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# Widespread Occurrence of Pesticides in Organically Managed Agricultural Soils—the Ghost of a Conventional Agricultural Past?

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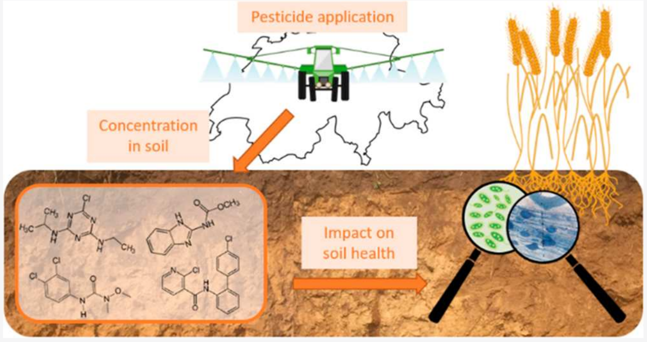
**ABSTRACT:** Pesticides are applied in large quantities to agroecosystems worldwide. To date, few studies assessed the occurrence of pesticides in organically managed agricultural soils, and it is unresolved whether these pesticide residues affect soil life. We screened 100 fields under organic and conventional management with an analytical method containing 46 pesticides (16 herbicides, 8 herbicide transformation products, 17 fungicides, seven insecticides). Pesticides were found in all sites, including 40 organic fields. The number of pesticide residues was two times and the concentration nine times higher in conventional compared to organic fields. Pesticide number and concentrations significantly decreased with the duration of organic management. Even after 20 years of organic agriculture, up to 16 different pesticide residues were present. Microbial biomass and specifically the abundance of arbuscular mycorrhizal fungi, a widespread group of beneficial plant symbionts, were significantly negatively linked to the amount of pesticide residues in soil. This indicates that pesticide residues, in addition to abiotic factors such as pH, are a key factor determining microbial soil life in agroecosystems. This comprehensive study demonstrates that pesticides are a hidden reality in agricultural soils, and our results suggest that they have harmful effects on beneficial soil life.



**KEYWORDS:** *Multiresidue analysis, herbicides, fungicides, insecticides, organic farming, no tillage, environmental impact, soil ecology*

## INTRODUCTION

Pesticides constitute an integral part of modern agriculture and contribute to the control of weeds, plant diseases, and pests. Over the past two decades, the use of pesticides has increased over 40%, and currently, over 4.1 million tons are used worldwide each year.[1] Despite their benefits for crop yield, the intensive and widespread use of pesticides raises environmental concerns due to the contamination of natural resources.[2] Depending on their application, only a minor fraction of the applied pesticides reaches their targets,[3] with the rest (30 to 50%) ending up on the soil surface and thereafter getting dispersed through several abiotic processes including volatilization, wind erosion, leaching, or runoff.[4]

The occurrence of pesticide residues in agricultural soils has been reported in a limited number of recent studies.[5−7] To date, it has been poorly investigated whether pesticides are also present in soils where they have not been applied, such as soils under organic management. One study compared residues of currently used pesticides in agricultural soils under conventional and organic management, considering five neonicotinoid insecticides.[8] However, broad scale investigations of various groups of pesticides (e.g., fungicides, herbicides, and insecticides) in organically managed soils are missing. Testing this is of great importance, as pesticide residues of past agricultural management or contamination from conventional fields could especially affect organic agriculture. Organic agriculture relies more on healthy soils that are capable of sustaining ecosystem services than systems under different management practices, such as conventional management where external inputs (e.g., synthetic pesticides and fertilizers) are allowed.[9] It is therefore important to know how long pesticides persist in those organically managed agricultural soils and whether they threaten soil health, which is indispensable for these sustainable systems.

Pesticides, i.e. their active ingredients, and their transformation products (TPs) are known to pollute aquatic

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environments[10] and to impact aquatic communities.[11] In terrestrial systems they have directly and indirectly been linked to decreasing bird, insect and pollinator populations.[12−15] Studies in model systems with individual pesticides on single organisms further showed that specific pesticides constitute a threat to soil microorganisms,[16] which drive pivotal soil processes such as carbon and nutrient cycling.[17] In the field, studies tested effects of individual pesticides, such as for example the herbicide nicosulfuron,[18] on soil microorganisms. They showed that these individual pesticides negatively affected microbial biomass as well as arbuscular mycorrhizal fungi (AMF) by inhibiting enzyme pathways and eventually stopping protein production. As soil life provides a wide range of ecosystem services and influences ecosystem multifunctionality,[19,20] these deleterious effects of pesticides on beneficial soil life could thus potentially affect soil health,[21] which is crucial for agricultural production.[22] The influence on AMF is of particular interest, as these fungi engage in symbiotic associations with the majority of land plants, including many crops. They provide nutrients and other services to plants in return for carbohydrates.[23,24] Up to 80% of the plant's phosphorus requirements can be contributed by AMF pointing to their importance for plant nutrition. AMF further provide a number of ecosystem services such as the promotion of soil structure and aggregation and the reduction of nutrient losses through leaching and denitrification.[25] While many studies looked into effects of individual pesticides in model or field studies, those on farm studies that link the occurrence of multiple pesticides to soil life, such as AMF, are missing so far. Therefore, it is still poorly understood whether pesticides in soil act as potential stressors for soil life under farm conditions and how it is affected by the amount of pesticide residues.

