

# Pesticide Residues in French Soils: Occurrence, Risks, and Persistence

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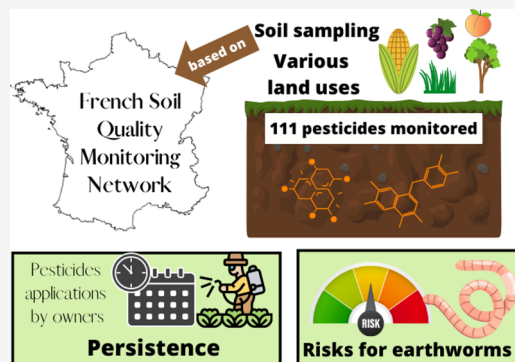
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**ABSTRACT:** Contamination of the environment by pesticide residues is a growing concern given their widespread presence in the environment and their effects on ecosystems. Only a few studies have addressed the occurrence of pesticides in soils, and their results highlighted the need for further research on the persistence and risks induced by those substances. We monitored 111 pesticide residues (48 fungicides, 36 herbicides, 25 insecticides and/or acaricides, and two safeners) in 47 soils sampled across France under various land uses (arable lands, vineyards, orchards, forests, grasslands, and brownfields). Pesticides were found in 98% of the sites (46 of the 47 sampled), including untreated areas such as organic fields, forests, grasslands, and brownfields, with up to 33 different substances detected in one sample, mostly fungicides and herbicides. The concentrations of herbicides were the highest in soils with glyphosate, and its transformation product, AMPA, contributed 70% of the cumulative herbicides. Risk assessment underlined a moderate to high risk for earthworms in arable soils mostly attributed to insecticides and/or acaricides. Finally, the comparison with pesticide application by farmers underlines the presence of some residues long after their supposed 90% degradation and at concentrations higher than predicted environmental concentrations, leading to questions their real persistence in soils.

**KEYWORDS:** herbicides, fungicides, insecticides, soil monitoring, contamination, glyphosate, earthworms, persistence



## 1. INTRODUCTION

Pesticide use is the base of modern agriculture, with more than 2.7 million tons of active substances applied worldwide in 2020 and an increase of 50% since the 1990s, leading to 1.8 kg/ha applied on cropland each year. France is the largest consumer of pesticides in Europe<sup>1</sup> and the seventh largest country in the world in terms of total pesticide use, reaching 65 000 tons in 2020. This intensive use of pesticides raises concerns about their environmental fate and the resulting impacts on ecosystems. Although pesticides have been widely monitored in water through the European water framework directive,<sup>2</sup> limited literature has presented pesticide residues in soils.<sup>3–8</sup> Recent studies conducted mostly on arable soils have reported the widespread occurrence of multiple pesticide residues. In addition, some studies showed a substantial risk for soil organisms and concentrations above the predicted environmental concentrations.<sup>9–11</sup> However, few studies have underlined the presence of pesticides long after their application, questioning the persistence of these substances in agricultural practice.<sup>12</sup> Consequently, there is a deep need for the assessment of pesticide residues in soils at broad scale under multiple land uses, including a comparison with application records to better highlight substances that should be monitored.

In this study, 110 active substances and one transformation product were measured in 47 sites sampled across France as a part of the ongoing French soil quality monitoring network (RMQS), already including the analysis of soil characteristics (C, N, texture, etc.)<sup>13,14</sup> and some contaminants (trace elements and persistent organic pollutants).<sup>15</sup> The selected sites included mostly arable lands, vineyards, and orchards and also forests and permanent grasslands. The targeted pesticides were currently used or recently banned substances. This pilot study aimed to evaluate the need to monitor pesticide residues in French soils and the applicability of monitoring them on a broad scale.

The objectives of this work were (1) to assess the occurrence of pesticide residues in French soils regarding land use, (2) to evaluate the impact of pesticides on earthworms (*Eisenia fetida*) based on cumulative risk assessment, and (3) to compare the results to application data and

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predicted environmental concentrations to assess the persistence of those substances in soils.

## 2. MATERIALS AND METHODS

**2.1. Sampling Sites and Procedure.** A total of 47 sampling sites were selected from the list of sites collected in 2019 and 2020 by the RMQS.<sup>16</sup> The sampling strategy of the RMQS is based on a regular grid of 16 km × 16 km, and approximately 180 sites are sampled each year.

Conditioned Latin Hypercube Sampling (cLHS)<sup>17</sup> was used to define a subset of samples representative of the marginal distribution based on soil characteristics (see the detailed procedure in Figure S1). As the study objectives were mostly focused on cultivated soils, a majority of soils under arable lands, vineyards, and orchards were selected: 29 sites, one site, and three sites, respectively. Five forests and six permanent grasslands were also selected and considered as “controls” because they should not have received pesticides for a long time. Finally, three brownfields previously cultivated were also selected (Table S2).

The soils were sampled in 2019 and 2020. Most of the samples (33 of 47) were collected during late autumn and winter periods (October to March). The 14 remaining sites were sampled throughout the spring and summer periods (see Table S2). At each site, in a 20 m × 20 m grid, 25 core samples of topsoil (0–20 cm) were taken. The core samples were bulked to obtain a composite sample stored at −20 °C before pesticide analysis at Bordeaux University. An aliquot was directly sent from the field within 2 days to the INRAE Laboratory of Soil Analysis (LAS) in Arras, France, in charge of the physicochemical analyses.

Agricultural and forestry practices were collected from the owners during the year following sampling through a questionnaire. The survey included crop rotations and pesticides applied at least throughout the year before sampling (see section 1 of the Supporting Information and Table S2).

**2.2. Physicochemical Analysis.** Physicochemical parameters were analyzed by the LAS, which is a certified laboratory for analysis of soil parameters. The soil was air-dried at ambient temperature and sieved at 2 mm before analyses of particle size fractions, pH, total C, N, and P concentrations, CaCO<sub>3</sub> content, CEC, and exchangeable cations that were determined according to international reference methods. The detailed analysis and reference methods are reported in the Table S1 along with the results for each sample (Table S2).

**2.3. Substance Selection.** The active substances were selected by the French Agency for Food, Environmental and Occupational Health & Safety (i.e., ANSES) based on the amount of usage (from the national database of pesticide sales<sup>18</sup>), toxicity to both soil organisms (earthworms) and humans,<sup>19</sup> mobility in the environment, occurrence in soils according to the literature studies, and analytical determinability. A total of 110 active substances and one transformation product were selected (Table S3), mostly pesticides currently authorized in Europe or recently banned, including 48 fungicides, 36 herbicides, 25 insecticides and/or acaricides, and two safeners. The selection focused on active substances, but considering the current concern about glyphosate by public authorities, its main transformation product AMPA was integrated in the final list.

