# Pesticide residues in agricultural soils in light of their on-farm application history☆

Judith Riedo [a],[1], Daniel Wächter [a],[1], Andreas Gubler [a], Felix E. Wettstein [b], Reto G. Meuli [a], Thomas D. Bucheli [b],*

[a] *Swiss Soil Monitoring, Agroscope, 8046, Zurich, Switzerland*
[b] *Environmental Analytics, Agroscope, 8046, Zurich, Switzerland*

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## ABSTRACT

The application of synthetic pesticides to agricultural fields for the protection of crops leads to the formation of residues in soils. While the short-term behavior of pesticide residues in soils after an application is generally known from laboratory and field studies required for authorization (prospective risk assessments), there is still a lack of *in-situ* observations that address their long-term fate. Long-term soil monitoring programs, with comprehensive site-specific records of pesticide application data, constitute an invaluable, complementary, retrospective exposure assessment tool to address this gap. Considering the pesticide applications over the past 10–15 years, this study assessed the occurrence of pesticides in agricultural soils of Switzerland and put their presence or absence, as well as their concentrations, in the context of their previous application. The results showed that pesticides could also be detected at sites without a connection to previous applications and that small residual mass fractions of pesticides, even of some non-persistent compounds, were found in soils, years or decades after their last application. This finding points to an environmental issue that may not be adequately captured in prospective risk assessment and calls attention to the need for comprehensive long-term recording and monitoring as a complementary retrospective exposure assessment.

## 1. Introduction

The intensification of agriculture, which is necessary to meet increasing global demands for food, has primarily been achieved through the increase of external inputs, such as fertilizers and pesticides (Pretty, 2018). As a result, pesticides have become a fundamental part of modern agriculture, safeguarding agricultural production by reducing yield losses caused by diseases, pests, and weeds (Food and Agriculture Organization of the United Nations, 2017; Savary et al., 2019). Generally, pesticides are defined as compounds used to eliminate or control pests, such as unwanted insects, animals, and plants or disease-carrying organisms (Food and Agriculture Organization of the United Nations, 2017). The active ingredients (AI) of pesticides and their transformation products (TP) represent a large and heterogeneous group of chemical compounds with varying molecular properties (University of Hertfordshire, 2020). Over the past two decades, global pesticide use has increased by over 40%, and since 2017 has stabilized at around 4.1 million tons per year (FAOSTAT, 2021). Herbicides, fungicides, and insecticides comprise more than 95% of the total pesticides used in agriculture (Food and Agriculture Organization of the United Nations, 2006). In Switzerland, around 2000 tons of pesticides are sold each year, although the amount of synthetic pesticides has steadily decreased since 2014 (Federal Office for Agriculture, 2022b).

In theory, pesticides are designed to act primarily on target organisms, to decompose rapidly, and to not translocate from the original application site (Rosell et al., 2008). In reality, however, a large percentage of the applied substances miss their target and end up elsewhere in the environment (Food and Agriculture Organization of the United Nations, 2017; Rodríguez-Eugenio et al., 2018). During application, the majority of AI reach the soil surface, either directly or via wash-off from crop canopy, or undergo abiotic distribution processes, such as drift and volatilization to the atmosphere. After application, AI can be subjected

to various abiotic and biotic processes, such as sorption and biodegradation by soil organisms (Copaja and Gatica-Jeria, 2021; Fenner et al., 2013). Recent studies have demonstrated that AI indeed are omnipresent in agricultural soils in Switzerland (Chiaia-Hernandez et al., 2017; Riedo et al., 2021), and other regions of Europe (Geissen et al., 2021; Hvězdová et al., 2018; Kosubová et al., 2020; Silva et al., 2019; Ukalska-Jaruga et al., 2020). The reported concentrations of AI residues span a wide range from below 1 μg/kg to a few 100 μg/kg per site, reflecting diverse application patterns, varying amounts applied, and differing subsequent dissipation in soil. Residues of AI were also detected in soils under organic agriculture and soils without agricultural exploitation, typically at the lower end of this concentration range (Geissen et al., 2021; Humann-Guilleminot et al., 2019; Riedo et al., 2021; Silva et al., 2019). This constant exposure to pesticides in soil potentially impacts both the diversity and the activity of flora, fauna, and funga. The associated changes in soil enzymatic activities and the harmful effects on beneficial organisms may impair soil fertility, as well as ecosystem services provided by soils (Bünemann et al., 2006; Johnsen et al., 2001; Sannino and Gianfreda, 2001). While the awareness of the potential problems pesticides pose to ecosystems has increased, pesticides with high-risk potential, meaning AI that are classified as potentially harmful to humans and ecosystems and/or are persistent in soils, still account for roughly 10%–14% of the amounts sold in Switzerland (Federal Office for Agriculture, 2019; Federal Office for Agriculture, 2020). In the European context, nearly 50% of currently used AIs are bioaccumulative and 25% are persistent in soil (Geissen et al., 2021).