Here we provide a comprehensive overview of the presence and abundance of 46 widely applied pesticides (16 herbicides, 8 herbicide TPs, 17 fungicides, and 7 insecticides) in soils of 100 agricultural fields, including 40 under organic management. The following four objectives were addressed: (i) Sixty arable and 40 vegetable fields were compared and it was assessed whether management systems (conventional, conventional without soil tillage (no-till), and organic management) influenced the occurrence of pesticides. (ii) Further, it was investigated whether the duration of organic management affected the occurrence and concentration of pesticides in the soil. (iii) We also evaluated whether soil characteristics influenced the occurrence of pesticide residues and (iv) additionally tested whether the occurrence of pesticide residues detected in this on farm study are linked to indicators of soil life (soil microbial biomass and respiration as well as the abundance of AMF).

## ■ METHODS

**Study Sites and Soil Sampling.** *Arable Farming.* Soil samples from 60 agricultural sites with different management systems (conventional tillage, conventional without soil tillage, and organic) were sampled in early May 2016 for an on-farm study throughout Switzerland.[26] The farmlands were distributed equally in two sampling areas in the northeast and southwest of Switzerland with 20 sites per management system. The conventional fields implemented soil tillage (20−25 cm depth) and usually applied synthetic fertilizers and pesticides. The no-till cropping systems were managed without soil tillage and with use of synthetic fertilizers and pesticides. Both farming systems followed the 'Proof of Ecological Performance' guidelines from the Swiss Federal Office for Agriculture.[27] The organic fields did not apply synthetic pesticides and synthetic fertilizers, applied tillage (20−25 cm depth), and were managed according to the guidelines of the Federation of Swiss Organic Farmers.[28] Winter wheat was seeded in all fields the year before. All soils were characterized as Cambisols and varied in soil texture, elevation, and mean annual temperature. However, none of these parameters differed significantly between farming systems.[26] The median soil characteristics are listed in Table S2 of the Supporting Information (SI).

Details on each farm's agricultural management were collected directly from the farmers through a questionnaire about management practices applied on the selected field in the last five years (for details see Büchi et al.[26]). Management indices for the degree of plant diversification and soil disturbance as well as amount of mineral fertilizer and organic amendments applied could be deducted from the survey. The farmers further provided an overview of the pesticides applied throughout the year before sampling.[26]

Soil sampling and processing were performed as described by Banerjee et al.[29] and Büchi et al.[26] Twenty soil cores (4 cm diameter) were collected over two transects of 20 m length. To reduce the risk of contamination from neighboring fields a 20 m buffer zone from the field edge was maintained. The 20 cores were mixed and pooled to obtain a representative sample. Due to the high degree of stratification in soils without tillage, the top 5 cm of the soils were sampled representing the most exposed soil layer. Soil samples were processed by removing plant materials, homogenization, and sieving (2 mm). Until further analysis, the samples were stored at −20 °C.

*Vegetable Farming.* The vegetable farming network consisted of 40 fields (20 under conventional and 20 under organic management) in eastern Switzerland. The soils were also characterized as Cambisol. The organic and conventional systems were managed as described above. The median soil characteristics are listed in SI Table S2. Information on each farm's agricultural management practices, such as the duration for which the organic sites were managed organically, were collected directly from the farmers through a questionnaire.

Soil samples from the vegetable fields were taken in December of 2016 and were part of a different field study with a slightly different sampling regime. Ten soil cores were randomly collected at each site. The cores were then immediately mixed and pooled to obtain a representative sample for each field. Samples were kept on ice and transported to the laboratory where they were sieved (5 mm) and stored at −20 °C until further analysis. As all vegetable fields were frequently ploughed, a sampling depth of 10 cm has been chosen. Consequently, the sampling depth between arable and vegetable sites differed.

**Physicochemical Soil Analyses.** The soil physicochemical properties, organic C, texture, pH, and soil nutrients (N, K and P), were determined according to the Swiss reference methods of the Federal Agricultural Research Station.[30] Organic C was determined with the Walkley−Black method. The texture was analyzed with a pipetting method with clay <2 μm, silt 2 to 50 μm, and sand >50 μm as cut-offs, and pH was determined in water. The total nitrogen was determined with the Dumas method. Potassium was extracted with 0.5 M ammonium acetate−EDTA solution at pH 4.65. Total P was extracted by washing the soil sample and using 0.6 M HCl as extractant. Potassium and total P were only measured for the arable fields.[30]

**Selection of Analyzed Pesticides.** The analyzed synthetic pesticides were selected by the Swiss Soil Monitoring Network taking into account their analytical determinability,[7] the amount and frequency of usage, the expected amounts in soil based on the predicted environmental concentrations, and estimations by experts in the field. All 46 chosen substances, including 38 parent substances and 8 TPs (SI Table S1), are modern pesticides, which are designed to be less persistent and more easily biodegradable than previously used pesticides such as for example organochlorines.[31,32]