**2.4. Pesticide Analysis.** All analyses were performed at Bordeaux University (EPOC-LPTC, UMR 5805 CNRS),<sup>20</sup>

and the detailed analysis protocol is reported in the section 3 of the Supporting Information.

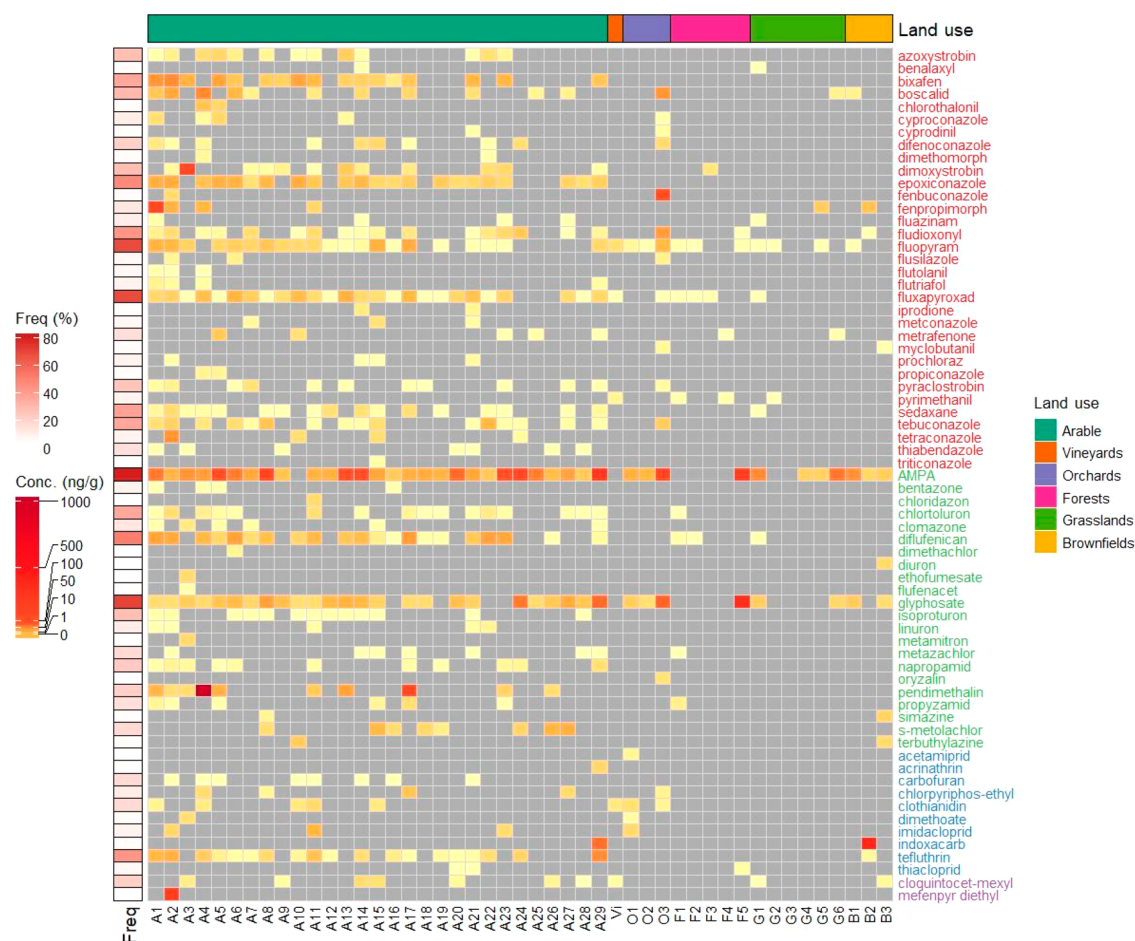
Each soil sample was freeze-dried at −40 °C, sieved at 2 mm, and ground in a ball mill. Hydrophilic and polar substances were extracted from 300 mg of a soil sample using methanol prior to microwave-assisted extraction for 15 min and centrifugation for 15 min at 3000 rpm. A 5 mL volume was then evaporated to 1 mL, diluted in ultrapure water (UP), and acidified to pH 2 (HCl). Solid phase extraction was then performed on Oasis HLB SPE cartridges (60 mg, 3 cm<sup>3</sup>) conditioned with methanol and acidified UP water to pH 2. The analytes were eluted with 3 mL of MeOH, and the solute was then concentrated under a nitrogen flux to a final volume of 300 μL. A 100 μL aliquot was directly injected into the HPLC-MS/MS instrument for determination. A second 100 μL aliquot was then evaporated to dryness under a nitrogen flux and diluted with 100 μL of dichloromethane (DCM) for GC-MS/MS determination.

Hydrophobic substances were extracted from 1 g of a soil sample by microwave extraction using 15 mL of DCM for 15 min. The extract solutions were then filtered and evaporated using a Rapid Vap vacuum evaporation system to a final volume of 2 mL. The solutions were then concentrated to a volume of 300 μL under a nitrogen flux before analysis using GC-MS/MS.

Extraction of glyphosate and its product of transformation AMPA was performed using 10 mL of KOH (0.6 M) before ultrasound extraction for 30 min and centrifugation for 15 min at 3500 rpm. The soil samples were adjusted with HCl to pH 9 and derived for 30 min in the dark with 300 μL of sodium borate (5%) and 500 μL of FMOC-Cl (6.5 M). The derivation was stopped with 50 μL of formic acid, concentrated under a nitrogen flux, and filtered at 0.2 μm before analysis by HPLC-MS/MS.

Pesticides were analyzed by high-performance liquid chromatography coupled to a quadrupole mass spectrometer (HPLC-MS/MS) and gas chromatography coupled to a triple quadrupole mass spectrometer (GC-MS/MS). Analyses by HPLC-MS/MS were performed with a reversed phase instrument using acetic acid or formic acid and methanol as mobile phases. The separated substances were then ionized by an electrospray source in positive or negative mode before detection by the quadrupole mass spectrometer. Glyphosate and AMPA were analyzed by reversed phase HPLC using Milli-Q water and acetonitrile. All of the quality assurance/quality control (QA/QC) data, including quantification limits and recovery, are reported in section 3.5 of the Supporting Information and Table S9.