Even though measures have been taken to limit the input of pesticides, the surveillance of the substances, which had already been applied in the past, is still important but often missing for the soil environment. In particular, mass balances of applied substances and observations of dissipation over a temporal scale are lacking so far. Soil monitoring programs are therefore a valuable resource to assess this exposure (Topping et al., 2020), particularly in cases where pesticide application records are available. While the short-term behavior of pesticide residues in soils after applications is known from laboratory and controlled field studies required for the authorization of new AI (prospective risk assessments), observations addressing the long-term fate and *in-situ* occurrence of residues in soils under real-world conditions, that would allow for retrospective exposure assessments, are still lacking (Silva et al., 2019).

To reduce this knowledge gap, this study investigated the occurrence of synthetic pesticides in agricultural soils of Switzerland and put the presence or absence of AI and TP, and their concentrations, in the context of previous pesticide applications. In addition, quantified soil concentrations were also compared with predicted concentrations derived from actual and accurate application data, which has not been studied before. To this end, soil samples from the Swiss Soil Monitoring Network (NABO), for which long-term agricultural management records are available, were analyzed for 34 AI and 7 TP. With this dataset, the following questions were assessed: (i) What were the occurrences and concentrations of pesticides present in the assessed soils? (ii) How could the presence or absence of the investigated AI and TP be interpreted in relation to the pesticide applications reported? (iii) And how do pesticide residues in soil develop over time periods after application beyond those addressed by registration?

## 2. Material and methods

### 2.1. Study sites and soil sampling

Soil samples from 31 agricultural sites were collected. Each site was sampled once between 2005 and 2009 during the routine monitoring of the NABO, which operates more than 100 long-term monitoring sites throughout Switzerland (Gubler et al., 2015; Gubler et al., 2019; Swiss Soil Monitoring Network, 2022). The selection of sites for this study comprised all monitoring sites for which land management data,

including pesticide applications, were available for the last 10–15 years before sampling (since 1996), depending on the year of sampling of the respective site. The pesticide application record of one exemplary site over time is presented in Figure S1 and Table S1. The corresponding last applications of the investigated substance are listed in Table S2. The monitored sites included 22 croplands (c, featuring varying crop rotations), 3 orchards (o), and 3 vineyards (v) under conventional agricultural management. All sites were managed according to the Swiss "Proof of Ecological Performance" guidelines after its implementation in 1999 (Federal Office for Agriculture, 2022a). Data on the pesticide applications were documented by NABO according to the farmers' declarations (Gross et al., 2021). In addition, 3 sites under organic management (org), which did not receive any synthetic pesticide input for decades (between 15 and 75 years), were added for comparison and as "negative controls".

Soil sampling and processing were performed as described by Gubler et al. (2015). For each site, four replicates of topsoil (0–20 cm), each being a bulked sample of 25 sub-samples, were collected from an area of $10 \times 10 \, m^2$ using a stratified random sampling design. Soil samples were then processed by removing plant materials, drying (oven-dried at 40 °C for 48 h), and sieving (2 mm). Until further analysis in 2018, the samples were stored in high-density polyethylene containers under cold (12–15 °C), dry (30–40% humidity), and dark conditions. Per site, 2 of the 4 replicated soil samples were analyzed.

### 2.2. Physico-chemical soil analyses

Soil physicochemical properties were characterized following the Swiss reference methods of our institute (Agroscope, 2022). The soil pH was determined in 0.01 M $CaCl_2$ (1:2.5 v/v). Organic carbon ($C_{org}$) was analyzed using the modified Walkley-Black method and texture was measured using a pipetting method with clay <2 μm, silt 2–50 μm and sand >50 μm as the cutoff values. The bulk density was determined via the volume and dry weight of the fine soil. The soil properties of the considered sites are summarized in Table S7.

### 2.3. Selection of analyzed pesticides

The analyzed substances were selected based on their (i) frequency of application within the monitoring network and the frequency of occurrence in our previous study (Chiaia-Hernandez et al., 2017), (ii) predicted environmental concentrations, which were estimated based on the AI applied within the network sites, and their expected dissipation rates ($DT_{50}$) taken from their registration data, (iii) analytical feasibility to be integrated into a multi-residue method, and (iv) importance based on expert knowledge. Overall, the multi-residue analysis included 34 AI and 7 TP synthetic pesticides (Riedo et al., 2021). Because pesticide selection, method development, and sample analysis followed different timelines, some substances were not approved until after the samples were collected. However, in order to keep the assessment as broad as possible, they were included. The selection criteria and the approval date of each pesticide are listed in Table S3. Relevant physicochemical properties of the pesticides (e.g. organic carbon-water partition coefficients ($K_{oc}$)), determining their environmental fate, were obtained from the literature (University of Hertfordshire, 2020), and are listed in Table S3.

### 2.4. Sample extraction and pesticide analysis with high-performance liquid chromatography-tandem mass spectrometry

Pesticides were extracted and measured as described by Riedo et al. (2021). Samples were mixed with a Turbula® shaker before a 6 g sub-sample was collected for further analysis. Accelerated solvent extraction (Dionex ASE 350, Thermo Scientific) was subsequently carried out to extract the pesticide residues from the soil. Two extraction steps were performed. In the first step, an organic mixture of acetone, methanol and