**Sample Extraction and Analysis with LC-MS/MS.** Accelerated Solvent Extraction (Dionex ASE 350, Thermo Scientific) was used to extract the pesticide residues from the soil samples. Soil samples were thawed 2 h before extraction and were subsequently homogenized with a TURBULA (Bühler GmbH) for 15 min. Each 6 g ± 0.01 g of wet soil were weighed into an 11 mL stainless steel extraction cell, which was prefilled with 1 g of sea sand and topped with another 1 g of sea sand. Two glass fiber filters (Whatman GF/F) covered the top and the bottom of the cell. The soil was extracted twice: in a first step, an organic mixture of acetone, methanol, and acetonitrile at a ratio of 65:10:25 (% v/v) was used, and in a second, acidic step, the soils were extracted with a mixture of acetone and 1% phosphoric acid in Millipore water at a ratio of 70:30 (% v/v). Detailed information on extraction parameters such as temperature and pressure are provided in SI Table S3.

Due to the expected large concentration range of the pesticides in the soil samples, two different aliquots of each extract were processed. Two different volumes, 4 mL and 0.4 mL, of extract were evaporated under a gentle stream of compressed air down to 0.4 mL or down to dryness. Subsequently, the extracts were diluted to 1 mL with a mixture of Millipore water and methanol at a ratio of 90:10 (% v/v). A mixture of 23 isotopically labeled internal standards was spiked, and the samples were filtered through 0.20 $\mu$m PTFE filters (Fisher Scientific). Lastly, the samples were transferred into HPLC-vials.

Pesticides were analyzed by high-performance liquid chromatography coupled to a triple quadrupole tandem mass spectrometer (HPLC-MS/MS). Chromatographic separation was performed by reversed phase HPLC using water and methanol as mobile phase. The detection was performed after electrospray ionization with a triple quadrupole mass spectrometer (QTrap 5500, Sciex) in positive and negative ionization mode. All detected pesticide concentrations ($\mu$g/L) were converted into $\mu$g per kg of dry soil. Further details about the analytical method, quantification, and quality control can be found in the SI (Chapter 8. *Pesticide analysis in soils*).

**Root Sampling and Mycorrhizal Colonization.** Indicators of microbial soil life were only assessed in the arable sites, as they were sampled when an active agroecosystem with living roots was present (spring). Whereas the vegetable sampling campaign was conducted in wintertime during which not all sampled fields were growing vegetables and therefore had no active rhizosphere. The abundance of AMF in root and soil were determined as described by Banerjee et al.[29] Briefly, the root samples of 10 wheat plants per site were dug out, cut off 5 cm above the roots, and pooled in a plastic bag. Subsequently, the roots were cleaned with water and fine roots (<1 mm) were cut into pieces of about 1 cm and were thoroughly mixed. The mycorrhizal colonization was determined by an estimation of the abundance of arbuscules, hyphae, or vesicles. The abundance of AMF in soil was assessed by PLFA extraction followed by analysis on gas chromatography mass spectrometry.[33] We quantified the abundance of AMF in soil by using the PLFA 16:1$\omega$5, which is well regarded as a biomarker for AMF.[34]

**Microbial Biomass and Basal Respiration.** For the arable soil samples, microbial biomass carbon and nitrogen estimates by chloroform−fumigation−extraction were carried out according to Vance et al.[35] The extracted organic C was determined by infrared spectrometry after combustion (DIMA-TOC 100, Dimatec), and extracted N was measured by chemo luminescence (TNb, Dimatec). Soil microbial biomass was then calculated according to Joergensen[36] and Joergensen and Mueller.[37] Basal respiration was determined by preincubating soils for 7 days at 50% water holding capacity to stabilize microbial communities. Soils were then incubated in a closed system with a NaOH solution for 24 h and transferred to a new bottle to absorb the emitted $CO_2$ in a NaOH solution over 72 h. The resulting $Na_2CO_3$ was precipitated with $BaCl_2$, and the unused NaOH was determined by titration with HCl.[38]

**Statistical Analyses.** All statistical analyses were performed using R version 3.6.3.[39] Differences between management systems for the occurrence and sum of concentration of pesticide residues were determined by analysis of variance (ANOVA) and subsequent simultaneous multiple comparison of least-squares means (package "*lsmeans*"[40]). The heatmaps were created using the *levelplot* function of the *lattice* package.[41] To describe the relation of numbers of pesticide, as well as pesticide concentrations, with the duration of organic management, the sites were grouped in five-year intervals and the difference was identified with ANOVA. Pairwise correlations between single pesticides and soil properties of the different fields were tested with the *cor* function based on a Spearman rank correlation coefficient, and *p*-values were adjusted for multiple comparison with the *fdr* method. The plot was displayed with the *corrplot* package.[42]

