled off and the total sales of pesticides remained relatively stable between 2011 and 2020 at around 350 000 tonnes per year (Eurostat, 2022). Currently, in the EU pesticide market there is approval for 444 active substances, which are used in thousands of commercial products (EC, 2023a). The recently published European Union Farm to Fork strategy (F2F) takes action to reduce the overall use and risk of chemical pesticides by 50%, as well as the use and risk of most hazardous pesticides by 50% by 2030 (EC, 2020).

Water contamination by pesticides has been widely studied over the past 30 years (Casado et al., 2019) but much less data have accrued concerning soil contamination (Pelosi et al., 2021). The difference in available data is likely result of the regulatory context. In the European Union (EU), the Water framework directive 2000/60/EC directs monitoring of water quality and there are regulatory limits for pesticide residue concentrations in drinking, surface and ground waters (EC, 2000). A similar regulatory framework for soils does not exist but in certain European countries, regulations encompass reference or maximum levels for outdated but highly persistent pesticides like DDTs and atrazine (Carlon, 2007). However, while a few of these countries' directives outline permissible levels for unspecified “other pesticides,” there are currently no established thresholds for authorized and currently used pesticides. In their recent worldwide review of currently used pesticide monitoring in agricultural soils Sabzevari and Hofman (2022) reported that knowledge of pesticide contamination and accumulation risks in soils is still scarce while the occurrence of pesticide residues in the agricultural soils is a rule rather than an exception. Thus,

---

☆ This paper has been recommended for acceptance by Charles Wong.

* Corresponding author.

E-mail address: marleena.hagner@luke.fi (M. Hagner).

https://doi.org/10.1016/j.envpol.2024.124430
Received 16 February 2024; Received in revised form 7 May 2024; Accepted 22 June 2024

establishing regular and comprehensive monitoring programs for pesticide residues in soils is needed. In the Proposal for a Directive on Soil Monitoring and Resilience (EC, 2023b) (Soil Monitoring Law), currently under preparation, a selection of organic contaminants is suggested for inclusion in the monitoring framework covering the soils of the EU.

Recent national and regional scale studies have shown high occurrence of various no longer approved and currently used pesticides (CUP) or their transformation products in European arable soils (Chiaia-Hernandez et al., 2017; Gamón et al., 2003; Hvězdová et al., 2018; Karasali et al., 2016; Marković et al., 2010; Silva et al., 2019; Suszter and Ambrus, 2017; Zhao et al., 2018). For example, according to research conducted by Vašíčková et al. (2019), concentrations of CUPs surpassed the toxicological thresholds for soil fauna in 35% of the agricultural fields investigated in the Czech Republic. On a wider geographical scale, Silva et al. (2019) showed that 83% of tested European agricultural soils contained one or more pesticide residues. Pelosi et al. (2021) reported a high occurrence of pesticide residues also in seminatural habitats (e.g., hedgerows, field margins) and nontreated organic fields in France. Furthermore, Geissen et al. (2021) and Riedo et al. (2021) reported pesticide residues in the soils of organic farms, although at lower frequencies and concentrations than in conventional farms. The most recent global review of the subject by Sabzevari and Hofman (2022) considered over 80 monitoring studies and surveys on pesticide residues in agricultural soils published during the last 51 years. Notably, none of the studies covered by that review or those mentioned above included soils from northern European countries. Recently, the EU Soil Observatory and LUCAS 2018 soil module carried out a systematic assessment of the occurrence of pesticide residues in the soils of the EU by analyzing 118 active ingredients and selected metabolites from 3473 sample sites. This study also covered northern Europe, including 73 sites in Finland. The survey showed pesticide residues to be widespread in the soils of Europe – only ca. 25% of the samples were pesticide-free. In Finland residue concentrations were even higher than the EU average (Vieira et al., 2023).

In addition to the chemical properties of pesticides, their degradation in soil depends on environmental conditions such as vegetation, pH, temperature, moisture, organic matter and nutrient content (Marican and Durán-Lara, 2018). If the compounds bind strongly in the soil, their availability for (bio)degradation decreases and residues can be traced for a long time (Arias-Estévez et al., 2008). On the other hand, elements and molecules with similar sorption mechanisms may reduce the binding strength and enhance the desorption of pesticides. High plant-available phosphorus (P) content has been reported to reduce the sorption of glyphosate (de Jonge et al., 2001). In the boreal region, the growing season with an active period of biological activity is typically short (4–6 months) and may markedly restrict the degradation of pesticides (Laitinen et al., 2009; Stenrød et al., 2005). Therefore, pesticide residue accumulation in northern conditions is of special concern even though the annual pesticide use per unit land area in northern Europe is typically lower than in central and southern Europe (Eurostat, 2018). In Finland, for instance, the volume of pesticides sold for agricultural use was the sixth lowest per hectare in Europe in 2018 (Eurostat, 2018).

Presently, the ecological risk assessment of both pesticides' active ingredients and formulated pesticide products in the terrestrial environment is conducted in the EU following to the frameworks on placing of plant protection products (PPP) on the market (EC, 2009) and regulation on uniform principles (EC, 2013). The approach relies on comparisons of toxicity exposure ratios (TERs) with trigger values. TERs are derived by dividing ecotoxicologically relevant concentrations LC50 (concentration resulting in the mortality of 50% of the exposed individuals) or NOEC (highest No Observed Effect Concentration) for indicator organisms by the residue's highest PEC (Predicted Environmental Concentration). Assessment using measured environmental concentrations (MEC) from soil surveys are very scarce (Kudsk et al., 2018; Renaud et al., 2018; Vaj et al., 2011; Vašíčková et al., 2019). As the risk evaluation is mostly based on the results of laboratory tests, often considering a single compound and species, the extrapolation of potential risks to the natural environment is difficult due to the complexity and heterogeneity of the soil matrix, mixture toxicity uncertainties, and scarcity of ecotoxicological data, especially for non-standard endpoints and species. Currently, EFSA, among others, is making substantial progress towards more comprehensive and harmonized risk assessment methodologies for combined exposure to multiple chemicals for all relevant areas (EFSA, 2019). Consequently, the valid risk assessment demands more measured data on pesticide residues from field conditions.

In this study, we investigated the occurrence of 198 pesticide residues, including both banned and currently used substances in 148 agricultural field sites in Finland. The data encompassed 20 organically farmed fields with no direct pesticide inputs for at least 10 preceding years. The main aim of this study was to perform a survey on the level of pesticide residues in arable soils in Finland and to establish a base for the monitoring of the residues. In addition, the aim was to investigate if there is an association between the residues in soil and the geographical location of the field, soil type, crop rotation, soil organic carbon (SOC) content and soil phosphorus (P) concentration. We hypothesized that glyphosate and AMPA contamination 1) is higher in the north than in the south of Finland due to longer persistence times resulting from a colder climate, 2) is higher in fine textured soil types than in coarser ones due to differences in sorption capacity, 3) is higher in vegetable production and cereal dominated rotations than in rotations containing grass phases due to higher pesticide inputs, 4) is higher in conventional than organically farmed fields, under which soils are not directly targeted by synthetic pesticides, and 5) decreases with increasing soil P and SOC due to competition for binding sites and SOC-induced higher microbial activity. In addition, ecological risk of residues to soil organisms was performed using two methods: toxicity exposure ratios – TERs, and risk quotients – RQs, by combining the measured environmental concentrations and available ecotoxicological data for earthworms (*Eisenia fetida* L.).

2. Materials and methods

2.1. *Soil samples*

The study based on the soil samples collected under the latest sampling campaign of the Finnish national monitoring program for arable soils, conducted during the active growing season (June–August) in 2018 (Heikkinen et al., 2022; Soinne et al., 2022). The sampling campaign encompassed a total of 620 topsoil samples (0–15 cm) taken from GPS-tracked sites located throughout the agricultural regions of Finland (Fig. 1). At each sampling site, covering an area of 10 m × 10 m, a composite soil sample of 1 L was taken by bulking augered individual soil cores of 2 cm diameter. After breaking and thoroughly mixing the bulked cores, a 0.05–0.1 L subsample was separated into a plastic bag and directly placed in a cool box at the field. Samples were frozen at the first opportunity and stored at −18 °C. The main composite samples were air-dried, ground to pass through a 2 mm sieve and analyzed for 0.5 M ammonium acetate-acetic acid (pH 4.65) extractable macronutrients, i.e. soil test P, Ca, K, Mg and S (Keskinen et al., 2016), selected 0.5 M ammonium acetate-acetic acid–0.02 M ethylenediaminetetraacetic acid (pH 4.65) extractable microelements, hot water extractable boron, pH in 1:2.5 soil-water suspension (Soinne et al., 2022), and total C assumed to contain only organic C due to soil acidity (Heikkinen et al., 2022).

Of the frozen subsamples, a set of 148 samples was selected for pesticide residue analysis. The sample selection was based on farming system (conventional or organically farmed fields) and crop rotation history (specialty crops, cereal dominated, grass dominated, or cereal–grass rotation) over the previous 10 years (Table 1). This information was derived for the sites from the Finnish Food Authority's database of