acetonitrile in the ratio of 65:10:25 (% v/v) was used. In the second extraction step, the soils were further processed with an acidic mixture of acetone and 1% phosphoric acid in Millipore water (Milli-Q Gradient, Merck) at a ratio of 70:30 (% v/v) (Table S4). The extracts were evaporated under compressed air and then diluted to 1 mL with 90:10 (% v/v) Millipore water and methanol. Finally, the pesticides were quantified by high performance liquid chromatography coupled to a triple quadrupole tandem mass spectrometer (HPLC-MS/MS, QTrap 5500, Sciex). Reversed-phase HPLC, with water and methanol as mobile phases, both containing 5 mM $NH_4COOH$, was used for separation. Only the 20 substances measured with isotopically labeled internal standards (ILIS) were considered for the quantitative analysis. All quantified concentrations were converted to µg per kg of dry soil. The limits of quantification (LOQ) were determined from the concentration of the matrix-matched calibration standard, for which the analyte peak heights of the quantifier and qualifier ion transition fulfilled the required signal-to-noise ratios of at least 10 and 3, respectively. The LOQs were set at 0.3 µg/kg for all analytes to facilitate further analysis and it was confirmed that the necessary signal-to-noise ratios were still maintained in soil matrices with different interferences (high $C_{org}$ content or plant residues). For the other substances, only their presence/absence was qualitatively assessed via signal-to-noise ratios >3 and <3, respectively. Details on instrument conditions, quantification, method validation, and figures of merit are provided in Appendix (*1.3. Pesticide Extraction and Analysis*) and in Riedo et al. (2021).

## 2.5. Qualitative comparison of detected pesticide with the collected application data

Similar to Chiaia-Hernandez et al. (2017), we assessed the occurrences of the AI and TP in the soil samples and compared them to the application data reported by the farmers. For the qualitative analysis of the individual instances, meaning all possible combinations of substances and sites, four different cases were defined – case i: the pesticide was applied at the site and subsequently detected in the soil sample (true-positive), case ii: the pesticide was applied, but not detected later on (false-negative), case iii: no application of the pesticide is known, however, it was still detected (false-positive), and finally case iv: the pesticide was neither applied nor detected (true-negative). The categorization of TPs was done in relation to the (non-)application of their corresponding parent compounds.

## 2.6. Calculation of the predicted environmental concentrations and the observed half-lives

The dissipation of each substance was estimated for the quantitatively determined AI. For this, the detected concentrations in the soil samples were expressed as a percentage of the predicted environmental concentration (PEC), and the resulting observed half-lives ($DT_{50,obs}$) were approximated. First, the initial concentrations reaching the topsoil ($PEC_{soil,ini}$, [µg/kg]) after the last application was calculated according to eq. (1). To this end, the originally applied amount (App, [g/ha]) of the last known applications was considered. For the bulk density ($bd_{soil}$, [g/ cm$^3$]), the corresponding value per site was used. The relevant depth of the soil layer (d, [cm]) was assumed to be 20 cm (i.e., the standard plowing depth), and the fraction of the AI, which had been intercepted by plant cover ($f_{ini}$, [-]) was estimated to be 90%. This represents the worst-case scenario for most substances (except for herbicides applied prior to crop emergence) (Boesten et al., 2005). This chosen factor was considered the most realistic approach for pesticide applications in arable crops, whereas it might be more variable for permanent crops such as vineyards and orchards. Additionally to the $PEC_{soil,ini}$, the predicted environmental concentration of all applications (i, [-]) within the last 10–15 years prior to the sampling was estimated ($PEC_{soil,sum}$). A single first order (SFO) dissipation process was assumed between the applications, where the metabolic capacity of the degrading biomass

was expected to never be constrained (Kasteel et al., 2010). The $DT_{50,PPDB}$ values were taken from the Pesticide Properties DataBase (PPDB, Table S3) by using the geometric mean of the field-derived $DT_{50}$ values (University of Hertfordshire, 2020). If not available, the geometric mean of the laboratory $DT_{50}$ values was used. Afterward, the predicted concentrations of all applications (i, [-]) were added up according to eq. (2).

With the $PEC_{soil,ini}$, the measured concentration of the study $C_{soil,measured}$, and the time that had passed since the last application (t, [d]), the observed dissipation rate constant ($k_{obs}$, [1/d]) was calculated (eq. (3)). With this rate constant, the observed half-life ($DT_{50,obs}$) was then calculated according to eq. (4). This observed half-live was then set in relation to the half-life reported in the literature ($DT_{50,PPDB}$) to obtain a relative $DT_{50}$ value (eq. (5)).

$$PEC_{soil,ini} = \frac{10 * App * (1 - f_{ini})}{d * bd_{soil}} \tag{1}$$

$$PEC_{soil,sum} = \left( \sum_{i=1}^{n} \frac{10 * App_i * (1 - f_{ini})}{d * bd_{soil}} * e^{-\frac{\ln(2)}{DT_{50,PPDB}} * t_i} \right) + PEC_{soil,ini} \tag{2}$$

$$k_{obs} = -\frac{ln\left(\frac{C_{soil,measured}}{PEC_{soil,ini}}\right)}{t} \tag{3}$$

$$DT_{50,obs} = \frac{ln(2)}{k_{obs}} \tag{4}$$

$$relative\ DT_{50} = \frac{DT_{50,obs}}{DT_{50,PPDB}} \tag{5}$$

## 2.7. Visualization and statistical analysis

All statistical analyses were conducted using R version 4.2.3. (R Core Team, 2022). The visualization of individual pesticide concentrations was provided by heatmaps, generated using the levelplot function of the lattice package (Sarkar et al., 2020). Potential robust correlations between soil or substance parameters ($C_{org}$, clay, $K_{oc}$, Henry's law constant, etc.) potentially influencing for the occurrence and distribution of pesticides were tested using the *lmRob* and *step. lmRob* functions of the robust and robustbase packages (Wang et al., 2022; Maechler et al., 2022).