For arable fields, multimodel inference and random forest analyses were performed to investigate the possible influence of pesticide residues on the soil life parameters, microbial biomass, basal respiration, and abundance of AMF in roots and soil. Due to sample size limitations, insufficient degrees of freedom were available to test the effect of individual pesticide residues on different response variables. Therefore, only the number and the sum of the pesticide concentration were considered. In addition to these indices for the degree of soil pesticide pollution, all physicochemical soil properties, namely soil texture (sand, clay, including the quadratic terms sand$^2$, clay$^2$, and the interaction of sand * clay to account for nonlinear relationships), pH, organic carbon, bulk density, and total N, P, and K were considered as predictors. Further management practices, such as management system, plant diversification, tillage, mineral fertilizer, and organic amendments were also included as predictors. All predictors were tested for collinearity based on Spearman correlation with a threshold level of 0.7 (due to the high correlation of number of pesticide residues and sum of the pesticide concentrations, only the first could be considered). Multimodel inference was applied to assess which predictors across all possible models best predicted the difference in abundance for each of the soil life parameters. Multimodel inference was performed using the package *glmulti*.[43,44] The unconditional model-averaged parameter estimates and standard errors, *z*-values, *p*-values, and the relative importance were extracted with the *metaphor* package[45] to evaluate the predictors. In addition, random forest analysis was performed to identify the main predictors of abundance for each of the soil life parameters. The importance of each predictor variable was determined by reviewing the increase in the mean square error (MSE). These analyses were conducted using the *randomForest* package.[46] The significance of the importance of each predictor on multifunctionality was assessed by using the *rfPermute* package.[47]

## ■ RESULTS AND DISCUSSION

**Widespread Occurrence of Pesticide Residues.** The analysis revealed that pesticide residues were widespread in agricultural soils and that all of the 100 tested sites contained pesticide residues in the top soil layer. The number of detected pesticides per field varied from 3 to 32, with similar numbers in arable and vegetable fields. Soils under conventional management contained about twice as many detected residues (median = 18 different pesticides) compared to soils under organic management (median = 8 different pesticides) (Figure 1A). Arable sites under conventional and no-till management were similar and contained an average of 17 different pesticides. The soil with the highest number of residues (32 different pesticides) was an arable field under no-till management (Figure 1A).

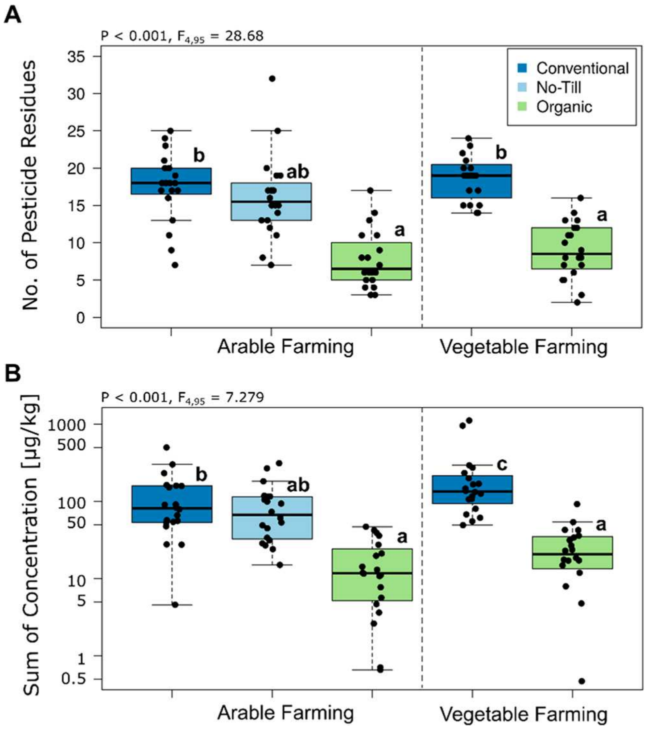

**Figure 1.** (A) Number of pesticide residues in arable and vegetable fields under conventional management with tillage, conventional management without tillage, or organic management. For each management system 20 fields were analyzed. (B) Sum of the concentrations of pesticides in arable and vegetable fields under conventional, conventional without tillage, or organic management.

The sum of the concentration of all residues (µg per kilogram of dry soil) also differed significantly between the management systems (see Figure 1B). Conventionally managed vegetable fields contained the highest pesticide loads with concentrations of up to 1170 µg/kg. The median total pesticide concentration in conventionally managed vegetable fields was 79% higher than the median of the conventionally managed arable fields. The median sum of pesticide concentration in organic sites under arable or vegetable production was in both cases 85% lower (arable production: max. 52 µg/kg, vegetable production: max. 90 µg/kg) than the median in conventionally managed sites. However, as the samples were taken from two different soil layers (0−5 cm for the arable fields and 0−10 cm for the vegetable fields) and because the farming systems varied in many aspects including application rate and the formulation of the pesticides being applied (e.g., application rates of pesticides in vegetable systems were much higher), the direct comparisons of residual pesticide concentrations between both systems are difficult. Since both sampling depths lay within the ploughing layer, soils from conventional and organic fields were well mixed, but due to the stratification in the no-till fields, concentrations in the latter are most likely overestimated in comparison to the former management practices. Nonetheless, the sites under no-till management did not differ clearly in their median sum of pesticide concentrations from either conventional or organic managed soils of the arable farming system (Figure 1B). It was expected that the fields under no-till farming would exhibit higher herbicide concentrations, as they are needed to control weeds, which are otherwise removed with tillage.[48] Furthermore, tillage is known to increase catabolic processes, such as oxidation and mineralization, and thus increase the degradation of pesticide residues.[49] However, only three no tillage sites showed high levels of herbicides and thus this hypothesis could not be confirmed.