**2.5. Risk Assessment.** The eco-toxicological risk induced by pesticides in soils was assessed on the basis of threshold values of chronic toxicity [i.e., non-observable effect concentration (NOEC)] for earthworms (*E. fetida*) collected from the “Pesticides Properties DataBase”<sup>21</sup> (<https://sitem.herts.ac.uk/aeru/ppdb/en/index.htm>). Risk assessment was performed by calculating individual risk quotients (RQ<sub>i</sub>) as ratios of concentrations of each substance in soils and the associated predicted non-effect concentration (PNEC). The PNEC values were computed by dividing NOEC values by an assessment factor of 10 adapted from instructions from the Environmental Risk Assessment Guidance published by the European Commission.<sup>22</sup> A cumulative risk assessment was then calculated by summing the individual RQ<sub>i</sub> of every substance to calculate a total risk quotient (RQ<sub>T</sub>). The obtained RQ<sub>T</sub>



**Figure 1.** Individual pesticide concentrations in nanograms per gram of the 67 residues detected in the sampling sites. Levels of the concentration range are displayed in the cells at the center of the heat map, and gray filling indicates an absence of quantification of the substance (i.e., <LOQ). Rows represent pesticides arranged by category (red, fungicides; green, herbicides; blue, insecticides and/or acaricides; purple, safener). Columns represent sampling sites arranged by land use, with each land use type being reported at the top of the heat map. The left column represents the detection frequency of pesticide residues in percent. The values indicated at the bottom correspond to sampling site identification numbers used by the French soil quality monitoring network.

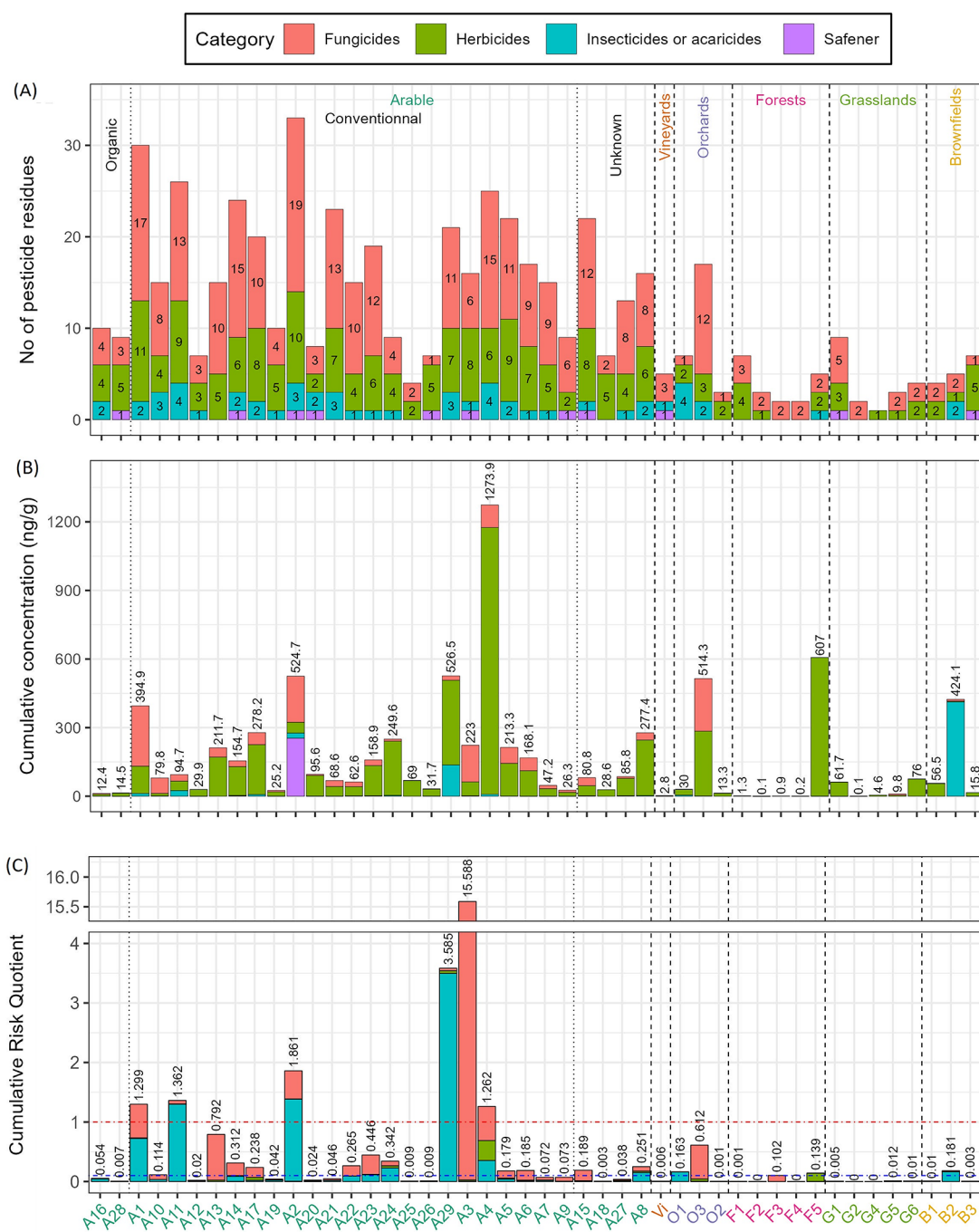
values were then classified into four categories: negligible risk ( $RQ_T < 0.01$ ), low risk ( $0.1 > RQ_T > 0.01$ ), medium risk ( $1 > RQ_T > 0.1$ ), and high risk ( $RQ_T > 1$ ).<sup>9,11</sup>