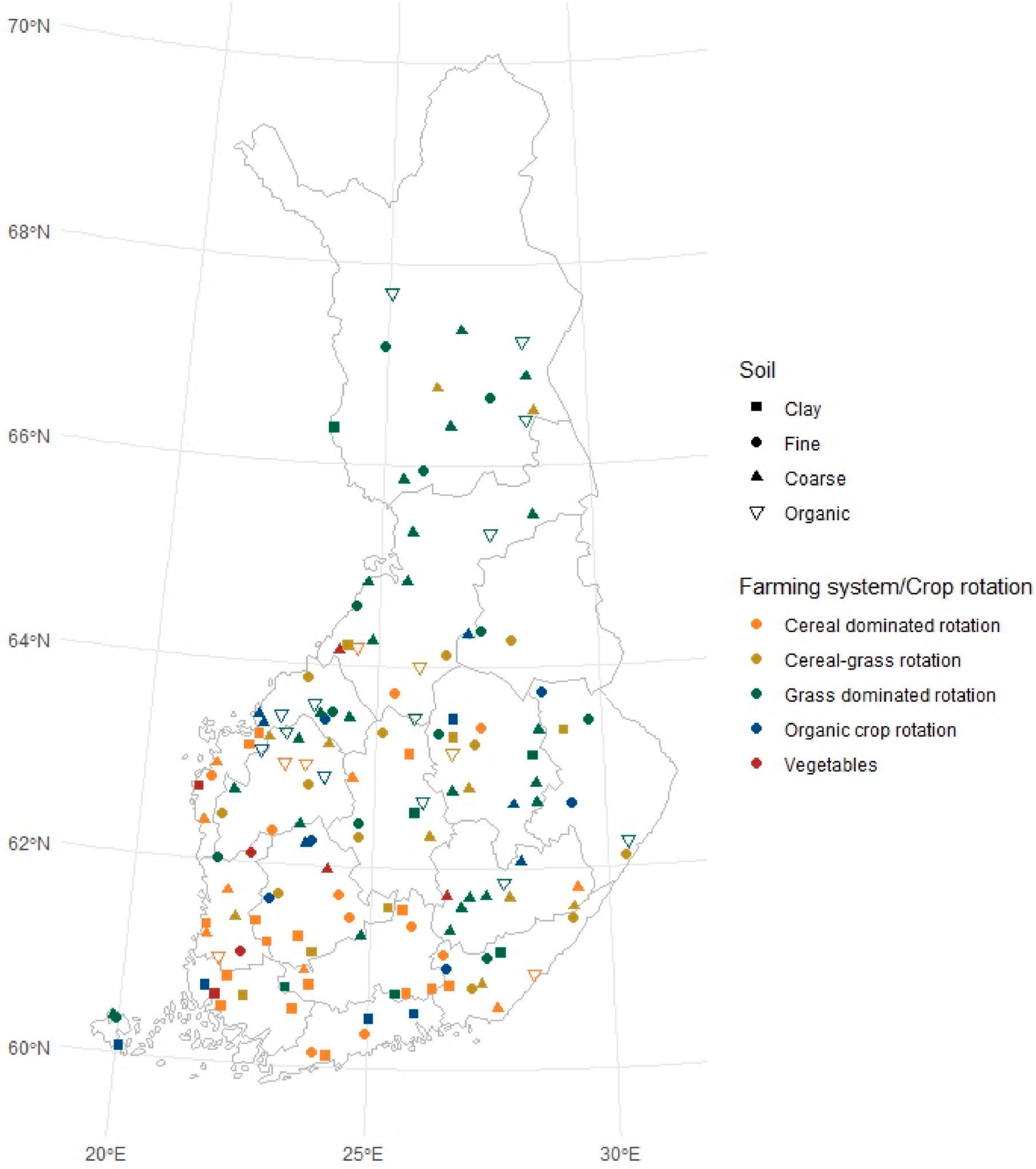


Fig. 1. Location of 148 sampling sites of the Finnish arable soil monitoring network that were utilized in the present study. N = 121 for conventional production including cereal dominated, grass dominated and cereal–grass rotations (see Table 1); n = 20 for organically farmed fields, n = 7 for vegetables (conventional). Farming system and crop rotation shown by colors and soil type by symbols. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

management and cultivated crop plants. Sites were classified into coarse, fine, clay and organic soils based on textural composition and organic matter content of the samples as in Keskinen et al. (2016). Pesticide application history of the fields was not available.

From all sites having been under organic farming throughout the previous ten years (n = 38), a set of 20 sites was randomly selected using stratified sampling by soil type with proportional allocation and spatial balancing to ensure a representative spread of the selected sites over the whole study area (Grafström et al., 2012). The remaining sites were selected from conventionally farmed field sites, in which either 1) cereal crops were grown for at least seven of the previous ten years, 2) grass was grown on at least seven of the previous ten years, or 3) grass and cereals were rotated (4–6 grass years per previous ten years); n = 432. All sites in which specialty crops, i.e. vegetables (potato and/or sugar beet) (n = 7), had been produced on at least four of the ten years before sampling were directly included in the sample set. However, only the samples taken from field parcels in which a single crop was grown each year (i.e. the field parcel was not split into two or more agricultural parcels) were considered, to ensure the accuracy of the crop data. From this sampling frame (n = 257), 121 samples were randomly selected by employing a balanced two-way stratification (Falorsi and Righi, 2008) by soil type, crop rotation and the local pivotal method (Grafström et al., 2012) to ensure a spatially regular design (Fig. 1). As a result, the marginal distributions of soil types and crop rotation classes were

Table 1
The number of soil samples (n) used in the study by farming system, crop rotation and soil type. The values for total carbon, pH and soil test phosphorus are medians with minimum and maximum in parentheses.

Farming system	Crop rotation	n	Soil type[a] (number of samples)				total C[b] (%)	pH[c]	Soil test P (mg/L)[d]
			Clay	Fine	Coarse	Organic			
Organic	–	20	5	6	6	3	3.3 [0.9; 29]	6.0 [5.4; 6.8]	8.7 [2.6; 47]
Conventional	Vegetables	7	2	2	3	0	2.0 [1.2; 6.6]	6.3 [5.6; 0.6.8]	21 [9.0; 65]
	Cereal dominated	39	16	10	8	5	3.4 [1.3; 27]	6.0 [4.9; 6.9]	9.6 [3.3; 37]
	Grass dominated	52	6	12	24	10	3.4 [1.3; 46]	5.9 [4.2; 6.8]	9.7 [3.1; 65]
	Cereal–grass rotation	30	6	12	10	2	3.1 [2.0; 36]	5.7 [4.8; 6.7]	6.7 [2.8; 20]

[a] Clay: <20% organic matter, >30% clay (<0.002 mm) particles; Fine: <20% organic matter, dominated by particles <0.06 mm but <30% clay; Coarse: <20% organic matter, dominated by particles >0.06 mm: Organic: >20% organic matter.

[b] Dry combustion (Leco TruMac CN).

[c] 1:2.5 soil:water suspension.

[d] 0.5 M ammonium acetate-acetic acid solution, pH 4.65 (Vuorinen and Mäkitie, 1955).

preserved in the sample, and it was spatially spread to cover the entire country.

To ensure that no bias was introduced by excluding the sites on field parcels with ambiguous crop information due to inclusion of several subplots in the parcel as explained above, the sampled set ($n = 121$), sampling frame ($n = 257$) and the whole target population ($n = 432$) were compared for relative distribution of soil groups, mean soil pH and soil test phosphorus (P) values. No significant differences between the sample sets were detected in any of these variables (data not shown).

2.2. Analysis of pesticide residues

The core of the pesticide residue analyses was conducted at Wageningen University. A list of analytes, developed under the scope of the H2020 SPRINT project (Sustainable Plant Protection Transition; https://sprint-h2020.eu/) was used. SPRINT had set a list of 209 pesticide residues to be analyzed in environmental and biological samples collected across ten European countries. The rationale behind the list was presented in Silva et al. (2021). In the present study 198 pesticide residues of the list were analyzed (Supplementary Tables S1). The list covered mostly synthetic organic pesticides but also some natural substances: azadirachtin, pyrethrins I/II, spinetoram, and spinosad. The list included 155 active substances (56 fungicides, 46 insecticides, and 53 herbicides), 1 synergist (piperonyl butoxide) and 42 metabolites. Of these, 49 are known to be very persistent in soil (PPDB, 2023a).

The concentrations of the 196 pesticide residues were measured by quantitative multi-methods based on Liquid Chromatography Tandem Mass Spectrometry (LC-MS/MS) and Gas Chromatography-Tandem Mass Spectrometry (GC-MS/MS). An overview of the methods is presented in the Supplementary Text T1, Tables S4, S5 and S6. Further details can be found in Khurshid et al. (in prep).

Glyphosate [N-(phosphonomethyl) glycine] and its main degradation product, aminomethylphosphonic acid (AMPA) residues were analyzed at the laboratories of Natural Resources Institute Finland as their 9-fluorenylmethyl chloroformate (FMOC) derivatives using the ultra-high performance liquid chromatography–tandem mass spectrometry (UHPLC-MS/MS) method according to Rämö et al. (2023) with minor modifications: glyphosate, AMPA and glufosinate-ammonium free soil (sampled from a home garden) were used for multi-point matrix-matched calibration. The recovery tests were made in four research samples with the same concentration as in the calibration level 6 (0.33 mg/kg in fresh weight). The recovery ranged between 102% and 108% for GLY and was 105–114% for AMPA.

Moisture content of samples was analyzed from separate subsamples by weighing the soil before and after drying (24 h, 105 °C). Concentrations of pesticide residues are expressed for μg/kg dry soil.

2.3. Risk assessment

Calculations for risk assessment were done for the 19 most frequently found pesticide residues. TERs were calculated based on the measured environmental pesticide residue concentrations in mg/kg (MEC) and the toxicity data for pesticides towards the earthworm *E. fetida* (LC50) as follows (Eq (1)).

$$\mathrm{TER} = \mathrm{LC50} / \mathrm{MEC} \tag{1}$$

where LC50 represents the concentration (mg/kg soil) which kills 50% of the earthworm population.

Threshold TER values for acute and chronic exposure risks for selected species are 5 and 10, respectively (EC, 2002). If the calculated TER is above these trigger values, the risk to certain species can be interpreted as negligible.

The risk quotient (RQ) for most frequent compounds was calculated using MECs and PNECs (predicated no-effect environmental concentration in mg/kg soil) as follows (Eq. (2)):

$$\mathrm{RQ} = \mathrm{MEC} / \mathrm{PNEC} \tag{2}$$

The PNEC was derived as follows (Eq. (3)): (see Supplementary Table S2)

$$\mathrm{PNEC} = \mathrm{LC50} \ / \ \mathrm{AF} \text{ or } \mathrm{NOEC} \ / \ \mathrm{AF} \tag{3}$$

where LC50 represents the concentration (mg/kg) that kills 50% of the population and NOEC represents no-observed-effect concentration. The LC50 and NOEC values for *E. fetida* were obtained from European Food Safety and Authority peer reviews, Pesticide Properties DataBase (PPDB, 2023b) and scientific literature (Vašíčková et al., 2019; Mu et al., 2023; Panico et al., 2022).

The AF represents an assessment factor (AF = 10–100 depending on the amount of available data) and is applied to reduce uncertainties related to the accuracy, model errors, lack and insufficiency of data used, and inherent variability between laboratory exposure and field conditions (Vašíčková et al., 2019). RQ values were classified into three levels of ecological risk according to Pérez et al. (2021): low ($\mathrm{RQ} < 0.1$), moderate ($0.1 < \mathrm{RQ} < 1.0$), and high ($\mathrm{RQ} > 1.0$).

SRQsite value, denoting the total ecological risk of the mixture for the given locality, was calculated by summing RQs for each pesticide residue quantified in the soil sample. In SRQsite calculations it was assumed that there is only the concentration addition (CA) effect among pesticide residues in the mixture. The risk ratios were classified into four risk levels: negligible (SRQsite <0.01), low (0.01 > SRQsite <0.1), medium (0.1 > SRQsite <1), and high (SRQsite >1) (Sánchez-Bayo et al., 2002; Vašíčková et al., 2019).

2.4. *Statistical analyses*

Generalized linear models, assuming independent and normally distributed model residuals, were used to study the factors influencing volume-based concentrations of glyphosate and AMPA residues. The other 196 pesticide residues could not be modelled (not even with generalized linear models) because of their rarity: individual pesticide residues were detected in 0–20% of the sample fields. Therefore, results for the most detected residues were presented with frequency tables. Furthermore, these concentrations were given on a mass basis to allow comparisons with previous studies.