Out of the 46 analyzed pesticides and transformation products (TPs), 41 were detected in at least one soil, including 12 herbicides, 8 herbicide TPs, 16 fungicides, and 7 insecticides (Figure 2). 2-Hydroxyatrazine, a TP of atrazine (a broad leaf herbicide), was detected most frequently, in 92% of the arable soils and in 100% of the vegetable soils. It further had the highest contribution to the pesticide load in organically managed sites. The herbicide residues atrazine, chloridazon, linuron, napropamide, and terbutylazine; the fungicide residues carbendazim and epoxyconazole; and the insecticide residues clothianidin and imidacloprid were also detected in more than half of the soils of all management systems, and in both arable and vegetable farming systems. The herbicides metamitron, S-metolachlor, and the TP 6-desisopropylatrazine were more abundant in soils from the arable farming system, whereas soils of the vegetable farming systems contained considerable amounts of the fungicides azoxystrobin and metalaxyl, as well as the insecticides pirimicarb and thiamethoxam. The two conventional vegetable sites with the highest loads of pesticide residues contained exceptionally high concentrations of the herbicide linuron and the fungicide azoxystrobin. In the conventional management fields without tillage, the concentrations of the herbicides S-metolachlor, terbutylazine, and its TPs stood out (Figure 2). The occurrence and concentrations of pesticides in agricultural soils can be strongly influenced by the time of sampling and the time of pesticide application. The questionnaires of the arable fields showed for instance that in some fields pesticides were applied in the week before sampling, explaining single high concentrations of epoxiconazole, boscalid, or tebuconazole.

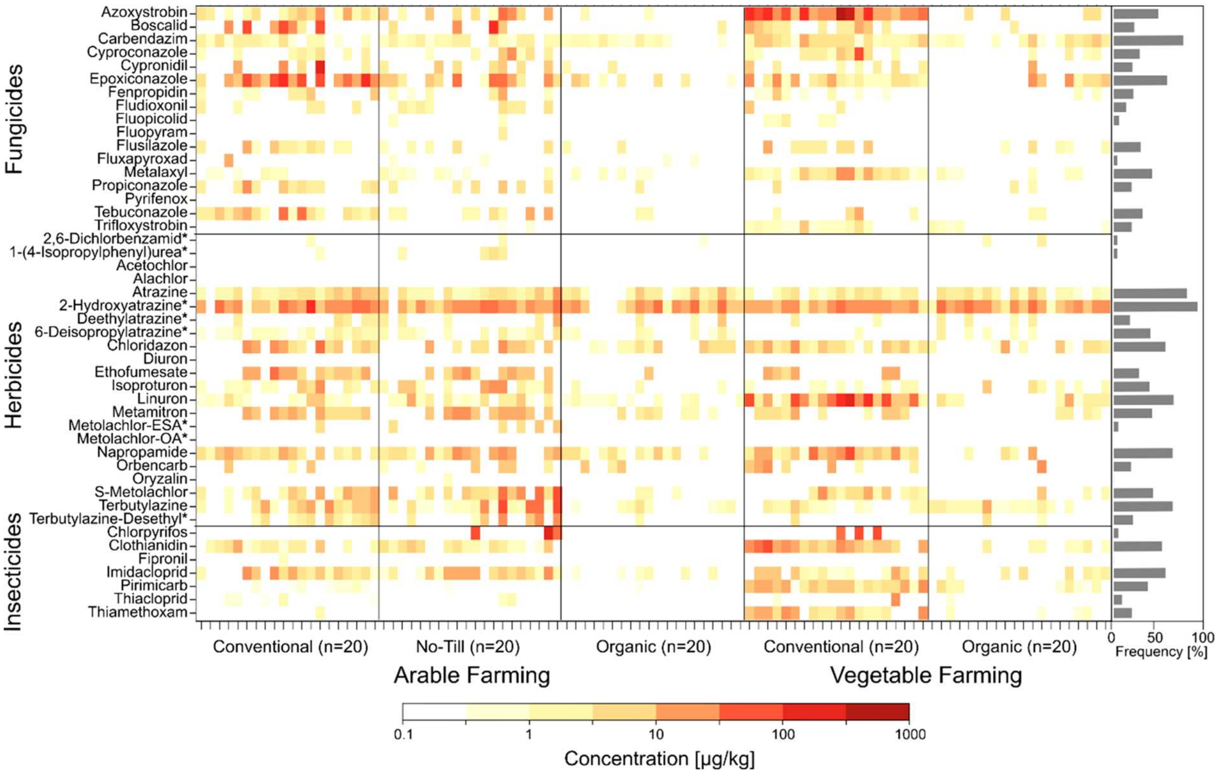

**Figure 2.** Abundance of 46 pesticides and transformation products (indicated with an asterisk) in the arable and vegetable fields under conventional, no-till, and organic management. Each row represents a pesticide, and each column, one field. The method limits of quantification (MLOQ) ranged between 0.064 μg/kg and 36 μg/kg depending on the substance (SI, Table S8). The color range represents the level of the detected concentrations, whereas empty (white) cells indicate no detects (<MLOQ). The bars on the right show the frequency of occurrence of a specific compound across all samples.