Predicted environmental concentrations ( $PEC_{max}$ ) were calculated on the basis of the pesticide applications recorded during the survey conducted with the farmers. Application rates of pesticide mixtures (in kilograms per hectare or liters per hectare) were indicated in 94% of the total applications. For the remaining missing application rates, the maximum recommended dose of the pesticide mixture for the ongoing culture was attributed. Those latest values were collected from the national database of pesticides (<https://ephy.anses.fr>). Among all of the doses of pesticides applied by the farmers, <5% were above the recommended dose. Calculations of the initial concentration ( $C_i$ ) of individual pesticides in soils in nanograms per gram were performed considering a soil depth of 20 cm and a soil density of  $1.5 \text{ g cm}^{-3}$ . The  $PEC_{max}$  in soils calculated at the sampling date can be considered as the “worst-case scenario” of predicted concentrations. We used degradation times of 90% and 50% of the substance to estimate the maximized levels of concentrations that could be found in soils if the delay between treatment and sampling was superior to those theoretical times. In this case, we avoid a possible

underestimation of predicted concentration calculated using degradation kinetic models determined in laboratories under controlled conditions. Three cases were considered. (1) When the delay between pesticide application (PA) and soil sampling was superior to  $DT_{90}$ , the  $PEC_{max}$  value considered was  $C_i$  after 90% degradation (i.e.,  $0.1C_i$ ). (2) When the PA delay was between  $DT_{50}$  and  $DT_{90}$  (or there was no  $DT_{90}$ ), the  $PEC_{max}$  value considered was  $C_i$  after 50% degradation (i.e.,  $0.5C_i$ ). (3) When the PA delay was under  $DT_{50}$ , the  $PEC_{max}$  value considered was  $C_i$ .

**2.6. Statistical Analyses.** Pesticide residues were considered as not detected when values were under the LOQ and concentrations were set to 0 for cumulative risk assessment and statistical analyses. All statistical analyses were performed using R version 4.1.3<sup>23</sup> and the package *stats*.<sup>24</sup> A Wilcoxon test was used to assess differences between cultivated and noncultivated areas for the risk assessment, the occurrence of residues, and the sum of pesticide concentrations. The difference between sampling month for pesticide number and cumulative concentrations was assessed with a Kruskal–Wallis test. Pairwise correlations between pesticide occurrence (values of 1 when detected and 0 when not detected) and soil properties were performed with the *cor* function (package *stats*) based on





**Figure 2.** (A) Number of pesticide residues detected, (B) cumulative concentrations in nanograms per gram, and (C) total risk quotient at each site displayed by usage category and organized by land use. Farming practices for arable lands (i.e., Arable) reported in the survey are indicated in black. “Unknown” indicates that the survey could not be conducted.

the Spearman’s rank correlations and plotted with the *corrplot* package.<sup>25</sup> Bar plots and box plots were displayed using the *ggplot2* package<sup>16</sup> and the *heatmap* with the *ComplexHeatmap* package.<sup>27</sup>

### 3. RESULTS AND DISCUSSION

**3.1. Occurrence of Pesticides.** The results demonstrated a widespread occurrence of pesticides in almost all of the soils, as 46 of the 47 sampling sites contained at least one substance in the topsoil layer. The only site where none of the 111 targeted substances was quantified (i.e., <LOQ) has been a site under permanent grassland since 1965. The concentrations of

pesticide residues in soils are summarized in Figure 1. A total of 67 different substances were detected. Fungicides were the most frequent showing a detection rate (DR) of 69%, followed by herbicides (DR of 61%) and insecticides (DR of 40%). Finally, the two safeners measured in the soil samples were both detected.

The most detected pesticide was AMPA, found in 83% of the soil samples, followed by glyphosate (DR of 70%). Fluopyram, fluxapyroxad, and diflufenican were detected in 69%, 68%, and 51% of the sites, respectively. Sixteen substances showed a DR between 20% and 50%, and 33 substances were detected in <10% of the sites (i.e., four sites).

Detailed statistical results of pesticide residue detection can be found in Table S10.

These results are supported by recent studies in which pesticide residues were detected in almost all of the soil samples collected from agricultural lands<sup>4–6</sup> or permanent grasslands and hedgerows.<sup>9</sup> Eighty-three percent of the 47 soils sampled contained more than three pesticide residues against approximately 60% of the agricultural soils from the European monitoring network LUCAS<sup>4</sup> and of arable soils from the Czech Republic.<sup>5</sup> Many studies have reported DR values of >60% of the initial targeted substances.<sup>5,6,9</sup>

Several substances widely found in agricultural soils have been highlighted in recent research with similar DR values (Table S12). The high occurrence of glyphosate and AMPA has been reported in arable soils collected in Europe<sup>28</sup> or western France.<sup>10</sup> Other herbicides (e.g., diflufenican, chlortoluron, isoproturon, napropamid, and pendimethalin) and fungicides (e.g., fludioxonil, boscalid, azoxystrobin, pyraclostrobin, and triazole substances) have been highlighted in several studies across Europe with comparable DR values.<sup>3–6,9,12,29</sup> Higher DR values would have been expected for imidacloprid, clothianidin, s-metolachlor, simazine, and terbuthylazine on the basis of the frequencies reported in studied sites from Switzerland,<sup>6,12</sup> France,<sup>9</sup> Spain,<sup>8,30–33</sup> and Portugal.<sup>30,34</sup> Conversely, this study revealed the widespread occurrence of fluopyram, fluxapyroxad, and dimoxystrobin that were detected in 69%, 68%, and 28% of the soils, respectively (Figure 1), compared to <5% of monitored soils reported in Switzerland<sup>6</sup> (for fluopyram and fluxapyroxad) and the Czech Republic<sup>5,29</sup> (for dimoxystrobin). Finally, tefluthrin, sedaxane, and propyzamid found in 43%, 38%, and 15% of the soils, respectively, have never been reported in the world soil monitoring literature to the best of our knowledge,<sup>3</sup> except for tefluthrin mentioned in one study on the urbanized area of the Pearl River Delta (China)<sup>35</sup> (Tables S12 and S16).

Individual pesticide concentrations ranged from 0.01 to 1115 ng g<sup>-1</sup>, and the maximum concentration was reached by pendimethalin (Figure 1 and Table S10). Mefenpyr-diethyl presented the highest mean concentration, reaching 254 ng g<sup>-1</sup> ( $n = 1$ ), followed by indoxacarb [246 ng g<sup>-1</sup> ( $n = 2$ )], pendimethalin [135 ng g<sup>-1</sup> ( $n = 10$ )], fenbuconazole [63 ng g<sup>-1</sup> ( $n = 2$ )], and AMPA [61.2 ng g<sup>-1</sup> ( $n = 39$ )]. The most detected substance, AMPA, ranged from 3.1 to 287 ng g<sup>-1</sup>, and glyphosate ranged from 1.1 to 365 ng g<sup>-1</sup>, with a mean value of 35 ng g<sup>-1</sup>. AMPA and glyphosate also presented the widest range of concentrations from <1 to >200 ng g<sup>-1</sup>, whereas other substances reached a maximum of 50 ng g<sup>-1</sup> (see Table S10). Seventeen substances presented a mean concentration in soil of >5 ng g<sup>-1</sup>, and nine substances among them were detected in >20% of the sites (i.e., 10 sites). Among the fungicides, fenbuconazole presented the highest mean concentration of 63 ng g<sup>-1</sup> ( $n = 2$ ), followed by fenpropimorph (n = 5; mean value of 35 ng g<sup>-1</sup>). The mean concentrations of bixafen, dimoxystrobin, boscalid, and epoxiconazole ranged from 8 to 15 ng g<sup>-1</sup>, with maximum values of 56.1, 138, 57, and 23.6 ng g<sup>-1</sup>, respectively.