For glyphosate and AMPA, measured mass-based concentrations were converted to volumetric concentrations to overcome bias caused by the low volume weight of organic soils (mean bulk density 0.6 ± 0.2 kg l^{-1}) in comparison with mineral soils (mean bulk density 1.0 ± 0.1 kg l^{-1}). The models were fitted to log- or square root transformed values due to highly skewed distributions of the concentrations: 27% of glyphosate and 18% AMPA residue values were zero (residues $<$ LOQ (limit of quantification)). To enable the transformations, zero values were first replaced with the half LOQ values, which were specific for each sample depending on the moisture content. The potential explanatory variables in modelling included region (south, east, west, north), soil type (coarse, fine, clay, organic), crop type (cereal dominated, grass dominated, cereal–grass rotation, vegetables, organic crop rotation), carbon content (C), phosphorus content (P) and acidity (pH). Crop type was formed as the combination of agricultural farming type (conventional, organic farming type) and crop rotation (cereal dominated, grass dominated, cereal–grass rotation), because crop rotation was related only to the conventional cereal/grass fields. Interaction terms for the explanatory variables were not included in the model as there were too few (or even none) observations from the variable combinations in the data. The Bonferroni method (with the overall significance level of $p = 0.05$) was used in pairwise comparisons of the model predicted class means. The statistical analyses were performed using SAS software, version 9.4.

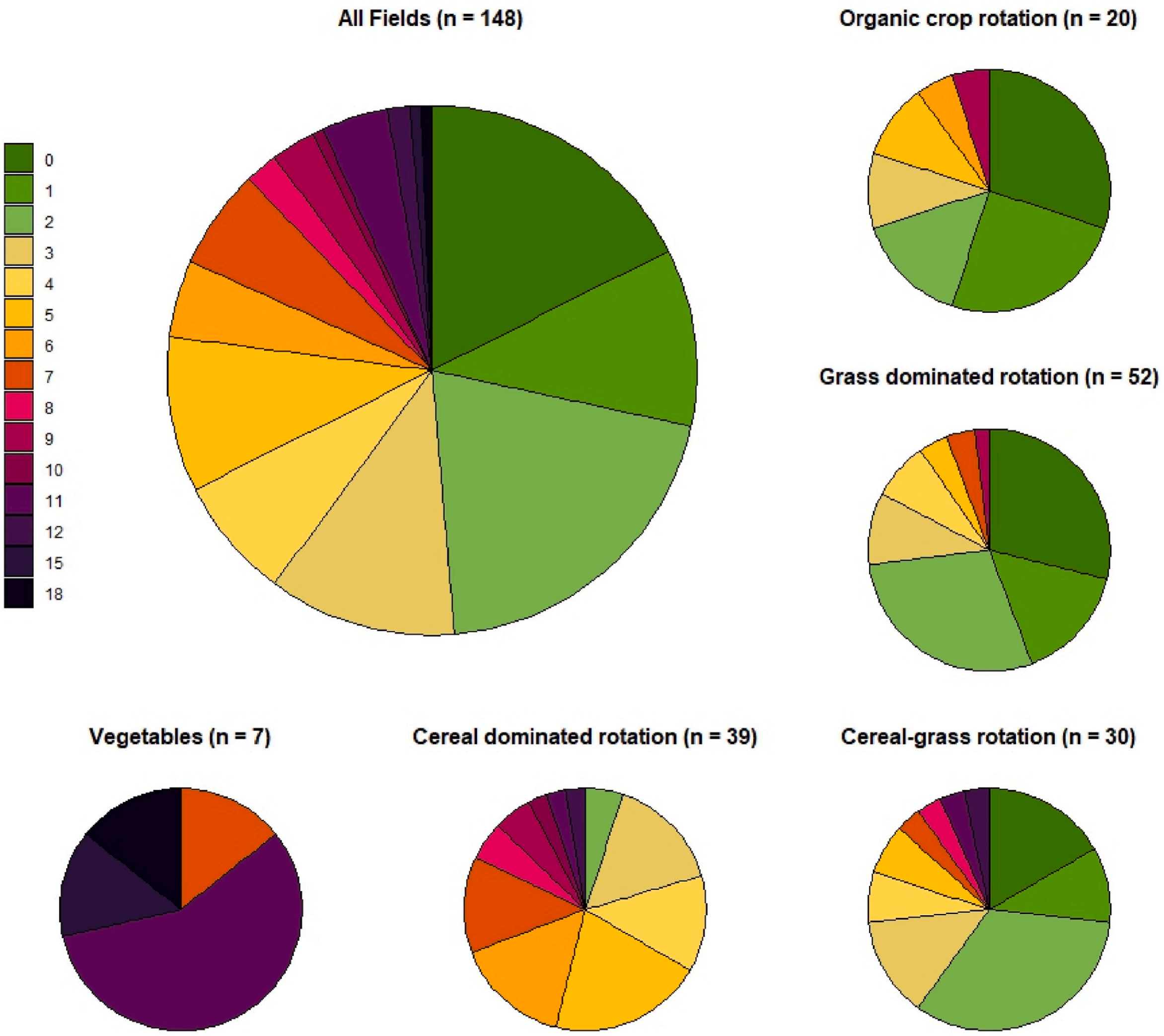
The final linear models for the glyphosate or AMPA residues, presenting the response and explanatory variables with used transformations, were:

(1) log(glyphosate volume) = Crop type, log(P)
(2) sqrt (AMPA volume) = Crop type, Region

3. Results

3.1. *Occurrence of pesticide residues in soils*

Among the 198 targeted pesticide residues, 64 were detected at levels exceeding respective LOQ. Among the 148 tested samples, 82% contained at least one residue, 32% of the samples contained five or more residues, and 7% encompassed over 10 different pesticide


All Fields (n = 148)

Organic crop rotation (n = 20)

Grass dominated rotation (n = 52)

Vegetables (n = 7)

Cereal dominated rotation (n = 39)

Cereal-grass rotation (n = 30)

Fig. 2. Proportion of soils (%) where given number (0–18) of pesticide residues was detected at a concentration above the limit of quantification (LOQ).

residues. In 18% of the samples, no pesticide residues were detected. The maximum number of residues found per sample was 18 (Fig. 2).

Among the conventional crop rotations, the number of pesticide residues detected (>LOQ) was highest in the fields growing vegetables (mean 12.6) followed by cereal dominated fields (5.7), cereal–grass rotation (3.0), and grass dominated fields (2.0) (Fig. 2). Under organic farming the corresponding mean value was 2.1.

3.2. *Type and concentrations of pesticide residues in soil*

Glyphosate and its degradation product AMPA were the most frequent residues in soil (Fig. 3, Table 2). In conventional farming, glyphosate was detected from 70% and AMPA 80% of soils (>LOQ). In cereal dominated fields both glyphosate and AMPA were detected in 100% of samples. The corresponding values were 80% and 67% for cereal–grass rotation, 65% and 50% for grass dominated fields, and 86% and 86% for vegetable production. In organically farmed fields, AMPA was detected in 65% and glyphosate in 40% of the samples.

Of the other pesticide residues addressed, 21 different substances were detected in ≥15% vegetable fields (Fig. 3d). Under cereal dominated rotation the consist of residues found from >5% of the studied soil samples was 17 (Fig. 3a), under cereal–grass rotation eight (Fig. 3b), and under grass dominated rotation four (Fig. 3c). Residues of clothianidin (insecticide) and MCPA (herbicide) were detected in soil associated with all management types. From fungicides, imazalil was most frequently found from cereal dominated and cereal–grass rotated fields followed by propiconazole. In vegetable fields, several residues that were scarcely detected from other treatments were prevalent, including fungicides (e.g. fenpropidin, fluopicolide, fluazinam, fluodioxonil, difenoconazole), insecticides (e.g. imidacloprid, thiamethozam), herbicides (e.g. metamitron, mandipropanid) and a metabolite (metamitron-desamino). Under organic farming, clothianidin, metamitron, propiconazole, DDT_pp, and DDE_pp were found >10 % of the examined soils (Fig. 3e).

The mean residue concentration for the whole dataset was 534 μg/kg being 608 μg/kg under conventional management and 138 μg/kg under organic farming. Altogether, in 30% of the sites total residue concentration was less than 100 μg/kg, in 66% of soils below 500 μg/kg and in 81% below 1000 μg/kg. In 18.9% of soils the total concentration of pesticide residues exceeded 1000 μg/kg. The maximum total residue concentration was 3043 μg/kg.

AMPA and glyphosate contributed most to the total pesticide residue concentration in both organic and conventionally farmed fields (Table 2). The maximum concentrations detected were 2045 μg/kg for glyphosate and 1967 μg/kg for AMPA in conventionally farmed and 81 μg/kg and 370 μg/kg in organically farmed soils, respectively. Maximum and mean concentrations of other residues such as imazalil, propiconazole, clothianidin and MCPA were tens to hundreds of times lower than those of glyphosate and AMPA (Table 2).

The most common pesticide residue combination in the conventionally cultivated (grass dominated, cereal dominated, cereal–grass