## 2.8. Potential limitations for data interpretation

To facilitate routine application to different soil types and (semi-) automated quantification of the multiple analytes of this multi-residue analytical method, the limit of quantification was set at 0.3 µg/kg for all substances, although quantification of some substances would have been possible below this limit in some soils. It is therefore possible that certain pesticides occasionally were present at very low concentrations but were not quantified. The number of substances present in individual sites could therefore be higher. In addition, the soils were stored for 9–13 years before analysis, and we cannot completely exclude changes in soil properties or analyte dissipation under the storage conditions mentioned above. Actual concentrations at the time of sampling might have been higher and consequently, the study does not show the worst-case scenario here either. Note however that the $C_{org}$ content determined by multiple analyses of one of our test soils was stable over several years (Figure S2) and the reanalysis of some soils after 8 years of storage resulted in comparable concentrations for all of the quantified pesticides (Figure S3). For details, see *1.4. Pesticide Stability during Sample Storage* in the appendix. Finally, it should also be noted that two of the investigated soils had $C_{org}$ contents above 10% (Table S7), which exceeded the validated range of the analytical method (3.9%; Riedo et al., 2021). As the $C_{org}$ content might influence pesticide sequestration and extractability (Schäffer et al., 2018), the quantified concentrations in

these two soils might not reflect true values.

## 3. Results and discussion

### 3.1. Pesticide applications within the monitoring sites

During the considered period of 10–15 years, pesticides were used at all sites under conventional agricultural management. Overall, 2647 AI applications took place in all sites, and according to the farmers' declarations they applied 4 to 47 AI per cropland site (median: 28). For orchards and vineyards, the number of different AI applied per site ranged from 13 to 31 and 15 to 29, respectively (median: 25 and 21, respectively). However, only 22% of all applications were covered by our analytical method, which included 34 AI. Of the qualitatively assessed AI, 0 to 13 were applied at individual cropland sites (median: 5). For orchards and vineyards, the number of assessed AI, which were applied per site, ranged from 1 to 7 and 3 to 8, respectively.

The broader range of pesticides used in cropland sites compared to orchards and vineyards was expected since various crops are cultivated at these sites, usually within a crop rotation of 6–8 years, whereas orchards and vineyards represent permanent cultures. Different crops require treatments with different pesticides, while a smaller number of pesticides is used repeatedly in permanent cultures. In addition, the number of applied pesticides varied strongly between the individual cropland sites. For the 3 cropland sites under organic management, no applications of synthetic pesticides were reported.

### 3.2. Qualitative comparison of the application and occurrence of pesticides

Most of the analyzed substances (i.e., 30 of 34 AI and all 7 TP) were found in one or more soil samples. Deisopropylatrazine, 2-hydroxyatrazine, atrazine, carbendazim, cyprodinil, imidacloprid, metamitron, napropamide, and propiconazole were the substances most frequently detected, while fluopicolide, fluopyram, fluxapyroxad, and fipronil were not detected in any of the studied soil samples (Figure S4). The detection pattern was mostly as expected: Imidacloprid, for instance, is rather

persistent (DT50 > 160 days) and is thus assumed to remain in the soils for longer periods, while fluopicolide, fluopyram, and fluxapyroxad are AIs that have only been recently approved for use and were not applied at any of the sites before soil sampling. Generally, in all sites - also the organically managed ones - residues were detected, whereby the number of different substances detected per site varied from 1 to 25 (median = 11). With the complete pesticide application history of the last 10–15 years prior to sampling, the qualitative occurrence of AI and TP in the soil samples (1271 instances from 31 sites and 41 analyzed substances) could be assigned to one of 4 cases (Figure S4).

For 195 of these instances, the farmers reported the application of a measured AI. The applied AI were detected for 146 of them, leading to true-positive results (case i - applied and detected, Fig. 1). Thus, for around 3 out of 4 instances where a pesticide was applied, the corresponding AI was still present in the soil at the date of sampling. Most case i instances were found in c22, c4, and c12, which were all cropland sites. An important factor, influencing the detection frequency of case i instances, is the time lag between the application and the soil sampling. As this is known for our dataset, it allowed an assessment of the dissipation of the AI in these case i sites. This will be discussed further below.

For the other 49 instances with a pesticide application, the AI was not detected anymore (case ii, false-negative). The proportion of instances differed strongly between the individual substances and soils (Fig. 1). For the sites c19 and c20, as well as the AI isoproturon and trifloxystrobin most case ii instances could be found. For these AI, the reported $DT_{50}$ values are rather short (Table S3). Thus, it seems reasonable that these substances had been degraded during the time from the application until the soil sampling (Figure S5, A and C). For half of the case ii instances, the application dates back more than 5 years, and over 100 half-lives had passed (Figure S5, B and D). These instances could thus also be considered as true-negative and could consequently be assigned to case iv. Correlations between management parameters, soil properties, or substance properties, responsible for the occurrence and distribution of the cases i and ii in the sites or substances were tested, however, revealed no conclusive information (data not shown).