**Pesticide Residues in Organically Managed Fields.** The questionnaires additionally gave information about how long the fields were managed organically. The number of pesticide residues as well as the sum of the total pesticide concentration declined significantly with the duration of organic farming by 70% or 90% respectively. However, even after 20 years of organic management, between 3 and 16 different pesticide residues were still detected (Figure 3, Figure S2). The herbicides linuron, napropamide, chloridazon, and atrazine (including TPs), as well as the fungicide carbendazim, were the pesticides that prevailed the longest after conversion to organic farming and were present in the soils, which converted to organic several years ago. As the organically managed fields had not been exposed to direct pesticide application for at least three years, our work suggests that either pesticides persisted in soil far longer than expected or that contamination occurred via an indirect pathway from adjacent conventional fields through particle drift, wind erosion, or runoff.[50]

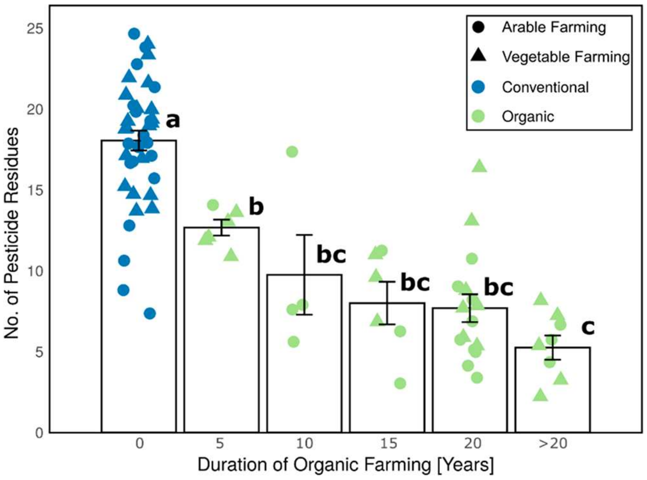

**Figure 3.** Decrease of the number of pesticide residues in soils, including both arable and vegetable farms, with the duration of organic management. The duration of organic management is expressed as the number of years since the conversion from conventional to organic. The sites were grouped in five-year time intervals.

For some of the detected pesticides, such as napropamide, chloridazon, and carbendazim, which are currently applied in many countries including Switzerland, this diffuse contamination via drift is possible.[1] However, for other residues, such as atrazine (and its TPs), which was banned in Switzerland in 2007,[51] an indirect pathway of contamination is not possible anymore. This implies that atrazine residues persist much longer than their half-lives (DT50) of 6−108 days as field studies suggest[52] (SI, Table S1). The half-lives of various other pesticides, such as chloridazon, carbendazim, and linuron, are also low (SI, Table S1), but they were still detected after 20 years of organic management. Older, formerly used pesticides, such as organochlorine pesticides (e.g., DDT), which were last used decades ago, had also been found in soils after conversion to organic management.[53] While the high persistence of compounds of earlier pesticide generations is a known drawback, the presence of pesticides approved in the past 30 years is against expectation, as they are considered less