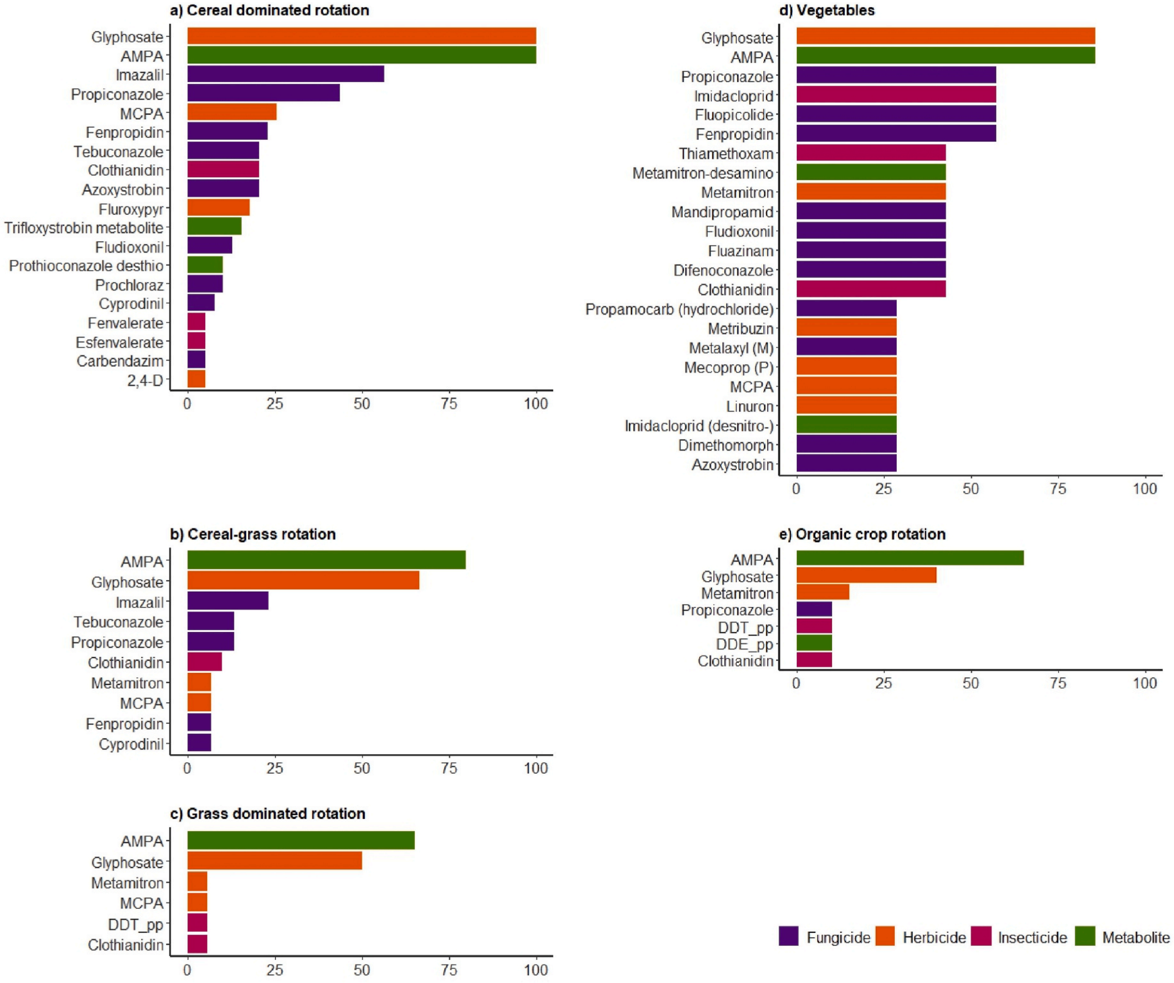


Fig. 3. The most frequently detected pesticide residues (>LOQ; percentage of samples) in conventionally farmed fields in Finland with a) cereal dominated (n = 39), b) grass dominated (n = 52), c) cereal–grass rotation (n = 30), d) vegetable production (n = 7) or in e) organically farmed fields (n = 20). Subfigures a), b) and c) consist of residues found from >5% of the studied soil samples, whereas in d) and e) the limit value is 10% due to lower number of sampled soils.

Table 2
Minimum, median, mean and maximum concentrations (μg/kg dm) of the most frequently detected pesticide residues in Finnish agricultural soils. Data includes conventionally farmed fields with cereal dominated, grass dominated or cereal–grass rotation, organically farmed fields and fields with conventionally farmed vegetable production. Values < LOQ marked as zero. A compound is classified as non-persistent (NP) when 90% of it degrades (DT90) in the laboratory at 20 °C in <30 d, moderately persistent (MP) when DT90 is 30–100 d, persistent (P) when value is 100–365 d and very persistent (VP) when >365 d (PPDB, 2023a).

Treatment	Compound	Percistency	Minimum	Median	Mean	Maximum
Conventional: Cereal dominated n = 39	AMPA	VP	132	662	703	1782
	Glyphosate	P	12.5	151	283	1343
	Imazalil	VP	0.0	1.6	2.2	15.3
	Propiconazole	P	0.0	0.0	2.1	15.8
	MCPA	MP	0.0	0.0	2.8	58.1
	Fenpropidin	VP	0.0	0.0	3.8	45.9
	Azoxystrobin	P	0.0	0.0	1.9	32.6
	Clothianidin	VP[a]	0.0	0.0	0.2	9.6
	Tebuconazole	P[a]	0.0	0.0	2.2	28.5
	Fluroxypyr	NP	0.0	0.0	1.1	22.2
	Trifloxystrobin metabolite	MP[b]	0.0	0.0	1.3	23.9
	Fludioxonil	–	0.0	0.0	0.2	2.1
	Cyprodinil	P	0.0	0.0	0.9	29.4
	Prochloraz	VP	0.0	0.0	1.5	25.5
	Prothioconazole desthio	P[b]	0.0	0.0	0.8	15.2
	Fenvalerate	–	0.0	0.0	0.2	3.3
	Esfenvalerate	P	0.0	0.0	0.2	4.7
	2,4-D	MP	0.0	0.0	0.2	3.9
	Carbendazim	P	0.0	0.0	0.1	2.6
Conventional: Cereal-gass rotation n = 30	AMPA	VP	0.0	281	396	1967
	Glyphosate	P	0.0	36.2	104	591
	Imazalil	VP	0.0	0.0	0.5	2.9
	Propiconazole	P	0.0	0.0	0.5	4.9
	Tebuconazole	P[a]	0.0	0.0	1.2	15.1
	Clothianidin	VP[a]	0.0	0.0	0.5	5.9
	Cyprodinil	P	0.0	0.0	0.6	11.4
	Fenpropidin	VP	0.0	0.0	0.3	6.0
	MCPA	MP	0.0	0.0	0.1	1.7
	Metamitron	MP	0.0	0.0	0.4	9.8
Conventional: Grass dominated n = 52	AMPA	VP	0.0	105	239	1933
	Glyphosate	P	0.0	7.2	114	2045
	DDT_pp	VP	0.0	0.0	0.6	26.1
	Clothianidin	VP[a]	0.0	0.0	0.2	7.4
	MCPA	MP	0.0	0.0	0.8	21.6
	Metamitron	MP	0.0	0.0	0.1	1.8
Organic crop rotation n = 20	AMPA	VP	0.0	76.2	121	370
	Glyphosate	P	0.0	0.0	12.7	81.2
	Clothianidin	VP[a]	0.0	0.0	0.3	5.0
	Metamitron	MP	0.0	0.0	0.9	11.3
	Propiconazole	P	0.0	0.0	0.2	2.4
	DDE_pp	VP	0.0	0.0	0.4	6.5
	DDT_pp	VP	0.0	0.0	0.8	14.0
Conventional: Vegetable n = 7	AMPA	VP	6.4	242	178	288
	Glyphosate	P	0.0	31.2	64.3	269
	Fenpropidin	VP	0.0	3.0	8.3	41.9
	Fluopicolide	VP	0.0	8.3	28.6	127.4
	Propiconazole	P	0.0	1.2	3.2	13.1
	Imidacloprid	P, VP[a]	0.0	1.5	3.9	12.2
	Clothianidin	VP[a]	0.0	0.0	4.5	13.0
	Difenoconazole	VP	0.0	0.0	22.6	78.8
	Fluazinam	P	0.0	0.0	4.2	16.1
	Fludioxonil	P[a]	0.0	0.0	3.9	14.5
	Metamitron	MP	0.0	0.0	12.6	46.1
	Metamitron-desamino	MP	0.0	0.0	13.2	61.9
	Thiamethoxam	VP	0.0	0.0	1.0	2.6
	Mandipropamid	P	0.0	0.0	9.4	29.9
	Dimethomorph	VP	0.0	0.0	1.2	6.6
	Imidacloprid (desnitro-)	–	0.0	0.0	1.2	5.4
	Linuron	P	0.0	0.0	1.8	9.7
	Azoxystrobin	P	0.0	0.0	2.0	7.1
	MCPA	MP	0.0	0.0	2.0	7.5
	Mecoprop (P)	NP	0.0	0.0	1.6	9.0
	Metalaxyl (M)	MP	0.0	0.0	0.3	2.3
	Metribuzin	NP	0.0	0.0	8.7	49.5
	Propamocarb (hydrochloride)	MP	0.0	0.0	0.6	4.5

[a] DT50 (lab at 20°C) used as no value for DT90 found from PPDB (2023a,b).

[b] Data from EFSA conclusion peer reviews.

rotation and vegetable) soils was glyphosate + AMPA (72% of samples), followed by glyphosate + AMPA + imazalil (22%), glyphosate + AMPA + MCPA (11%), glyphosate + AMPA + tebuconazole (10%), glyphosate + AMPA + propiconazole (10%), and glyphosate + AMPA + clothianidin (10%).

Of pesticides banned decades ago, DDT was still detected from 7 of 148 fields (4.7% of the samples) at a concentration range of 1.49–89.51 μg/kg. Of other substances banned before the sampling year 2018, only sporadic residues were found. HBC was found from 4 samples (1.31–13.5 μg/kg), fenvalerate from 3 samples (1.70–3.31 μg/kg), carbendazim from 2 samples (1.68–2.61 μg/kg) and linuron from 2 samples (2.57–9.71 μg/kg).

3.3. Patterns of glyphosate and AMPA contents according to soil properties and management

Farming systems and crop rotations differed regarding contents of both AMPA and glyphosate residues (Fig. 4). Concentrations of both substances were highest in cereal dominated rotations, although the difference between cereals and vegetables was not significant for glyphosate. Even though residues were found also from organically farmed fields, the concentrations were lower than for the conventionally farmed cereal fields.

Volume-based soil P showed a negative relationship with glyphosate concentration ($p = 0.0087$; Fig. 5c), whereas no clear association was established between P and APMA (Fig. 5d). Variation of soil type (coarse, fine, clay, organic), SOC (Fig. 5a; 5b) and pH were not statistically discernibly associated with the concentrations of glyphosate or AMPA ($p > 0.05$). Geographical location had no effect on the content of glyphosate residues ($p > 0.05$). Instead, the residues of AMPA varied among regions ($p < 0.001$) such that in northern Finland the mean concentration (0.028 mg/kg) was significantly lower than in the east (0.283 mg/kg), west (0.221 mg/kg) and south (0.260 mg/kg).

3.4. Risk assessment

For each assessed pesticide residue, TER-values derived from MEC-values and *E. fetida* LC50-values (Supplementary Table S2) exceeded the trigger values of 5 and 10 for acute and chronic exposure risks (EC, 2002), suggesting that the exposure risk to *E. fetida* can be interpreted as negligible (Supplementary Table S3).

Furthermore, RQ-values calculated using MECs and PNECs (Supplementary Table S3) showed low ecological risk for 94.2% of the conventionally farmed fields under cereal dominated, grass dominated and cereal–grass rotations (113 of 120 fields) and moderate ecological risk for 3.3% (4 of 120 fields; AMPA, thiamethoxam, imazalil) of these fields. High ecological risk was recognized for three fields (2.5%), where residues of DDE exceeded the limit values significantly. Under organic farming, RQ-values showed low ecological risk for 17 of 20 fields (85%). In two organically farmed fields, the assessment indicated moderate risk for soil organisms due to the concentration of DDE and in one field due to the imacloprid. In vegetable production, RQ-values for imidacloprid and fluazinam showed moderate risk for 2–3 of 7 fields and difenoconazole showed moderate risk for one and high risk for 2 of 7 fields (Supplementary Table S3).

Overall, under conventional farming, including cereal and grass dominated fields and cereal–grass rotated fields, the SRQsite values denoting the total ecological risk of the mixture showed negligible risk for 23.1%, low risk for 63.6%, medium risk for 9.9%, and high risk for 3.3% of the fields. More specifically, in cereal dominated fields, the proportion of fields showing medium ecological risk (20.5%) was higher than for those with cereal–grass rotation or grass dominated production (Table 3). From organically farmed fields most sites (85%) had negligible or low risk, but also medium risk was evident. In one of the seven analyzed vegetable fields the SROsite-value showed low risk, and in three fields moderate and in three fields high risk occurred for *E. fetida* (Table 3).