Similar ranges of pesticide concentrations have been reported in the literature,<sup>3</sup> reaching 2050 ng g<sup>-1</sup> in agricultural soils from Europe<sup>4,28</sup> and ~1000 ng g<sup>-1</sup> in arable soils sampled in Switzerland<sup>6</sup> and western France,<sup>9</sup> attributed to glyphosate, diflufenican, and azoxystrobin, respectively. Lower values have been reported for agricultural soils from the Czech Republic<sup>5,29</sup> and Spain,<sup>8,32</sup> showing maximum concentrations of <500 ng

g<sup>-1</sup>. However, higher concentration ranges for individual substances such as AMPA, glyphosate, epoxiconazole, tebuconazole, and boscalid were observed in arable soils from Europe,<sup>4,28</sup> reaching 1920, 2050, 160, 190, and 410 ng g<sup>-1</sup>, respectively. Those higher values could be due to soil sampling throughout the year in the latest study, including close to pesticide treatments, which was not the case in our study (Table S2).

**3.2. Influence of Land Use.** The number of pesticide residues quantified per site varied from 1 to 33 with a median value of nine substances, and the total cumulative concentration varied from 0.08 to 1274 ng g<sup>-1</sup>. The detailed results are reported in Figure 2.

Soils under arable farming were the most contaminated, with a median of 15 pesticide residues detected, ranging from 4 to 33. Almost all of the soils from arable lands contained at least seven residues (i.e., 28 sites of the 29 sampled). The mean cumulative concentration varied from 12.4 to 1274 ng g<sup>-1</sup> (Figure 2B). Five substances were detected in the vineyard soil collected during the study with a total concentration of 2.8 ng g<sup>-1</sup>. The number of detected residues in the three orchard soils ranged from 3 to 17, with large differences in cumulative concentrations varying from 13.2 to 514 ng g<sup>-1</sup> and a mean cumulative concentration of 186 ng g<sup>-1</sup>. Pesticide occurrence could not be explained by either soil characteristics or sampling period. No effect of the sampling period was observed on the number of pesticide residues or the cumulative concentration (Table S2 and Figure S5). No correlations between pesticide detection and soil properties were found for “cultivated soils” (arable lands, vineyards, and orchards) and “uncultivated lands or grasslands” [forests, brownfields, and permanent grasslands (Figures S6 and S7)].

The low pesticide concentrations of <3 ng g<sup>-1</sup> measured in the vineyard (Figure 2B) could result from soil sampling in April, probably before most of the applications of pesticides to the plot. This hypothesis is supported by the high variability of pesticide concentrations ranging from below the LOQ to >400 ng g<sup>-1</sup> in vineyard sites in Spain<sup>8</sup> attributed to both sampling period and location. For orchard sites, the lowest detection rate and cumulative concentrations reported at the O2 site (Figure 2) might be attributed to permaculture management since 2018 and the absence of recent pesticide application. The contamination of orchard sites O1 and O3 under conventional management was similar to that of orchard soils collected in Switzerland<sup>12</sup> and Spain.<sup>7</sup>

This difference in the number of pesticide residues and cumulative concentrations between “cultivated soils” (arable lands, vineyards, and orchards) and “uncultivated lands or grasslands” (forests, brownfields, and permanent grasslands) was statistically significant [ $p < 0.05$ , Wilcoxon (Figures S3 and S4)]. Those results were comparable to those of the literature studies with an average of 10–20 pesticide residues found in agricultural soils in Switzerland<sup>6,12</sup> and with a larger number of substances in arable lands despite lower rates of application of pesticides compared to vineyards and orchards. Similar total cumulated concentrations were measured in European agricultural soils,<sup>4</sup> reaching 2870 ng g<sup>-1</sup>, in Swiss arable soils,<sup>6</sup> showing a median value of approximately 100 ng g<sup>-1</sup> and a maximum of 1170 ng g<sup>-1</sup>. Soils under arable lands collected in the Czech Republic<sup>5,29</sup> presented maximum values of approximately 300 ng g<sup>-1</sup>.

Two sites under organic farming management since 2010 and 2018 contained fewer pesticide residues [i.e., 9 and 10

substances (Figure 2)] than sites under conventional farming (median of 16 pesticide residues). The most significant difference could be observed in the total cumulative concentrations of 14.5 and 12.4 ng g<sup>-1</sup> measured in soils under organic management compared to a median value of 155 ng g<sup>-1</sup> ( $n = 23$ ) in soils under conventional farming. Similar results were found in soils from organic fields in Switzerland,<sup>6</sup> Spain,<sup>7</sup> and France<sup>9</sup> also presenting fewer residues and lower concentrations.

Thirteen different substances were found in soils from forests and grasslands that were supposed to be untreated. Forests were contaminated by two to seven residues and grasslands by one to nine pesticide residues, mainly fungicides and herbicides. Fluopyram ( $n = 6$ ), AMPA ( $n = 5$ ), and fluxapyroxad ( $n = 4$ ) were the most frequent pesticides. Total cumulative pesticide concentrations were <2 ng g<sup>-1</sup> for forest soils except for F5, reaching 607 ng g<sup>-1</sup>, which was attributed to high concentrations of AMPA and glyphosate. The total cumulative concentrations measured under grasslands ranged from 0.1 to 76 ng g<sup>-1</sup> (mean value of 30.4 ng g<sup>-1</sup>). Four to seven pesticide residues and 13 different substances were detected in the three brownfields, presenting a total cumulative concentration varying from 15.8 to 424 ng g<sup>-1</sup> (mean value of 165 ng g<sup>-1</sup>). Brownfields B1 and B2 were arable lands until 2018 and 2010, respectively, and B3 was a vineyard until 2013. Surprisingly, the most contaminated site was the oldest uncultivated site (B2).