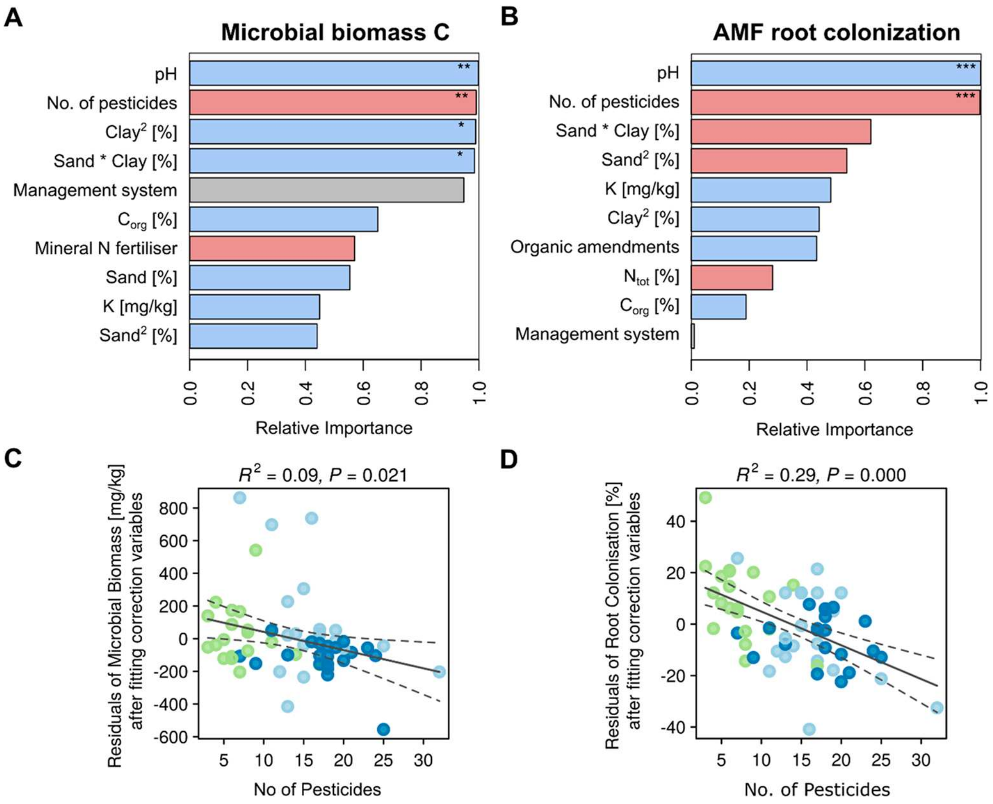

**Figure 4.** (A and B) Relative importance of various variables, which explained microbial biomass (A) and AMF root colonization (B) in arable farming using multimodel inference. The bars represent the importance of predictors (see methods for details on individual variables). The colors of the bars indicate the model's average estimate, where blue implies positive and red negative values. Management (gray bar as this is a categorical variable) is also included in the figure regardless of its rank as a predictor. Asterisks indicate the statistical significance of the variables ($*P < 0.05$; $**P < 0.01$; $***P < 0.001$). (C) Univariate relationship of microbial biomass C and numbers of pesticide residues corrected for pH, $C_{org}$, and sampling area (see methods: *Statistical analyses*). The colors represent the management systems (dark blue = conventional, light blue = conventional without tillage, green = organic); the solid line indicates the regression line, and the dotted line, the 95% confidence interval. (D) Univariate relationship of AMF and number of pesticide residues corrected for pH, $C_{org}$, and sampling area. The relationships between AMF colonization and the number of pesticide residues was also significant without correcting for pH, $C_{org}$, and sampling area (SI, Figure S5).

persistent and more rapidly biodegradable.[2] When the pesticides half-lives and their maximal application dosage are taken into account, traces of only five pesticides (boscalid, epoxiconazole, fluopicolid, flusilazole, and an S-metolachlor TP) should still be detectable after ten years. This suggests that, additional input pathways as specified above excluded, these residues remained in the soils even after the conversion from the previous conventional management to organic management and degrade slower than assumed.

**Influence of Soil Characteristics on the Occurrence of Pesticide Residues.** Additionally, it was tested whether the abundance of pesticide residues or their TPs was linked to specific soil characteristics (soil organic carbon, pH, total nitrogen, texture) (SI Figure S1). The number of pesticides and the sum of concentrations of all pesticide residues were generally not related to the tested soil characteristics. However, the abundance of specific pesticides such as terbutylazine-desethyl ($R^2 = 0.690$, $P < 0.001$) and fenpropidin ($R^2 = 0.256$, $P = 0.014$) was positively correlated to soil organic matter content (SI Figure S1). Indications for pH-dependent occurrence of pesticides were observed for individual pesticides including atrazine and its TPs ($R^2 = 0.228$, $P < 0.001$) as well as fenpropidin ($R^2 = 0.180$, $P = 0.044$), which showed a negative correlation (SI, Figure S1). This relation suggests that increasing soil pH decreases the biodegradation and mobility of these pesticide residues. This implies that these soil characteristics are at least partly responsible for the high concentrations of atrazine residues, even after many years of organic management. Soil pH is also known to be an important factor that can influence the mobility and degradation of pesticides.[54] For example, higher levels of pesticides were found in soils with a low soil pH, possibly because the ability of such soils to sorb pesticides is higher, resulting in increased persistence.[55] Moreover, microbial activity is reduced at low soil pH, which could impair the breakdown of pesticides[56] and adaptation to pesticide degradation is decreased in acidic soils.[57] In addition, compound properties can play a role in their sorption and degradation. As many of the analyzed pesticides are ionizable, and thus protonate or deprotonate in accordance to their $pK_A$ value (SI, Table S1), their sorption is expected to be pH dependent.[58]

**Pesticide Residues as a Negative Driver for Microbial Biomass and Arbuscular Mycorrhiza Fungi.** For the assessment of the influence pesticide residues on indicators of soil life, we focused on the subset of all 60 arable fields because these were sampled in spring when an active agroecosystem with living roots was present (e.g., for the vegetable fields samples were taken in winter). Furthermore, the arable fields all had the same crop (wheat), which facilitates the comparison, as plant host species has a big impact on AMF root colonization.[24]

Multimodel inference revealed that pH, the number of pesticide residues, and soil texture best predict microbial biomass C and AMF root colonization (Figure 4A and B). Microbial biomass and AMF root colonization were negatively correlated to the number of pesticides residues. This negative correlation was also visible when looking at the direct relationships of the two parameters and when correcting for variation explained by pH, soil organic matter content, and sampling area (Figure 4C−D). The negative correlation between the number of pesticide residues and AMF colonization was most pronounced (Figure 4D).