4. Discussion

4.1. Occurrence of residues

The survey showed that pesticide residues are common in the agricultural soils of Finland at various concentrations. We found at least one pesticide residue in 82% of the soils, and of those, 32% contained five or more residues, and 7.4% had over 10 different residues. Recently, European soils were screened for pesticide residues with similar outcomes. Silva et al. (2019) evaluated 317 agricultural topsoil samples across the EU and established that over 80% of them contained pesticide residues. Hvězdová et al. (2018) investigated 75 arable soils in the Czech Republic, where 99% of soils contained one or more residues and 51% more than five residues. In addition, Geissen et al. (2021) investigated

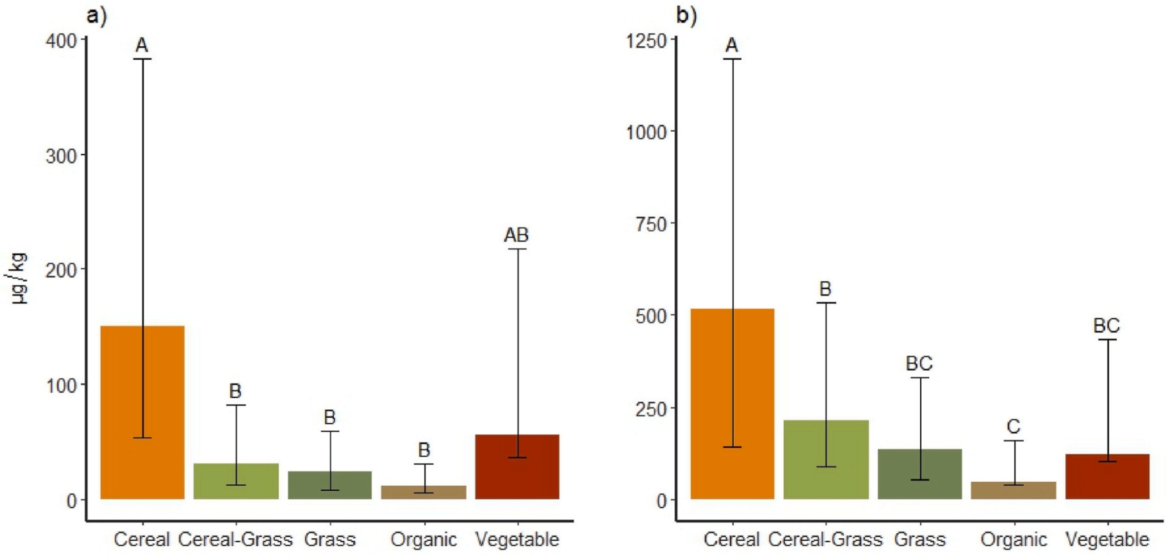


Fig. 4. Mean volume-based model estimates of glyphosate (a) and AMPA (b) concentrations and their 95% confidence intervals in various farming systems. Above bars, the same letter denotes non-significant difference ($p > 0.05$ in Bonferroni test) among cultivation systems. Note the different scales for y-axes.

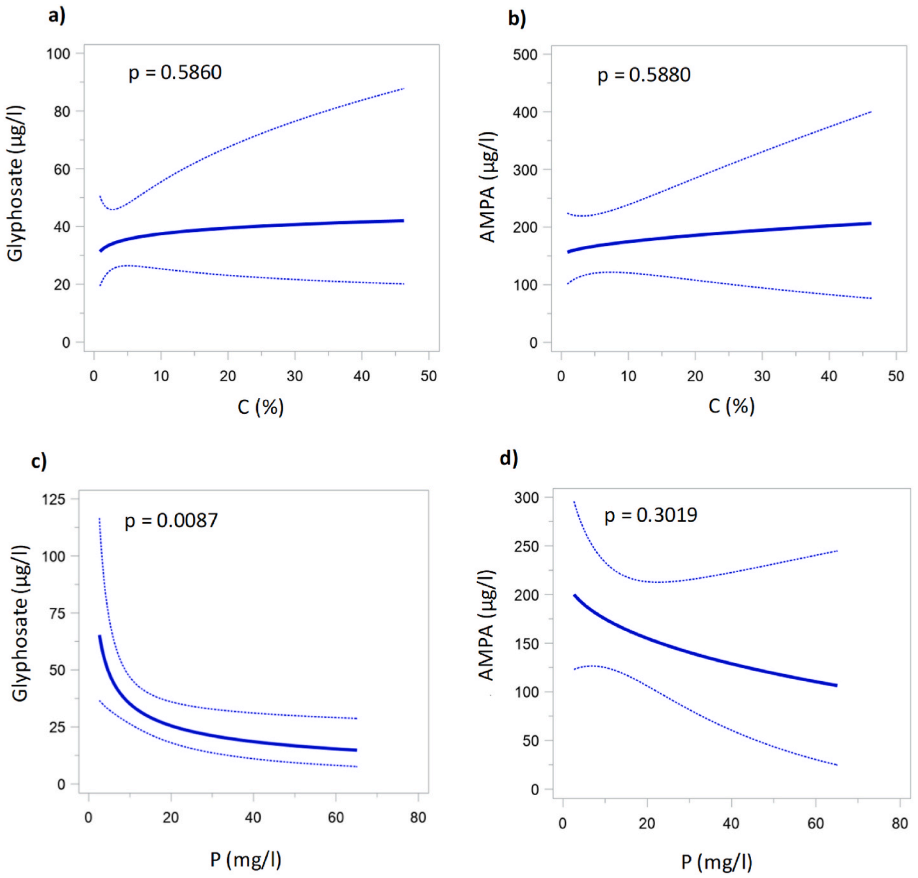


Fig. 5. Soil glyphosate (a, c) and AMPA (b, d) concentrations in relation to soil C (%) and soil test P concentration (mg/l) and their statistical significance (p-value of generalized linear model).

Table 3
Proportion of fields (%) belonging to the groups showing negligible (SRQsite <0.01), low (0.01 > SRQsite <0.1), medium (0.1 > SRQsite <1) or high (SRQsite >1) risk according the SRQsite values denoting the total ecological risk of the mixture of residues for the given locality (number of fields in parenthesis).

	Negligible (%)	Low (%)	Medium (%)	High (%)
Cereal dominated	0.00 (0)	76.9 (30)	20.5 (8)	2.56 (1)
Grass dominated	38.5 (20)	55.8 (29)	1.92 (1)	3.85 (2)
Cereal–grass rotation	26.7 (8)	60.0 (18)	10.0 (3)	3.33 (1)
Organic crop rotation	50.0 (10)	35.0 (7)	15.0 (3)	0.00 (0)
Vegetable	0.00 (0)	14.3 (1)	42.9 (3)	42.9 (3)

340 samples from Spain, Portugal and Netherlands. They found that 80% of conventional fields contained residues of two or more pesticides, with a maximum of 16 residues per sample. The study of Vieira et al. (2023) was the only survey that contained samples from northern Europe, including 73 samples from Finland. In their survey, 74% of samples contained at least one pesticide residue, and of those 11% had more than 10 pesticide residues. Our results agree with those of Vieira et al. (2023), indicating that the occurrence of pesticide residues in topsoil samples in Finland corresponds with their occurrence elsewhere in the EU.

Glyphosate and its metabolite AMPA were the most prevalent residues. Their predominance was expected as glyphosate-based herbicides are currently the most used herbicides globally, in Europe and in Finland (Antier et al., 2020; Tukes, 2023). Other frequently recorded herbicide residues in conventionally farmed fields were MCPA and fluoroxopyr, both of which are currently accepted for use in the EU. From other pesticide groups, residues of several accepted fungicides were detected (e.g. imazalil, tebuconazole, fenpropidin and fludioxonil). Also, residues of the recently (2018) banned fungicide propiconazole (EC, 2023a) were regularly found. The most frequently found insecticide residue was clothianidin, the use of which was banned in 2019 (EC, 2023a). Residues of DDT were still found in soils from both farming systems although it has been banned in Finland since 1975.

Earlier European studies produced results like ours. Vieira et al. (2023) showed that herbicide and fungicide residues are the most often found pesticide substances in Finnish arable soils. Silva et al. (2019) reported that glyphosate along with its primary metabolite AMPA are the most frequently found herbicide residues in European arable soils and Geissen et al. (2021) found that glyphosate, AMPA, and pendimethalin were the remains of herbicides detected most frequently and with the highest concentrations in soil. In the study of Hvězdová et al. (2018) in the Czech Republic, glyphosate and AMPA were not analyzed, and the most frequent occurrence was for triazine herbicides and conazole fungicides. In Silva et al. (2021), residues of DDT and its metabolites and the broad-spectrum fungicides (boscalid, epoxiconazole and tebuconazole), were detected in over 10% of samples. Triazoles are common agricultural fungicides. Residues of tebuconazole, propiconazole and prothioconazole were highest in cereal fields, while difenoconazole levels were relatively high in vegetable fields. The half-life of triazoles is relatively short, but as conjugates they can persist in soil (Dytrtová et al., 2014). The global use of triazoles in the environment promotes resistant fungal species (Verweij et al., 2016). This has led to the emergence of fungi resistant to azoles for medical application. The use of chemicals can have unforeseen consequences, therefore, the up-to-date information presented in this article is important.

4.2. Concentration of residues

Maximum total residue concentration among the conventionally farmed soils was 3043 μg/kg, of which AMPA and glyphosate contributed the most, reaching values as high as 2040 and 1967 μg/kg, respectively. These concentrations correspond with those measured in conventionally farmed soils elsewhere in Europe. Silva et al. (2019) reported maximum total pesticide residue content of 2870 μg/kg, from which glyphosate and AMPA had the highest share, with maximum values of 2050 and 1920 μg/kg, respectively. In Geissen et al. (2021), total residue content ranged between 800 and 12 000 μg/kg, the concentrations of glyphosate and AMPA being 10–7900 μg/kg and 10–430 μg/kg, respectively, the highest concentrations measured in fruit orchards. In their report, Vieira et al. (2023) concluded that pesticide residue concentrations in Finland were higher than the average values in the EU as in 65% of Finnish soils concentrations were between 150 and 1000 μg/kg and in 10% of soils values exceeded 1000 μg/kg. In our study the share of samples where residue concentrations exceeded 1000 μg/kg was even higher, 18.9%. This might be at least partly explained by differences in sampling depth being 0–15 cm in our study compared with 0–20 cm in Vieira et al. (2023). Our results indicate that even though the application level of pesticides in Finland is much lower than in central and southern Europe (Eurostat, 2018), the total residue concentrations in the soils are similar or higher. The most probable reason for this is the cold climate. Vieira et al. (2023) showed a greater incidence of pesticide residues in areas with mild temperatures unfavorable for the degradation of such compounds.