For 1076 instances the farmers reported no application of the respective substance, however, AI or TP were detected in 215 of these
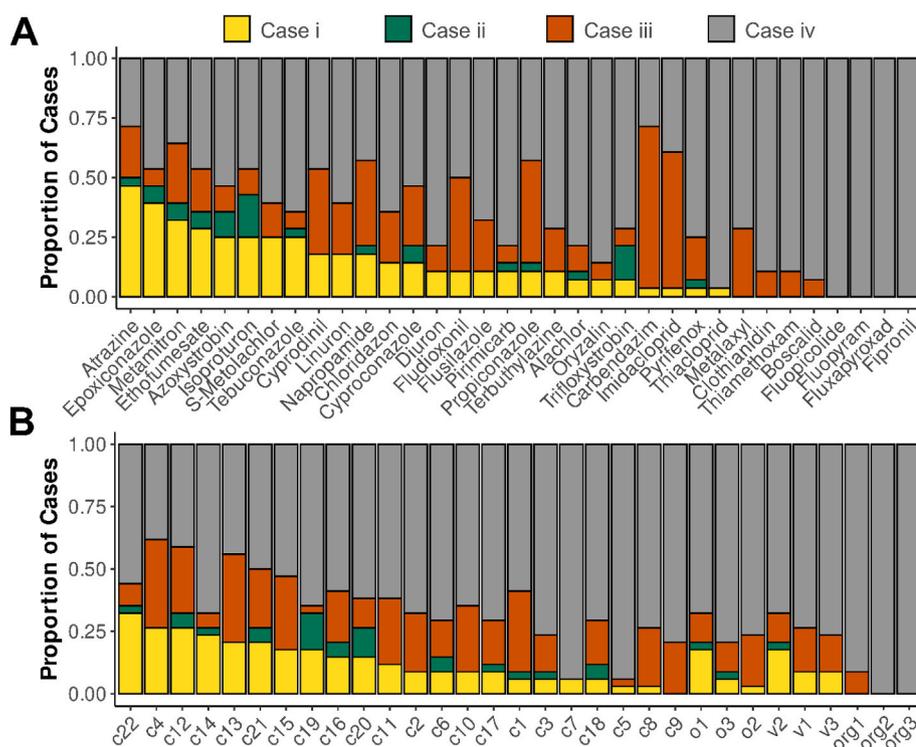


**Fig. 1.** Stacked bar plots showing the proportional distribution of the 4 cases of pesticide application-detection in soil (case i: applied-detected, case ii: applied-not detected, case iii: not applied-detected, case iv: not applied-not detected) for: **(A)** the respective active ingredients or transformation products (n each substance = 31, corresponding to the number of sites). **(B)** Each site (c = croplands, o = orchards, v = vineyards, and org = organically managed croplands; n each site = 34, corresponding to the number of active ingredients considered).

soils (case iii, false-positive). This corresponds to 17% of all instances, which is considerably less than the 38% reported by Chiaia-Hernandez et al. (2017). The detected concentrations for the case iii instances were within the same range as the case i concentrations (Figure S6). It is noticeable that case iii instances are particularly frequent for carbendazim, imidacloprid, propiconazole, fludioxonil, cyprodinil, metalaxyl, and napropamide (Fig. 1A, Figure S4). For these AI, the case iii instances exceeded the sum of instances found for cases i and ii. The occurrence of these false-positive cases can potentially be explained by unreported applications, applications before the records started, application of a substance whose TP is one of the analyzed AI, or contamination through other pathways. Examples of residues from unreported applications could be the detection of substances such as imidacloprid, fludioxonil, cyprodinil, and metalaxyl, which are also approved in Switzerland as seed coating (Wettstein et al., 2016). This is often not considered a classical pesticide application and therefore may have been neglected in the reporting of the farmers, as we did not specifically ask about it. The pesticide input via treated seed can reach levels comparable to a spray application on a field, as more than 90% of the applied amount enters the soil directly (Jones et al., 2014). Additionally, residues of applications prior to the considered period (1996–2009) might still be detectable. This could be the case for substances that were registered for application for multiple decades in Switzerland, such as carbendazim, metalaxyl, propiconazole, and napropamide. Carbendazim is moreover a TP of thiophanate methyl or benomyl and the detected concentrations may have resulted from their degradation. However, also no such applications were reported on the corresponding sites. Further input pathways could be drift from nearby applications, supply by surface runoff from neighboring plots, or atmospheric deposition. Previous studies showed that the detection of metalaxyl could potentially be explained by the repeated input through precipitation over the years, as its concentration in rainwater is accordingly high (Riedo et al., 2022). The sites c1, c4, c13, and c15 were the ones with the highest number of occurrences of case iii instances, however, no correlations could be found with site characteristics or management parameters that would explain this reduced dissipation at these sites, which is responsible for the limited availability of the residues for degradation or leaching from soils (data not shown). Also in all fields under organic management, in which no applications have taken place for extended periods (15–75 years), case iii instances could be found. All 3 sites contained residues of 2-hydroxyatrazine and the sample from the field converted most recently from conventional to organic agriculture additionally contained traces of boscalid and epoxiconazole (Figure S6). Concerning input pathways, atmospheric deposition is most likely not the reason for the concentrations of the atrazine TP 2-hydroxyatrazine, as it has been shown that the atrazine concentrations solely deposited by precipitation are not high enough to cause such concentration levels (Riedo et al., 2022). For boscalid and epoxiconazole, Décuq et al. (2022) showed that wet deposition could be a possible source of the concentrations measured in soil. However, since not all 3 sites exhibited these residues, this seems to be only the case on a local level, or the source of the substances must have been a different one.