Further statistical testing with random forest analysis confirmed the multimodel inference and regression analyses and highlighted the importance of the number of pesticides and pH in explaining the abundance of AMF in roots, but not for the microbial biomass (SI, Figure S4). The negative correlation for the abundance of AMF in roots was further confirmed by an AMF specific phospholipid fatty acid (PLFA) biomarker (SI, Figure S3). However, for the AMF biomarker the effect of the pesticide residues was not statistically significant throughout all models (SI, Figure S4). In contrast, for basal respiration, a metric of microbial activity, pesticide residues seem not to be a major driver and no correlation between basal respiration and number of pesticide residues was detected (SI, Figure S3).

We only performed our analysis with all pesticide residues together and not for separate pesticide types (e.g., fungicides, herbicides, and/or insecticides) as it was not possible to assess which type of pesticides was responsible for the observed effects because the occurrence of the types was highly correlated (SI, Figure S1). Furthermore, it was not possible to differentiate between the concentration and number of pesticide residues because these two variables were also highly correlated (SI, Figure S1).

The robust negative association between the number of pesticides and AMF reveals that pesticides in soil are likely a key driver of AMF abundance in the field. It is well established that mineral fertilization reduces the abundance and diversity of AMF and several studies also showed that soil pH influences AMF abundance.[59,60] However, the impact of pesticides on AMF is poorly understood and previous studies were performed under controlled conditions, applying pesticides one by one at rather high application rates, and led to an inconclusive picture.[61] Moreover, so far it has not yet been shown that pesticide residues in soil have such a big impact on AMF abundance in an on-farm study. In our study, the number of pesticide residues was even more important in explaining AMF abundance than mineral fertilization, indicating that the suppression of AMF in many agricultural soils not only is the result of fertilization but also comes from pesticide management. Furthermore, we observed that even though the highest amount of AMF root colonization could be found in organically managed fields and lowest levels in conventionally managed fields, in the statistical analyses pesticide residues and pH best explained AMF abundance and exceeded the effect of management system. Our analysis implies that pesticide management must be considered when explaining the distribution and abundance of AMF in agroecosystems. The mechanisms responsible for the effects of pesticides on AMF remain unclear and need further investigation. Pesticides in soil (e.g., fungicides) could directly impair the growth of fungal hyphae or interfere with specific physiological processes such as uptake and transport of metabolites and nutrients or the signaling between plant and mycorrhizal fungus. These findings are important because AMF, as mentioned above, form symbiotic associations with plants while providing a number of crucial ecosystem services and are thus indispensable for a healthy soil.[23]

**Insight and Future Research.** The results highlight that the ubiquitous contamination of agricultural soils with a variety of pesticides can have long-term negative effects on soil life. We demonstrate that organically managed sites experience a legacy effect of past conventional management. Moreover, our data indicate that the persistence of both banned and currently used pesticides is underestimated. Even though low concentrations were detected in soils of organically managed fields, the potential effect of this long-term contamination is especially critical, as fields under organic management rely much more on biological soil processes and beneficial soil life such as AMF. Further, the modeled data show that pesticide residues could have a detrimental influence on soil microbial life.

Our work indicates that future studies should not only focus on single pesticides but also consider a wide range of pesticide combinations (e.g., cocktails) and further investigate to what extent these pesticide residues affect soil organisms and consequently soil processes and functions. Additionally, studies should also investigate interactions of pesticide residues with other global change factors such as drought, antibiotics, or microplastic since these abiotic and anthropogenic stressors can synergistically or antagonistically affect soil microbiota and reduce soil functioning.[62]

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.0c06405.

1. Relation between soil characteristics and the occurrence of pesticide residues
2. Decrease of total pesticide concentration with duration of organic management
3. Effects of pesticide residues on basal respiration and PLFA for AMF
4. Results of the random forest analysis
5. Uncorrected univariate relationships
6. Pesticides and pesticide transformation products included in this study
7. Soil characteristics of the selected fields and the test soils used for method validation
8. Pesticide analysis in soils

8.1. Chemicals and reagents

8.2. Accelerated Solvent Extraction and further Sample Preparation

8.3. High-performance Liquid Chromatography coupled to Triple Quadrupole Tandem Mass Spectrometry (HPLC-MS/MS)

8.4. Quantification

8.5. Method Validation

9. Measured concentrations and method limits of quantification
10. Supplementary References

(PDF)

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M.v.d.H., R.C., F.W., and L.B. conceived and designed the study of the arable network, for which F.W. and L.B. conducted the sampling. M.vd.H., C.H., and S.B. conceived and designed the study of the vegetable network, for which C.H. and S.B. conducted the sampling. D.W. executed the pesticide selection. F.E.W. and T.D.B. developed the organic trace analysis. A.R. helped with data analysis and the writing of the Supporting Information. J.R. and F.E.W. performed the organic trace analysis. J.R. and F.W. performed statistical analyses. J.R. wrote the manuscript with substantial contributions from F.W., T.D.B., and M.v.d.H.; all authors edited the manuscript.

### Notes

The authors declare no competing financial interest.

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