According to Silva et al. (2019), European arable soils also contained residues of boscalid (27% of samples, median 40 μg kg^{-1}), epoxiconazole (24%, 20 μg/kg), DDE (23%, 20 μg/kg), phthalimide (19%, NA) and tebuconazole (12%, 20 μg/kg). In our survey, the fungicide boscalid was found from one vegetable field, the occurrence might have been higher if vegetable fields had been covered comprehensively. Residues of epoxiconazole were not found in the present study and residues of DDE/DDT existed only in six soils. Soil contamination with DDT has been widely studied in Europe, with a maximum of content 5810 μg/kg in some Romanian topsoils (Ene et al., 2012). In the European soil survey of Silva et al. (2019), the maximum DDT concentration was 310 μg/kg, a value much higher than the maximum in our study (81.5 μg/kg). We found tebuconazole in 18% of cereal fields and from 13% of cereal–grass rotated fields in concentrations significantly lower (mean $<$ 2.2 μg/kg) than those reported by Silva et al. (2019). The pesticide products used, their application rates and residue concentrations in soil depend highly on the type of crop (Räsänen et al., 2022). Our results concern mostly cereal and grass fields. If more vegetable or berry fields, where pesticides are more frequently used than in cereal production (Räsänen et al., 2022), had been included in the survey, the results would likely have been different. Thus, our study comprehensively represents only Finnish cereal and grass fields. In addition to cereal and grass production, future arable soil monitoring should therefore also target other crop types.

4.3. Pesticides in organically farmed soils

Pesticide residues were also found from organically farmed soils, the concentrations were 75–90% lower than in the conventionally farmed fields. In the European survey, Geissen et al. (2021) established that organic farmed soils had significantly fewer residues. When they looked at residues common to both systems, similarly to our results, organically farmed soils had 70–90% lower residue concentrations than the conventionally cultivated soils. In line with Geissen et al. (2021), AMPA was the most frequently found residue in organically farmed fields in our study. The AMPA concentrations we found from organically farmed fields (max 370 μg/kg) were several times higher than those reported from organic potato production in northern Netherlands (max 14 μg/kg) but lower than those in organic orange production in eastern Spain (max 593 μg/kg) (Geissen et al., 2021). Further in line with Geissen et al. (2021), we found glyphosate residues from 50% of organically farmed fields. Even though the concentrations were quite low (max 81 μg/kg), they were comparable with those reported from organic orange production in eastern Spain (max 105 μg/kg) (Geissen et al., 2021). Also, residues of other compounds, such as clothianidin, metamitron, and DDT, were found in the organically farmed fields of our study, although the concentrations were low. The presence of glyphosate and AMPA residues in organically farmed fields indicates that degradation of some pesticides in boreal conditions may take longer than expected. Residues can be detected over 10 years after the abandonment of pesticide use, as shown also by Laitinen et al. (2009). It is also possible that drift and atmospheric deposition from nearby conventional farms may contribute to the residue concentrations in organically farmed soils (Riedo et al., 2022).

4.4. Factors affecting glyphosate and AMPA residues

We found that the crop rotation history affects the contents of both AMPA and glyphosate residues in soil, being significantly higher in cereal dominated rotations than in grass dominated or cereal–grass rotation. This is likely explained by higher glyphosate inputs for annual crops than for rotations containing perennial phases because annual spring or autumn applications of glyphosate have become common in Finnish cereal production (Laitinen et al., 2009). Our results are also in line with those of Pelosi et al. (2021), who detected glyphosate more frequently and in higher concentrations in soils of cereal fields and hedgerows (93–95% of the samples) than in grassland soils (75%).

Degradation of glyphosate and AMPA is temperature dependent, being faster at warm temperatures (Bento et al., 2016). We therefore hypothesized that their contamination levels would differ among geographic locations, due to a decreasing gradient in annual mean temperature and length and effective temperature sum of the growing season towards the north (Heikkinen et al., 2022). In a previous study conducted in western Finland, Laitinen et al. (2009) recovered 72% of the applied glyphosate in soil, either as glyphosate or AMPA twenty months after application. Overall, glyphosate is considered to degrade relatively fast, while AMPA is taken to be more resistant, although the estimated half-lives vary greatly according to study conditions, from a few days up to years (Borggaard and Gimsing, 2008). Geographical location had, however, no effect on the glyphosate residues, rather the residues of AMPA were lower in the north than in the other parts of Finland. This may relate to differences in glyphosate application rates among the regions as most intensive cereal production, and thus likely higher glyphosate use, is centered on southern parts of the country. In general, long persistence of these compounds in boreal conditions may also have impeded recognition of potential regional differences (Vieira et al., 2023).

Decelerated degradation and accumulation of glyphosate and AMPA in soil are favored by the strong sorption of the compounds through their phosphonate group on to aluminum and iron oxides, poorly ordered aluminum silicates and edges of layer silicates (Borggaard and Gimsing, 2008). Thus, accumulation could be expected to be favored in soils rich in these adsorbing surfaces (Okada et al., 2016), i.e. in fine rather than in coarse textured soils (Keskinen et al., 2022). However, no significant relationship between glyphosate or AMPA with soil type or SOC was established. Glyphosate mainly adsorbs on to mineral surfaces, the possible effects of organic matter occurring indirectly by inhibition of sorption through blocking of sorption sites (Gerritse et al., 1996) or boosting of degradation through increased microbial activity (Muskus et al., 2019). In an earlier study with a variable set of Finnish soil samples, organic carbon content did not predict the mobility of glyphosate (Autio et al., 2004).

Glyphosate, AMPA and phosphate share the same retention mechanism on the soil mineral components and are thus known to compete for the same binding sites such that phosphate is often preferred (Borggaard and Gimsing, 2008). Decreasing glyphosate sorption with increasing soil P was demonstrated by Laitinen et al. (2009) and Munira et al. (2016), among others. The current finding of decreasing glyphosate residues with increasing soil P status agrees with this phenomenon as freely occurring compounds are more vulnerable to degradation and transport via leaching than those protected by binding on to soil surfaces (Ghafoor et al., 2011; Simonsen et al., 2008).

4.5. Ecological risks of residues in soil for earthworms

In the EU the maximum allowed concentrations after the application of glyphosate-based herbicides are 5974 μg/kg and 6616 μg/kg for annual and permanent crops, respectively (EC, 2015; EFSA, 2015; Pelosi et al., 2022). For AMPA, the corresponding values are 3072 μg/kg and 6180 μg/kg (Pelosi et al., 2022). Residue concentrations in our study did not exceed these values in any sample. In addition, measured concentrations of all other residues were tens or hundreds of times below LC50-values for *E. fetida*. To assess the risk more comprehensively, we estimated the risk of the most frequently found residues in soils to earthworms using TER- and RQ-approaches. For each assessed pesticide residue, TER-values were above trigger values for acute and chronic exposure risks (EC, 2002), suggesting negligible risk to *E. fetida.* RQ-values for conventional fields, including cereal dominated, grass dominated and cereal–grass rotation, likewise showed low ecological risk for the vast majority (94.2%) of fields.

Pelosi et al. (2021) investigated glyphosate, AMPA and glufosinate concentrations in soils and earthworms in a French arable landscape and, similarly to us, reported TER-values which indicated negligible risk for earthworms. However, they criticized the protocol where risk assessment values are obtained from regulatory documents with the model species and by the consideration of endpoints. *E. fetida,* typically used in risk assessment procedures, is known to be less sensitive to pesticides than other earthworm species (Pelosi et al., 2013), which can underestimate the calculated risks. For example, glyphosate-based herbicide products may have detrimental effects on earthworm (re)production, growth, and activity at much lower concentrations. The product Grassate®, a glyphosate-based herbicide, has, for instance, exhibited an average LC50 at 3045 mg/kg on the earthworm *Aporrectodea longa* (Ogeleka et al., 2017). This concentration is near to those found in our study. According to Pelosi et al. (2021) in an intensive agricultural landscape in France, pesticide residues, at levels that could endanger earthworms, were found from 54% of nontarget beneficial soil organisms. However, this topic is complex, considering the differences in product formulations, application rates, surfactants, toxicity endpoints used and due to the exposure to chemical mixtures in natural environments.

The SRQsite values denoting the total ecological risk of the mixture for the given locality (Sanchez-Bayo et al., 2002; Vašíčková et al., 2019) indicated that in 21% of cereal dominated fields, pesticide residues caused medium ecological risk. In cereal–grass rotated or grass dominated fields the comparable value was $\leq$10%. In 2023, total cultivated area in Finland was 2 007 000 ha, of which cereals covered 52%, grasses 38%, the rest of the field area being mainly vegetables (Luke, 2023). In this survey, the number of vegetable fields was low and our sampling campaign during the growing season corresponds to a worst-case scenario. However, for only one of the studied vegetable fields the ecological risk was low, and the remaining six sites represented either moderate or high ecological risk. Thus, even though pesticide residues were also found from grass dominated crop rotations and organically farmed fields, the number of different residues, their concentrations, and thus also risks for the ecosystem was much lower than for those of conventionally cultivated cereal and vegetable fields, as was also shown by Vieira et al. (2023). To obtain a more comprehensive picture of ecological risks associated with pesticide use and residues in agricultural soils of Finland and boreal region, in addition to cereal fields, future assessments should also focus on vegetable production, although the area proportion of vegetable fields in Nordic countries is relatively low.

5. Conclusions

The survey showed that pesticide residues are commonly found in the agricultural soils of Finland. Residues of AMPA and glyphosate were the most frequently found substances from both conventional and organically farmed fields. Even though the application rates of pesticides in Finland is lower than for most parts of central and southern Europe, the number of pesticide residues and total residue concentrations in the soils were at similar or higher levels than the EU average. The most probable reason for this is the cold climate, which slows down their degradation. However, the comparison of residue concentrations in the present study and those from other regions of Europe is difficult and impractical because selection of fields and crops has a huge effect on pesticides used and, consequently, their residues. Risk analyses for individual substances indicated low ecological risk for most of the fields. Also, the total ecological risk associated with the mixtures of residues was mostly low, except for 21% of cereal dominated fields where they represented a medium risk. In most of the vegetable fields, the ecological risk was shown to be moderate or high. To obtain a more comprehensive picture of ecological risks of pesticide residues in agricultural soils of Finland, in addition to cereal fields, future sampling and risk assessment should also include vegetable production. Our results showed that the presence of mixtures of pesticide residues in soils is a rule rather than an exception also in boreal soils. In highly chemicalized modern agriculture, the follow-up of the residues of currently used pesticides is imperative in soil monitoring programs as an important soil quality indicator and to support sustainable environment policies.

CRediT authorship contribution statement

M. Hagner: Writing – original draft, Project administration, Investigation, Funding acquisition. **S. Rämö:** Writing – review & editing, Methodology. **H. Soinne:** Writing – review & editing, Visualization, Conceptualization. **V. Nuutinen:** Writing – review & editing, Supervision, Resources, Funding acquisition, Conceptualization. **R. Muilu-Mäkelä:** Writing – review & editing, Investigation. **J. Heikkinen:** Writing – review & editing, Resources, Formal analysis, Conceptualization. **J. Heikkinen:** Writing – review & editing, Software, Formal analysis. **J. Hyvönen:** Writing – review & editing, Software, Formal analysis. **K. Ohralahti:** Writing – review & editing, Investigation. **V. Silva:** Writing – review & editing, Methodology. **R. Osman:** Writing – review & editing, Methodology. **V. Geissen:** Writing – review & editing, Supervision. **C.J. Ritsema:** Writing – review & editing, Supervision. **R. Keskinen:** Writing – original draft, Resources, Investigation, Conceptualization.