The last case includes instances in which the investigated AI was neither applied nor detected (case iv, true-negative). This applies to 861 of the total 1271 instances, and thus explained the majority of the instances (68%). Case iv was the only case for the substances fluopicolide, fluopyram, fluxapyroxad, and fipronil (Fig. 1A). Regarding sites, only in one site (c7) solely true cases (case i or case iv) could be detected (Fig. 1B). During the 15 years prior to sampling, this site was mostly managed as grassland and thus only received comparably few pesticide treatments during the single season where it was used for wheat growing, potentially explaining this finding.

### 3.3. Detected residue concentrations and quantitative comparison to other studies

The AI and TP, for which an ILIS was used allowed for additional, quantitative analysis. The quantified concentrations for each site and each substance are listed in Table S8. The resulting concentrations strongly differed for individual substances and ranged from 0.3 µg/kg to 430 µg/kg (median = 1.3 µg/kg). For certain substances, individual sites stand out with comparably high concentrations, for example for tebuconazole (max = 170 µg/kg), diuron (max = 160 µg/kg), linuron (max = 79 µg/kg), and carbendazim (max = 61 µg/kg, Fig. 2). These elevated concentrations are in line with corresponding documented applications shortly before sampling. As for the sites, the two sites c4 and c13 had higher concentrations than the others. These sites are peat soils with high soil $C_{org}$ content, which is known to retain contaminants in the soil for longer periods of time, limiting their degradation (Spark and Swift, 2002). Also, the concentrations of the most frequently detected substances – atrazine, imidacloprid and carbendazim - correlated with the content of $C_{org}$ (Figure S7). In addition to $C_{org}$, other physicochemical properties, such as pH or clay content, and climatic conditions measured at the sampling site, such as mean annual precipitation or temperature, were considered to explain the concentrations, but no trend was observed (Figure S7).

The concentrations of the individual substances reported here (0.30 µg/kg to 430 µg/kg, median = 1.3 µg/kg) are generally at the lower end of published data for agricultural soils in Switzerland and various regions in Europe (0.094 µg/kg to 330 µg/kg, median = 2.0–20 µg/kg, Table S9). In direct comparison to the concentrations from earlier Swiss studies, which used a similar or the same method for the AI quantification, Chiaia-Hernandez et al. (2017) found values ranging from 0.70 µg/kg to 330 µg/kg (median = 9.7 µg/kg). These higher concentrations might be explained by a higher fraction of soils from specialty crops, such as vineyards and orchards, which correspondingly have higher application rates and frequencies of the same pesticides (Federal Office for Agriculture, 2022b). Riedo et al. (2021) reported very similar concentrations (0.094 µg/kg to 230 µg/kg, median = 2.0 µg/kg). The direct comparison with results from other European countries is more complicated, as in these studies different soil layers were sampled and other analytical methods, with different extraction methods, quantification limits, and substance choices, were used (Kosubová et al., 2020; Silva et al., 2019). For instance, since the limit of quantification employed here was 0.3 µg/kg, as opposed to 10 µg/kg (Silva et al., 2019) and 3 µg/kg to 10 µg/kg (Kosubová et al., 2020), most of the concentrations detected in this study were below the limit of quantification of the other studies. Those concentrations that were above these higher limits of quantification were in the same range.

### 3.4. Proportion of pesticide residues remaining in soil over time

In addition to the separation of residues into different cases, the application data allows estimations about the dissipation of the individual substances. For this, only substances out of case i, which were quantitatively determined, were considered. The detected concentrations in the soil samples were expressed as a percentage of the $PEC_{soil,ini}$ right after application (see methods for calculations, eq. (1)). This percentage was then related to the period between the last application before sampling and the sampling itself, expressed in terms of the number of $DT_{50}$ values elapsed for the respective AI (Fig. 3, for a zoom on the lower figure part see Figure S8). For this, the absolute duration in days was divided by the respective geometric mean $DT_{50}$.