The major hypothesis for pesticide contamination of uncultivated lands could be the proximity of treated fields, as two of the five forests (i.e., F1 and F2) were located near arable lands and the most contaminated brownfield (B2) was close to a vineyard. The high level of contamination by glyphosate of forest site F4 could be due to pesticide applications in an oak stand overhanging the sampling site. Nevertheless, the two remaining forests were surrounded by grasslands and forests, suggesting other factors influencing soil contamination such as long-range atmospheric transfer induced by adverse atmospheric conditions as evidenced in South American forests<sup>36,37</sup> or the “hopping” effect (i.e., multiple deposition and volatilization of a substance).<sup>38,39</sup>

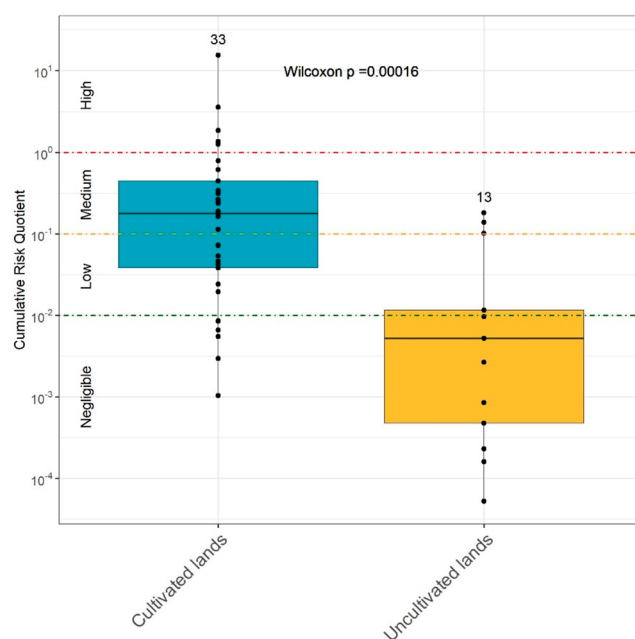
Some pesticides have been reported in forest soils from Switzerland;<sup>40</sup> however, those were mostly banned pesticides such as DDT. Studies of South American forests reported the significant contamination of forest soils attributed to air pollution and transfer from treated areas. Our results on grassland soil contamination by pesticide residues were similar to results reported in agricultural soils sampled in France<sup>9</sup> and Switzerland,<sup>12</sup> with means of 7.5 substances and 5 substances detected, respectively.

In terms of cumulative concentrations, herbicides were the major contributors to the total pesticide concentration (Figure 2 and Figure S8). The largest contributions were reported for indoxacarb [median of 56% ( $n = 2$ )], followed by AMPA [median of 49% ( $n = 39$ )] and Pyrimethanil [median of 46% ( $n = 4$ )]. Fenbuconazole, simazine, s-metolachlor, terbuthylazine, glyphosate, bixafen, and pendimethalin presented median contributions between 5% and 12% of the total concentrations. Consequently, the cumulative contributions of AMPA and its parental molecule glyphosate reached a median value of 63% ( $n = 40$ ) of the total concentration of pesticide residues in soils (Figure S8).

**3.3. Risk Assessment.** Risk assessment conducted on soil samples revealed a nonnegligible risk for soil organisms

induced by pesticide residues at many sites, with a total RQ<sub>T</sub> reaching 15.6 in arable land (Figure 2C). Among the 47 sites considered, six sites presented high risk with RQ<sub>T</sub> values of >1 (i.e., 13%); all were arable lands under conventional management. The total risk quotient indicated a medium risk (i.e., between 0.1 and 1) for 14 sites, including two forest soils, and pesticide residues induced a low risk (i.e., RQ<sub>T</sub> between 0.1 and 0.01) for nine sites. Consequently, the total content of pesticide residues posed a medium or high risk in 43% of the soils collected. Insecticides or acaricides and fungicides contributed the most to the cumulative risk quotient. The highest risks were obtained for dimoxystrobin, reaching an RQ<sub>i</sub> of 15.5 ( $n = 1$ ), and tefluthrin, showing RQ<sub>i</sub> values of 3.4 and 1.2, in two arable soils under conventional management. The highest median RQ<sub>i</sub> values were attributed to imidacloprid [median of 0.16 ( $n = 4$ ) (Figure S9)], indoxacarb [median of 0.08 ( $n = 2$ )], dimoxystrobin [median of 0.08 ( $n = 13$ )], tefluthrin [median of 0.04 ( $n = 20$ )], and difenoconazole [median of 0.03 ( $n = 10$ )]. The major contribution of triazole compounds and insecticides such as imidacloprid to the cumulative risk has been evidenced in a French arable landscape soil study.<sup>9</sup>