Declaration of competing interest

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

Data availability

Data will be made available on request.

Acknowledgments

We thank Luke's field personnel for the collection of the soil samples and Luke's soil laboratory for the pretreatment of the samples. Special thanks for Luke's laboratory employee Leena Holkeri for her valuable help with glyohosate and AMPA analysis. The study was funded through Valse V -project (Ministry of Agriculture and Forestry of Finland) and PesResValse-project (Luke's strategic funding).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2024.124430.

References

Antier, C., Kudsk, P., Reboud, X., Ulber, L., Baret, P.V., Messéan, A., 2020. Glyphosate use in the European agricultural sector and a framework for its further monitoring. Sustainability 12, 5682. https://doi.org/10.3390/su12145682.

Arias-Estévez, M., López-Periago, E., Martínez-Carballo, E., Simal-Gándara, J., Mejuto, J.-C., García-Río, L., 2008. The mobility and degradation of pesticides in soils and the pollution of groundwater resources - a review. Agric. Ecosyst. Environ. 123, 247–260. https://doi.org/10.1016/j.agee.2007.07.011.

Autio, S., Siimes, K., Laitinen, P., Rämö, S., Oinonen, S., Eronen, L., 2004. Adsorption of sugar beet herbicides to Finnish soil. Chemosphere 55, 215–2226. https://doi.org/10.1016/j.chemosphere.2003.10.015.

Bento, C.P., Yang, X., Gort, G., Xue, S., van Dam, R., Zomer, P., Mol, H.G., Ritsema, C.J., Geissen, V., 2016. Persistence of glyphosate and aminomethylphosphonic acid in loess soil under different combinations of temperature, soil moisture and light/darkness. Sci. Total Environ. 572, 301–311. https://doi.org/10.1016/j.scitotenv.2016.07.215.

Borggaard, O.K., Gimsing, A.L., 2008. Fate of glyphosate in soil and the possibility of leaching to ground and surface waters: a review. Pest Manag. Sci. 64, 441–456. doi:10.1002/ps.1512.

Carlon, C. (Ed.), 2007. Derivation Methods of Soil Screening Values in Europe. A Review and Evaluation of National Procedures towards Harmonization. European Commission. Joint Research Centre, Ispra, EUR, p. 306, 22805-EN.

Casado, J., Brigden, K., Santillo, D., Johnston, P., 2019. Screening of pesticides and veterinary drugs in small streams in the European Union by liquid chromatography high resolution mass spectrometry. Sci. Total Environ. 670, 1204e1225. https://doi.org/10.1016/j.scitotenv.2019.03.207.

Chiaia-Hernandez, Keller, A.C., Wächter, A., Steinlin, D., Camenzuli, C., Hollender, L., Krauss, M., 2017. Long-term persistence of pesticides and TPs in archived agricultural soil samples and comparison with pesticide application. Environ. Sci. Technol. 51, 10642–10651. https://doi.org/10.1021/acs.est.7b02529.

De Jonge, H., De Jonge, L.W., Jacobsen, O.H., Yamaguchi, T., Moldrup, P., 2001. Glyphosate sorption in soils of different pH and phosphorus content. Soil Sci. 166, 230–238. https://doi.org/10.1097/00010694-200104000-00002.

Dytrtová, J., Fanfrlik, J., Norková, R., Jakl, M., Hobza, P., 2014. Theoretical insight into the stabilization of triazole fungicides via their interactions with dications. Int. J. Mass Spectrom. 359, 38–43. https://doi.org/10.1016/j.ijms.2013.11.011.

EC (European Commission), 2000. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. https://eur-lex.europa.eu/eli/dir/2000/60/oj.

EC (European Commission), 2002. EC Guidance Document on Terrestrial Ecotoxicology Under Council Directive 91/414/EEC. SANCO/10329/2002 rev 2 final, p. 39.

EC (European Commission), 2009. 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 and repealing Council Directives 79/117/EEC and 91/414/EEC. http://data.europa.eu/eli/reg/2009/1107/oj.

EC (European Commission), 2013. Regulation (EU) no 1306/2013 of the European Parliament and of the council of 17 December 2013 on the financing, management and monitoring of the common agricultural policy and repealing Council Regulations (EEC) No 352/78, (EC) No 165/94, (EC) No 2799/98, (EC) No 814/2000, (EC) No 1290/2005 and (EC) No 485/2008. https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2013:347:0549:0607:EN:PDF.

EC (European Commission), 2015. Final Addendum to the Renewal Assessment Report.

EC (European Commission), 2020. Farm to Fork Strategy. For a Fair, Healthy and Environmentally-Friendly Food System. European Union. https://food.ec.europa.eu/system/files/2020-05/f2f_action-plan_2020_strategy-info_en.pdf. (Accessed 30 January 2024).

EC (European Commission), 2023a. European Commission EU-pesticides-database. https://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/start/screen/active-substances. (Accessed 20 November 2023).

EC (European Commission), 2023b. Proposal for a directive on soil monitoring and Resilience. https://environment.ec.europa.eu/publications/proposal-directive-soil-monitoring-and-resilience_en. (Accessed 20 November 2023).

EFSA (European Food Safety Authority), 2015. Conclusion on the peer review of the pesticide risk assessment of the active substance glyphosate. EFS2 13. https://doi.org/10.2903/j.efsa.2015.4302.

EFSA (European Food Safety Authority), 2019. Guidance on harmonised methodologies for human health, animal health and ecological risk assessment of combined exposure to multiple chemicals. EFSA J. https://doi.org/10.2903/j.efsa.2019.5634.

Ene, A., Bogdevich, O., Sion, A., 2012. Levels and distribution of organochlorine pesticides (OCPs) and polycyclic aromatic hydrocarbons (PAHs) in topsoils from Romania. Sci. Total Environ. 439, 76–86. https://doi.org/10.1016/j.scitotenv.2012.09.004.

Eurostat, 2018. Pesticide sales statistics. https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Archive:Pesticide_sales_statistics. (Accessed 20 November 2023).

Eurostat, 2022. Agri-environmental indicator - consumption of pesticides. https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Agri-environmental_indicator_-_consumption_of_pesticides. (Accessed 17 February 2023).

Falorsi, P., Righi, P., 2008. A balanced sampling approach for multi-way stratification designs for small area estimation. Surv. Methodol. 34, 223–234.

Gamón, M., Sáez, E., Gil, J., Boluda, R., 2003. Direct and indirect exogenous contamination by pesticides of rice-farming soils in a Mediterranean Wetland. Arch. Environ. Contam. Toxicol. 44, 141–151. https://doi.org/10.1007/s00244-002-2008-3.

Geissen, V., Silva, V., Lwanga, E.H., Beriot, N., Oostindie, K., Bin, Z., Pyne, E., Busink, S., Zomer, P., Mol, H., Ritsema, C.J., 2021. Cocktails of pesticide residues in conventional and organic farming systems in Europe - Legacy of the past and turning point for the future. Environ. Pollut. 278, 116827 https://doi.org/10.1016/j.envpol.2021.116827.

Gerritse, R.G., Beltran, J., Hernandez, F., 1996. Adsorption of atrazine, simazine, and glyphosate in soils of the Gnangara Mound, western Australia. Aust. J. Soil Res. 34, 599–607.

Ghafoor, A., Jarvis, N.J., Thierfelder, T., Stenström, J., 2011. Measurements and modeling of pesticide persistence in soil at the catchment scale. Sci. Total Environ. 409, 1900–1908. https://doi.org/10.1016/j.scitotenv.2011.01.049.

FAOSTAT (Food and Agriculture Organization of the United Nations), 2024. Online database. http://www.fao.org/faostat/en/#data/. (Accessed 17 February 2024).

Grafström, A., Lundström, N.L.P., Schelin, L., 2012. Spatially balanced sampling through the pivotal method. Biometrics 68, 514–520. https://doi.org/10.1111/j.1541-0420.2011.01699.x.

Heikkinen, J., Keskinen, R., Kostensalo, J., Nuutinen, V., 2022. Climate change induces carbon loss of arable mineral soils in boreal conditions. Global Change Biol. 28, 3960–3973. https://doi.org/10.1111/gcb.16164.

Hvězdová, M., Kosubová, P., Košíková, M., Scherr, K.E., Šimek, Z., Brodský, L., Šudoma, M., Škulcová, L., Sáňka, M., Svobodová, M., Krkošková, L., Vašíčková, J., Neuwirthová, N., Bielská, L., Hofman, J., 2018. Currently and recently used pesticides in Central European arable soils. Sci. Total Environ. 613–614, 361–370. https://doi.org/10.1016/j.scitotenv.2017.09.049.

Karasali, H., Marousopoulou, A., Machera, K., 2016. Pesticide residue concentration in soil following conventional and Low-Input Crop Management in a Mediterranean agro-ecosystem, in Central Greece. Sci. Total Environ. 541, 130–142. https://doi.org/10.1016/j.scitotenv.2015.09.016.

Keskinen, R., Ketoja, E., Heikkinen, J., Salo, T., Uusitalo, R., Nuutinen, V., 2016. 35-year trends of acidity and soluble nutrients in cultivated soils of Finland. Geoderma Reg. 7, 376–387. https://doi.org/10.1016/j.geodrs.2016.11.005.

Keskinen, R., Hillier, S., Liski, E., Nuutinen, V., Nyambura, M., Tiljander, M., 2022. Mineral composition and its relations to readily available element concentrations in cultivated soils of Finland. Acta Agric. Scand. B Soil Plant Sci. 72, 751–760. https://doi.org/10.1080/09064710.2022.2075790.

Kudsk, P., Jørgensen, L.N., Ørum, J.E., 2018. Pesticide Load—a new Danish pesticide risk indicator with multiple applications. Land Use Pol. 70, 384–393. https://doi.org/10.1016/j.landusepol.2017.11.010.

Laitinen, P., Rämö, S., Nikunen, U., Jauhiainen, L., Siimes, K., Turtola, E., 2009. Glyphosate and phosphorus leaching and residues in boreal sandy soil. Plant Soil 323, 267–283. https://doi.org/10.1007/s11104-009-9935-y.

Luke, 2023. Statistics Database. Natural Resources Institute Finland.

Marican, A., Durán-Lara, E.F., 2018. A review on pesticide removal through different processes. Environ. Sci. Pollut. Res. 25, 2051–2206. https://doi.org/10.1007/s11356-017-0796-2.