Since the AI from the most recent application experienced the least dissipation and thus accounts for the majority of detected concentrations, only this input was considered instead of all applications in the 10–15 years prior to the sampling. The calculations of the PECs were conducted including all recorded applications within the last 10–15 years instead of only the last application before sampling ($PEC_{soil,sum}$,
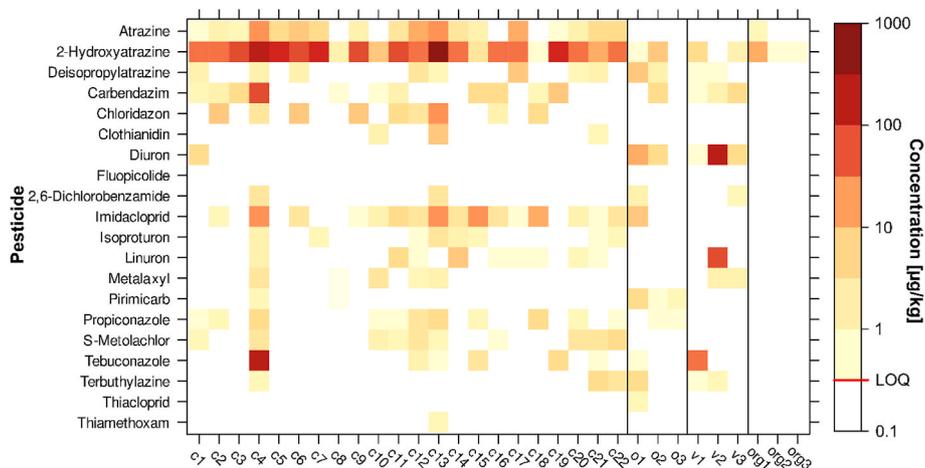
**Fig. 2.** Concentrations of 20 active ingredients (AI) and transformation products (TP) quantified with isotope-labeled analogous internal standards in the croplands (c), orchards (o) vineyards (v), and organically managed croplands (org). Each row represents an AI or TP and each column is one site. The color range represents the level of the quantified concentrations, whereas empty (white) cells indicate concentrations below the limit of quantification (<LOQ), which was 0.3 µg/kg.
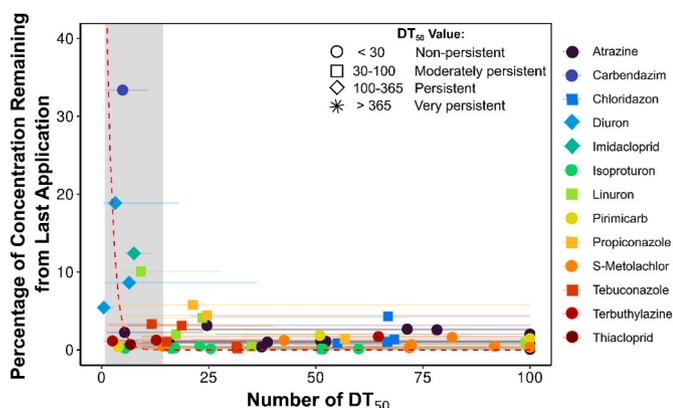


**Fig. 3.** Percentage of the most recent application of an active ingredient (AI) remaining in the soil as a function of time elapsed between application and sampling, expressed as the number of $DT_{50}$ evolved for each AI. The x-axis is cropped at $100 \times DT_{50}$, and observations with an even longer time span (up to $2400 \ DT_{50}$) are shifted to $100 \times DT_{50}$. The horizontal lines display the number of $DT_{50}$ values resulting from using the respective minimum and maximum $DT_{50}$ values taken from the Pesticide Properties Database (PPDB) (University of Hertfordshire, 2020). As long as these lines intersect the red, dashed line, a single first-order dissipation cannot be excluded *a priori*. The shape of the points indicates different $DT_{50}$ categories. The red, dashed line indicates an assumed single first-order dissipation, and the grey area specifies the range of the number of $DT_{50}$ values (0.75–14) that passed in the 120 days considered during the registration of a new AI (Boesten et al., 2005). For a zoom on the lower figure part see Figure S8.

see methods for calculations, eq. (2)). The corresponding plot qualitatively looks very similar to the one shown in Fig. 3 and only differed in that the initial application quantity was slightly larger and thus the remaining percentage differs by 1–2%, the pattern, however, remained the same (Figure S9). While most concentrations detected in the soils represented only a few percent of the most recent application, in some instances more than 5% was still present in the soil with a maximum of more than 35% (Fig. 3).

Laboratory soil incubation experiments to derive dissipation rates and $DT_{50}$ values conducted according to the OECD test guideline No. 307 (OECD, 2002), are usually carried out over a period of 120 days, as requested e.g. in the European pesticide authorization process. $DT_{50}$ values for substances, which are not degraded to 50% of the initial concentration after this time are extrapolated beyond the study duration

(Boesten et al., 2005). Depending on the half-life of the AI included in this study, these 120 days correspond to a range of around 0.75 to 14 × $DT_{50}$ values (geometric mean, PPDB) (University of Hertfordshire, 2020). Most of the elevated residue concentrations (>5% of $PEC_{ini}$) lay within the duration of this range. Beyond this time, no observations exceeded 10%. Therefore, we consider the end of this range as the division of the observations into two phases; a dynamic phase and a long-term residue phase.

During the first phase, elevated concentrations of AI and TP are observed as a result of pesticide applications followed by a decrease. During the second phase, some of the extractable amounts of AI and TP seemed to be stabilized at a few percent of the initial concentration (Fig. 3). The cessation of the dissipation at a later stage, leading to this continuous residue concentration, violating the assumption of an SFO dissipation, could be due to physico-chemical processes limiting the abiotic and biotic degradation, therefore, resulting in longer persistence of the AI in soil (Schäffer et al., 2022). Further temporal interpretation of the results is complicated by the fact that soil samples were taken at different time points within the year and in different years, hindering the comparison between sites. Furthermore, for the majority of the instances (77%) presented in this study, the most recent application was reported more than one year prior to sampling, and for 25% of case i instances, the time between application and sampling even exceeded 5 years (Figure S5, C), leading to incubation periods that spread over different seasons and consequently complicate the analyses.