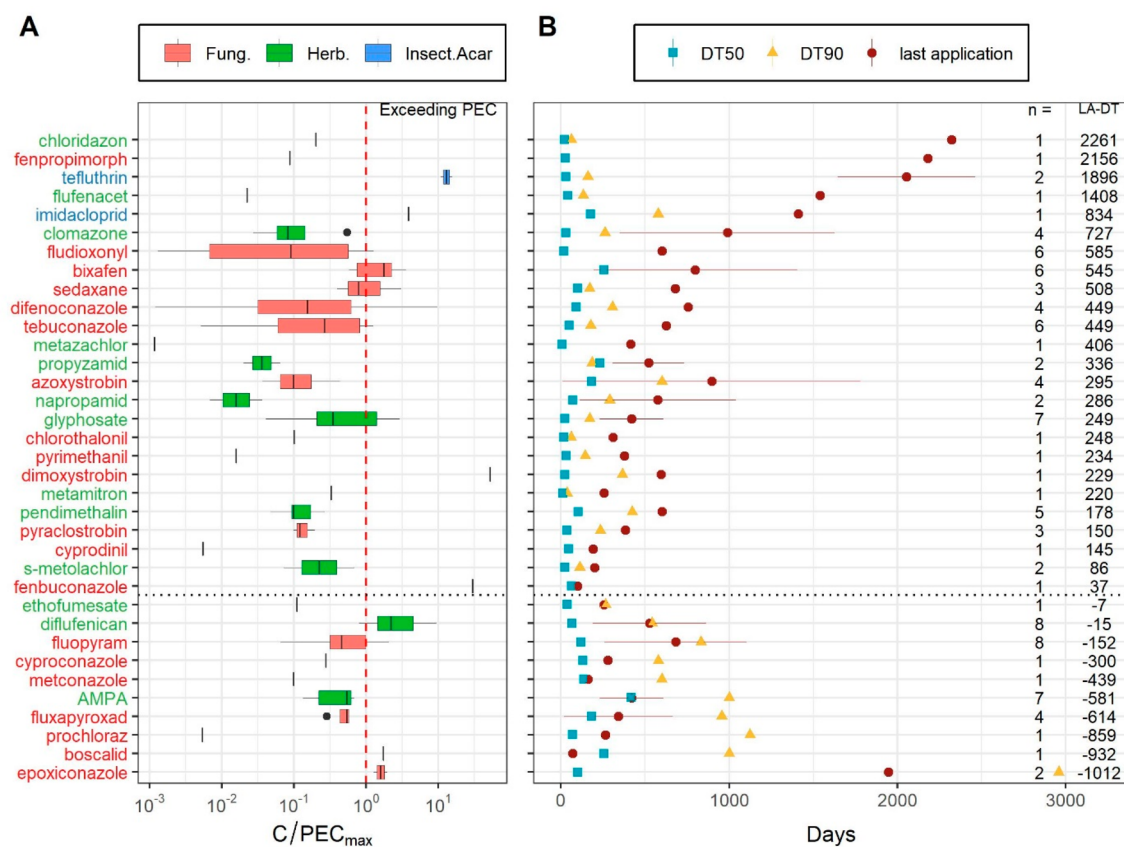
The pesticide mixture induced higher risks in soils under “cultivated lands” (i.e., arable lands, vineyards, and orchards) than in soils under “uncultivated lands”, including forests, brownfields, and permanent grasslands, as shown in Figure 3.



**Figure 3.** Cumulative risk quotient calculated by site displayed by land use group along with the number of values considered and the risk category for earthworms (i.e., negligible, low, medium, or high risk).

Most of the soils under uncultivated lands displayed a negligible or low risk for earthworms (76%), while 58% of the soils under cultivated lands showed a medium to high risk. All of the high risks concerned soils under arable lands. The medium risks obtained for soils under uncultivated lands were observed in two forest soils and a brownfield soil. Almost all of the total pesticide residues found in grasslands posed a negligible risk for soil organisms.





**Figure 4.** (A) Ratios of measured pesticide concentrations in soils and  $PEC_{max}$  and (B) comparison of the delay between the last pesticide application and soil sampling with the theoretical degradation times  $DT_{50}$  and  $DT_{90}$ . In panel B, the number of sites is reported (i.e.,  $n$ ), as well as the difference in days between the mean value of the last application delay and the theoretical degradation time ( $DT_{90}$  or  $DT_{50}$  when  $DT_{90}$  is missing) displayed as “LA – DT”. For panels A and B, the group of pesticides above the dotted black line showed a last application delay longer than the theoretical degradation time (i.e., LA – DT > 0). The residues displayed under the black dotted line were applied closer to the sampling date and within the delay of theoretical degradation (i.e., LA – DT < 0).

The risk assessment performed by Pelosi et al. in 2021<sup>9</sup> on agricultural soils in western France reported similar results with a higher rate of arable lands in the high-risk class, reaching 85% and a mean  $RQ_T$  of 10 for conventional farming ( $n = 48$ ) against 20% in our study and a mean  $RQ_T$  value of 4.2 ( $n = 6$ ). In the same study, grassland soils showed the lowest risks, with 75% of them in the medium- and low-risk classes, whereas 10% of the 60 sites fell in the negligible-risk class. The lower risks found in our study could be due to soil sampling far from pesticide application, mostly during winter, when sampling was conducted in spring by Pelosi et al. In addition, a sampling depth of 5 cm could explain the higher concentrations in this latest study<sup>9</sup> as pesticide residues tend to concentrate in the top centimeters of soils and dilution could occur in deeper samples of 0–20 cm, which we used in our study. Finally, the risk assessment conducted was based on NOEC values for one species of earthworm (i.e., *E. fetida*) not considered to be the most sensitive for toxicity assessment.<sup>41,42</sup> Therefore, such results question the real risk for other earthworms species and other soil organisms that can bioaccumulate pesticides and be severely affected by cocktail effects of pesticides.<sup>43</sup>

### 3.4. Comparison with Application and $PEC_{max}$ .

Information about targeted pesticide applications collected from the owners reported a total of 232 applications of 61 different substances in the 21 sites with a survey on agricultural practices. In addition, numeric records from field practice

software were provided by seven farmers, some of whom gave numeric records of pesticide application since 2011. A total of 2 to 35 pesticides were applied by site with two to eight substances for vineyards and orchards [mean of 5 ( $n = 3$ )] and 3–35 pesticides for arable lands [mean of 12 ( $n = 18$ )]. Pesticides were either reported to be applied or detected in soils in 485 cases (see Figure S10). The presence of pesticides was confirmed in 21% of the cases, but in 27% of the cases, substances were not detected despite a reported application (Figure S10 and Table S13). Seventeen substances were never detected when applied (Table S13), including lambda-cyhalothrin, applied 11 days before sampling in an arable site and not detected despite a  $DT_{50}$  of 27 days. In 52% of the cases, pesticides were detected in soils but were not reported as applied in at least one site, including 19 substances that were never reported as applied. In the sites with numeric records, 39 pesticide residues were detected but never indicated as applied, and 16 of those substances showed a  $DT_{90}$  of <400 days (Table S15). Dimoxystrobin, AMPA, boscalid, epoxiconazole, and fluxapyroxad were detected but not reported applied in sites showing long-term records (back to 2015 at least). Isoproturon, napropamid, pyraclostrobin, and sedaxane showed  $DT_{90}$  values of <1 year but were detected at four sites where no application was reported. However, the presence of some substances such as thiabendazole, linuron, and metrafenone, detected in seven, four, and four sites,

respectively, could be attributed to ancient application, which is supported by their long degradation times, which reach 55 000 days ( $DT_{90}$ ) for metrafenone. In monitored agricultural soils from Switzerland,<sup>12</sup> pesticides were detected despite no reported application in 38% of the cases.