Marković, M., Cupać, S., Ðurović, R., Milinović, J., Kljajić, P., 2010. Assessment of heavy metal and pesticide levels in soil and plant products from agricultural area of Belgrade. Serbia. Arch. Environ. Contam. Toxicol. 58, 341–351. https://doi.org/10.1007/s00244-009-9359-y.

Mu, H., Yang, X., Wang, K., Tang, D., Xu, W., Liu, X., Ritsema, C.J., Geissen, V., 2023. Ecological risk assessment of pesticides on soil biota: an integrated field-modelling approach. Chemosphere 326, 138428. https://doi.org/10.1016/j.chemosphere.2023.138428.

Munira, S., Farenhorst, A., Flaten, D., Grant, C., 2016. Phosphate fertilizer impacts on glyphosate sorption by soil. Chemosphere 153, 471–477. https://doi.org/10.1016/j.chemosphere.2016.03.028.

Muskus, A.M., Krauss, M., Miltner, A., Hamer, U., Nowak, K.M., 2019. Effect of temperature, pH and total organic carbon variations on microbial turnover of 13C315N-glyphosate in agricultural soil. Sci. Total Environ. 658, 697–707. https://doi.org/10.1016/j.scitotenv.2018.12.195.

Ogeleka, D., Onwuemene, C., Okieimen, F., 2017. Toxicity potential of Grassate® a nonselective herbicide on snails (Achachatina marginata) and earthworms (Aporrectodea longa). J. Chem. Ecol. 33, 447–463.

Okada, E., Costa, J.L., Bedmar, F., 2016. Adsorption and mobility of glyphosate in different soils under no-till and conventional tillage. Geoderma 263, 78–85. https://doi.org/10.1016/j.geoderma.2015.09.009.

Panico, S.C., van Gestel, C.A.M., Verweij, R.A., Rault, M., Bertrand, C., Barrigae, C.A.M., Coeurdassier, M., Fritsch, C., Gimbert, F., Pelosi, C., 2022. Field mixtures of currently used pesticides in agricultural soil pose a risk to soils invertebrates. Environ. Pollut. 305, 11929 https://doi.org/10.1016/j.envpol.2022.119290.

Pelosi, C., Toutous, L., Chiron, F., Dubs, F., Hedde, M., Muratet, A., Ponge, J.-F., Salmon, S., Makowski, D., 2013. Reduction of pesticide use can increase earthworm populations in wheat crops in a European temperate region. Agric. Ecosyst. Environ. 181, 223–230. https://doi.org/10.1016/j.agee.2013.10.003.

Pelosi, C., Bertrand, C., Daniele, G., Coeurdassier, M., Benoit, P., Nélieu, S., Lafay, F., Bretagnolle, V., Gaba, S., Vulliet, E., Fritsch, C., 2021. Residues of currently used pesticides in soils and earthworms: a silent threat? Agric Ecosyst. Environ. 305, 107167 https://doi.org/10.1016/j.agee.2020.107167.

Pelosi, C., Bertrand, C., Bretagnolle, V., Coeurdassier, M., Delhomme, O., Deschamps, M., Gaba, S., Millet, M., Nélieu, S., Fritsch, C., 2022. Glyphosate, AMPA and glufosinate in soils and earthworms in a French arable landscape. Chemosphere 301, 134672. https://doi.org/10.1016/j.chemosphere.2022.134672.

Pérez, D.J., Iturburu, F.G., Calderon, G., Oyesqui, L.A., De Gerónimo, E., Aparicio, V.C., 2021. Ecological risk assessment of current-use pesticides and biocides in soils, sediments and surface water of a mixed land-use basin of the Pampas region, Argentina. Chemosphere 263, 128061. https://doi.org/10.1016/j.chemosphere.2020.128061.

PPDB, 2023a. The University of Hertfordshire agricultural substances databases - background and support information. http://sitem.herts.ac.uk/aeru/iupac/docs/Background_and_Support.pdf. (Accessed 24 January 2024).

PPDP, 2023b. Pesticide Properties Database. http://sitem.herts.ac.uk/aeru/ppdb/en/. (Accessed 10 November 2023).

Rämö, S., Välimäki, J., Siimes, K., Uusi-Kämppä, J., 2023. Determination of glyphosate and aminomethylphosphonic acid residues in Finnish soils by ultra-high performance liquid chromatography–tandem mass spectrometry. MethodsX 11, 102397. https://doi.org/10.1016/j.mex.2023.102397.

Räsänen, K., Hannukkala, A., Kurppa, S., Aaltonen, M., Rahkonen, A., Kukkonen, J.V.K., Vänninen, I., 2022. The use of chemical plant protection products in field vegetable farms in a central industrial vegetable growing area in Finland. Agric. Food Sci. 31, 54–69. https://doi.org/10.23986/afsci.112827.

Renaud, R., Akeju, T., Natal-da-Luz, T., Leston, S., Rosa, J., Ramos, F., Sousa, J.P., Azevedo-Pereira, H.M.V.S., 2018. Effects of the neonicotinoids acetamiprid and thiacloprid in their commercial formulations on soil fauna. Chemosphere 194, 85–93. https://doi.org/10.1016/j.chemosphere.2017.11.102.

Riedo, J., Wettstein, F.E., Rösch, A., Herzog, C., Banerjee, S., Büchi, L., Charles, R., Wächter, D., Martin-Laurent, F., Bucheli, T.D., Walder, F., van der Heijden, M.G.A., 2021. Widespread occurrence of pesticides in organically managed agricultural soils-the ghost of a conventional agricultural past? Environ. Sci. Technol. 55, 2919–2928. https://doi.org/10.1021/acs.est.0c06405.

Riedo, J., Herzog, C., Banerjee, S., Fenner, K., Walder, F., van der Heijden, M.G.A., Bucheli, T.D., 2022. Concerted evaluation of pesticides in soils of extensive grassland sites and organic and conventional vegetable fields facilitates the identification of major input processes. Environ. Sci. Technol. 46, 13686–13695. https://doi.org/10.1021/acs.est.2c02413.

Sabzevari, S., Hofman, J., 2022. A worldwide review of currently used pesticides' monitoring in agricultural soils. Sci. Total Environ. 812, 152344 https://doi.org/10.1016/j.scitotenv.2021.152344.

Silva, V., Mol, H.G.J., Zomer, P., Tienstra, M., Ritsema, C.J., Geissen, V., 2019. Pesticide residues in European agricultural soils – a hidden reality unfolded. Sci. Total Environ. 653, 1532–1545. https://doi.org/10.1016/j.scitotenv.2018.10.441.

Sánchez-Bayo, F., Baskaran, S., Kennedy, I.R., 2002. Ecological relative risk (EcoRR): another approach for risk assessment of pesticides in agriculture. Agric. Ecosyst. Environ. 91, 37–57. https://doi.org/10.1016/S0167-8809(01)00258-4.

Silva, V., Alaoui, A., Schlünssen, V., Vested, A., Graumans, M., van Dael, M., Trevisan, M., Suciu, N., Mol, H., Beekmann, K., Figueiredo, D., Harkes, P., Hofman, J., Kandeler, E., Abrantes, N., Campos, I., Martínez, M.Á., Pereira, J.L., Goossens, D., Gandrass, J., Debler, F., Lwanga, E.H., Jonker, M., van Langevelde, F., Sorensen, M.T., Wells, J.M., Boekhorst, J., Huss, A., Mandrioli, D., Sgargi, D., Nathanail, P., Nathanail, J., Tamm, L., Fantke, P., Mark, J., Grovermann, C., Frelih-Larsen, A., Herb, I., Chivers, C.-A., Mills, J., Alcon, F., Contreras, J., Baldi, I., Pasković, I., Matjaz, G., Norgaard, T., Aparicio, V., Ritsema, C.J., Geissen, V., Scheepers, P.T.J., 2021. Collection of human and environmental data on pesticide use in Europe and Argentina: field study protocol for the SPRINT project. PLoS One 16 (11), e0259748. https://doi.org/10.1371/journal.pone.0259748.

Simonsen, L., Fomsgaard, I.S., Svensmark, B., Spliid, N.H., 2008. Fate and availability of glyphosate and AMPA in agricultural soil. J. Environ. Sci. Health B. 43, 365–375. https://doi.org/10.1080/03601230802062000.

Soinne, H., Kurkilahti, M., Heikkinen, J., Eurola, M., Uusitalo, R., Nuutinen, V., Keskinen, R., 2022. Decadal trends in soil and grain microelement concentrations indicate mainly favourable development in Finland. J. Plant Nutr. Soil Sci. 185, 578–588. https://doi.org/10.1002/jpln.202200141.

Stenrød, M., Eklo, O.M., Charnay, M.P., Benoit, P., 2005. Effect of freezing and thawing on microbial activity and glyphosate degradation in two Norwegian soils. Pest Manag. Sci. 61, 887–898. https://doi.org/10.1002/ps.1107. PMID: 16041712.

Suszter, G.K., Ambrus, Á., 2017. Distribution of pesticide residues in soil and uncertainty of sampling. J. Environ. Sci. Health B 52, 557–563. https://doi.org/10.1080/03601234.2017.1316171.

Tukes, 2023. Finnish Safety and Chemical Agency. Sales volumes of plant protection products. https://tukes.fi/en/chemicals/plant-protection-products/sales-volumes. Accessed 1.12.2023.

Vaj, C., Barmaz, S., Sørensen, P.B., Spurgeon, D., Vighi, M., 2011. Assessing, mapping and validating site-specific ecotoxicological risk for pesticide mixtures: a case study for small scale hot spots in aquatic and terrestrial environments. Ecotoxicol. Environ. Saf. 74, 2156–2166. https://doi.org/10.1016/j.ecoenv.2011.07.011.

Vašíčková, J., Hvězdová, M., Kosubová, J., Hofman, P., 2019. Ecological risk assessment of pesticide residues in arable soils of the Czech Republic. Chemosphere 216, 479–487. https://doi.org/10.1016/j.chemosphere.2018.10.158.

Verweij, P., Chowdhary, A., Melchers, W.J., Meis, J.F., 2016. Azole resistance in Aspergillus fumigatus: can we retain the clinical use of mold-active antifungal azoles? Clin. Infect. Dis. 62, 362–368. https://doi.org/10.1093/cid/civ885.

Vieira, D., Franco, A., De Medici, D., Martin Jimenez, J., Wojda, P., Jones, A., 2023. Pesticides Residues in European Agricultural Soils - Results from LUCAS 2018 Soil Module. Publications Office of the European Union, Luxembourg.

Vuorinen, J., Mäkitie, O., 1955. The Method of Soil Testing in Use in Finland, vol 63. Agroecol. Publ., p. 44

Zhao, P., Wang, Z., Li, K., Guo, X., Zhao, L., 2018. Multi-residue enantiomeric analysis of 18 chiral pesticides in water, soil and river sediment using magnetic solid-phase extraction based on amino modified multiwalled carbon nanotubes and chiral liquid chromatography coupled with tandem mass spectrometry. J. Chromatogr., A 1568, 8–21. https://doi.org/10.1016/j.chroma.2018.07.022.