### 3.5. Observed concentrations compared to the probable dissipation rate

While the retrospective exposure assessment of this study confirms that small amounts of AI and TP rated as persistent build temporally stable residue levels, which are detectable in soils for years, it also shows that substances, which are not regarded as persistent, can form long-term residue concentration as well. Of the applied and detected substances (case i, true-positive) chloridazon, diuron, and tebuconazole fall into the above-mentioned category of persistent compounds (moderately persistent $DT_{50} = 30$–100 days, persistent: $DT_{50} = 100$–365 days) However, Fig. 3 shows that a residual amount of a few percent can be found regardless of the classification of substances according to their half-life values (indicated by the shapes of the data points).

Therefore, we took a closer look at the residual concentrations in light of their probable dissipation rates. To this end, we estimated the $DT_{50}$ values for our observations ($DT_{50,obs}$, see methods for calculations, eqs. (3)–(5)) by assuming an SFO dissipation (Kasteel et al., 2010). For compounds and sites, for which the time between application and

sampling lay within the above-determined phase 1 ($0.75-14 \times DT_{50}$, geometric mean, PPDB) (University of Hertfordshire, 2020), the observed $DT_{50}$ fell mostly within this predicted range (Fig. 4, pink symbols). For imidacloprid, the AI with the highest $DT_{50}$ values of the displayed substances, the observed $DT_{50}$ exceeded the maximum of the reported $DT_{50}$. In contrast, the observed $DT_{50}$ fell below the minimum of the reported $DT_{50}$ for pirimicarb, the AI with the lowest $DT_{50}$. Apart from one observation for diuron, the observations for the other AI were within the predicted range. Therefore, the simple SFO model, with a soil unspecific $DT_{50}$, seems capable of explaining the decrease of AI residual concentrations during the dynamic phase. For compounds, for which the period between application and sampling was longer than 14 $DT_{50}$ (phase 2, geometric mean, PPDB; Fig. 4, dark green symbols) (University of Hertfordshire, 2020), only AI with relatively long half-lives (e.g. tebuconazole) were within the predicted range. For all other AIs the assumption of an SFO and its extrapolation beyond 14 times the $DT_{50}$, which is the case for most AI (Figure S5 D), does not seem suitable (European Food Safety Authority, 2014).

## 4. Conclusions

In this work, we compared the occurrence and concentrations of pesticides in agriculturally managed soils to an extensive pesticide application history. With this knowledge about pesticide application in the last 10–15 years prior to sampling, we were able to demonstrate that at almost all sites pesticides occurred even though no application had been reported. Furthermore, small residual mass fractions (2%–8% of the initial application) of several AI and TP, commonly considered as non- or only moderately persistent, were found in the soil even years after their last recorded application. This might point to an environmental concern not covered during the current prospective risk assessment. Therefore, a retrospective long-term exposure assessment of pesticides complementary to the evaluation during registration seems mandated. Thus, the presented work advocates for the introduction of an iterative process that combines the already mandatory prospective risk assessment of pesticides with additional soil monitoring in real agricultural practice. In this way, dissipations of newly approved pesticides can be followed and their use and application rates can potentially be adjusted if they appear in soils for longer than accepted. This retrospective exposure assessment should contain periodical analyses, as well as analyses that account for seasonal variability of residues. Further, it should include the exact application times of pesticides in the planning process, to make sites better comparable among each other. In addition, individual fields should be monitored over a longer period and for a larger range of commonly used pesticides, going beyond single product and single crop assessment, which is currently used (Topping et al., 2020).

## Author statement

RM, AG, and DW conceived and designed the study. FEW conducted the analyses. DW, AG, and JR performed the data analyses. JR wrote the manuscript with substantial contributions from DW, AG, and TDB; all authors edited the manuscript.

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## 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.
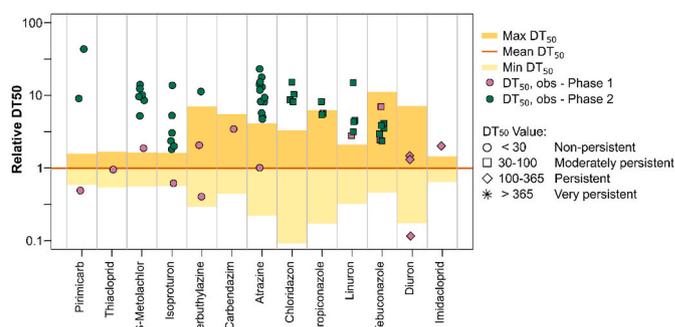


**Fig. 4.** Observed $DT_{50}$ values of pesticides in soil, assuming a single first-order dissipation, relative to the reported mean $DT_{50}$ value from the Pesticide Properties Database (PPDB) (University of Hertfordshire, 2020). The estimations are separated according to the two identified phases (phase 1: $<14 \times DT_{50}$, phase 2: $>14 \times DT_{50}$). Minimum, mean, and maximum $DT_{50}$ reported by PPDB are displayed as reference ranges. The active ingredients (AI) were ordered according to their increasing half-life.

## Data availability

Data will be made available on request.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2023.121892.

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