Maximized predicted environmental concentrations ( $PEC_{max}$ ) were compared to the measured concentrations through the  $C/PEC_{max}$  ratio, as shown in Figure 4A. The  $PEC_{max}$  values correspond to the highest concentrations that could be found in soils under the “worst-case scenario” of pesticide degradation based on theoretical degradation times [i.e.,  $DT_{50}$  and  $DT_{90}$  (see section 2.5)]. Consequently,  $C/PEC_{max}$  ratios of  $>1$  would indicate that pesticide concentrations were measured in soils at rates much higher than expected on the basis of the information (application date and dose) reported by the farmer. The  $C/PEC_{max}$  ratio ranged from  $1.2 \times 10^{-3}$  to 52 with a median value of 0.32 for a total of 101 values. The  $PEC_{max}$  in soils was exceeded for 14 pesticide residues (Figure 4A) in 14 different sites [i.e., 67% of the 21 sites with completed surveys (Table S14)]. Diflufenican and bixafen exceeded  $PEC_{max}$  values in the largest number of sites (i.e., at six and four sites, respectively). The 12 remaining pesticides showed concentrations higher than the  $PEC_{max}$  values at one or two different sites. The highest mean  $C/PEC_{max}$  ratios were reported for dimoxystrobin ( $n = 1$ ), fenbuconazole ( $n = 1$ ), and tefluthrin ( $n = 2$ ), with mean values of 52, 30, and 13, respectively (Figure 4A). Imidacloprid ( $n = 2$ ), diflufenican ( $n = 8$ ), and difenoconazole ( $n = 4$ ) showed concentrations up to 9 times the  $PEC_{max}$  in soils with mean ratios of 3.8, 3.6, and 2.5, respectively. Bixafen ( $n = 6$ ), boscalid ( $n = 1$ ), epoxiconazole ( $n = 2$ ), and sedaxane ( $n = 1$ ) showed mean  $C/PEC_{max}$  ratios of  $\sim 1.5$ . In the literature, residues such as diflufenican, boscalid, epoxiconazole, and imidacloprid showed concentrations exceeding the  $PEC$  in some French soils.<sup>9</sup>

The delays between the last pesticide applications indicated in the surveys were compared to the theoretical degradation times ( $DT_{90}$  and  $DT_{50}$ ) for 35 different substances, as shown in Figure 4B. Ten substances showed application delays within the range of degradation time, explaining their occurrence in soils. Among those 10 substances, diflufenican, epoxiconazole, boscalid, and fluopyram showed concentrations above the  $PEC_{max}$  highlighting the presence of those substances at rates higher than expected. In addition, nine of those 10 substances show  $DT_{90}$  values of  $>500$  and  $\leq 3000$  days (i.e., 8 years) for epoxiconazole, which are higher than those of the rest of the  $DT$  substances reported in Figure 4.

Twenty-five pesticides were detected after their theoretical degradation (Table S16). Among them, 18 substances showed concentrations under the  $PEC_{max}$  despite their detection long after the theoretical degradation times, such as chloridazone, fenpropimorphe, and flufenacet detected between 1400 and 2200 days after their  $DT_{90}$  delay. Seven residues, including tefluthrin, imidacloprid, bixafen, sedaxane, and difenoconazole, were detected between 400 and 1900 days after  $DT_{90}$  (except for bixafen, for which  $DT_{50}$  was considered) and presented measured concentrations  $\leq 15$  times the  $PEC_{max}$  values (Table S16). Dimoxystrobin was found at a concentration of 52 times the calculated  $PEC_{max}$  in a soil that was sampled 229 days after the  $DT_{90}$  of this substance. Glyphosate was detected approximately 250 days ( $n = 7$ ) after the  $DT_{90}$  delay, with two measured concentrations exceeding the  $PEC_{max}$  values. These results are supported by literature studies, as 45% of the

applied pesticides were detected in agricultural soils from Switzerland<sup>12</sup> long after their application despite their short dissipation half-life ( $<1$  year). If the persistence of some substances such as tefluthrin and fenbuconazole could be explained by their low mobility in soils attributed to a high  $K_{foc}$ , this is not the case for most of the other substances such as dimoxystrobin, imidacloprid, and difenoconazole, which are considered slightly to moderately mobile in soils (Table S16 and Figure S11). Finally, several substances highlighted in this study as potentially overly persistent, including bixafen, sedaxane, tefluthrin, and fenbuconazole, have been poorly or not even monitored in soils to the best of our knowledge<sup>3</sup> (see Table S16).

**3.5. Main Insights.** The widespread occurrence of pesticide residues in almost all of the sampled soils, including organic fields and nontreated areas such as forests and permanent grasslands, exposes the knowledge gap on the dispersion of pesticides in the environment. Several pesticides, such as glyphosate, AMPA, pendimethalin, diflufenican, triazole compounds, boscalid, prochloraz, and imidacloprid, already highlighted in the literature, were confirmed as frequent and highly concentrated compounds. The high number of residues of  $\leq 35$  compounds questions the risk induced by those cocktails of molecules for soil biodiversity, given the first results of simple cumulative risk quotients for arable lands. Finally, the presence of those residues long after their application and their theoretical degradation at rates above the predicted concentrations in soils raises concerns about their persistence in the environment under real agricultural practices, especially considering that some substances highlighted in this study have never been targeted in major literature studies<sup>3</sup> (see Tables S12 and S16). The results advocate for the integration of pesticide residue in soil monitoring at national scales and a revision of homologation procedures to ensure the accurate persistence of pesticides under real farming practices. Furthermore, those substances should be considered in the construction of the future regulations on soil protection and particularly the European Soil Health Law currently being discussed.<sup>44</sup>

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.2c09591>.

A detailed description of the statistical procedure for the selection of studied sites along with their characteristics, chemical characteristics of all targeted substances, detailed analysis protocols and QA/QC, and several additional tables and figures based on the results (PDF)

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### Author Contributions

C.J., A.B., N.P.A.S., and C.F. designed and coordinated the study, including soil sampling based on the French Soil Quality Monitoring Network coordinated by C.J. and A.B. H.B. and M.P. conducted pesticide analysis, and G.C. the analysis of physicochemical parameters of soil samples. C.F. wrote the first draft of the manuscript with subsequent contribution of all of the authors, including D.A.

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### Notes

The authors declare no competing financial interest.

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### ABBREVIATIONS

RMQS, French Soil Quality Monitoring Network; LOQ, limit of quantification; DR, detection rate; PEC, predicted environmental concentration; DT<sub>50</sub> and DT<sub>90</sub>, 50% and 90% degradation times, respectively; NOEC, non-observable effect concentration; RQ, risk quotient.

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