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Concerted Evaluation of Pesticides in Soils of Extensive Grassland Sites and Organic and Conventional Vegetable Fields Facilitates the Identification of Major Input Processes

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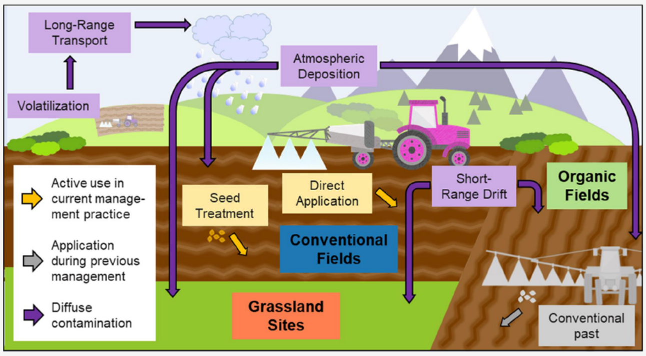

ABSTRACT: The intensive use of pesticides and their subsequent distribution to the environment and non-target organisms is of increasing concern. So far, little is known about the occurrence of pesticides in soils of untreated areas—such as ecological refuges—as well as the processes contributing to this unwanted pesticide contamination. In this study, we analyzed the presence and abundance of 46 different pesticides in soils from extensively managed grassland sites, as well as organically and conventionally managed vegetable fields (60 fields in total). Pesticides were found in all soils, including the extensive grassland sites, demonstrating a widespread background contamination of soils with pesticides. The results suggest that after conversion from conventional to organic farming, the organic fields reach pesticide levels as low as those of grassland sites not until 20 years later. Furthermore, the different pesticide composition patterns in grassland sites and organically managed fields facilitated differentiation between long-term persistence of residues and diffuse contamination processes, that is, short-scale redistribution (spray drift) and long-scale dispersion (atmospheric deposition), to offsite contamination.

KEYWORDS: *multiresidue analysis, organic farming, grasslands, short-range spray drift, atmospheric deposition*

■ INTRODUCTION

Pesticides are indispensable in today's agriculture, where they are used against diseases, pests, and weeds to secure crop yield and quality.[1] However, a large proportion of pesticides miss their target organisms,[2,3] leading to an unintentional but widespread contamination of pesticides in other areas through spray drift, infiltration, runoff, volatilization, and long-range atmospheric deposition.[4−8] Drift and volatilization are the main contributors to environmental contamination, leading to dispersion of up to 9% of the applied substances on small or large scales, respectively.[9] Spray drift is the process that is responsible for pesticides to be carried away during application[10] and tends to result in short-range transport.[11] In this way, pesticides can be transported several meters away from their application source depending on the application technique.[12] This off-target displacement can occur through aerosols or dust during application[13] and is largely influenced by wind speed and direction as well as the application methods, the formulation of the product, and the environmental conditions.[5,14] In contrast, volatilization of the substances is a continuous process,[15] which occurs mainly after application.[9] Volatilization is the origin of long-range transport via air and subsequent wet or dry deposition, causing pesticide contamination in places where they most likely were never applied, such as the Arctic or pristine mountain regions.[16−20] Whether and to which degree volatilization takes place is dependent on meteorological and environmental conditions, such as humidity and nature of the surface as well as temperature, wind, and the chemical's vapor pressure.[16] For atrazine, for instance, it has been shown that it can be volatilized, transported, and detected in rain water years after application.[21,22] However, recent studies showed that this is not only the case for older and more persistent pesticides but also for currently used ones including alachlor, chlorpyrifos, chlorothalonil, and S-metolachlor.[18,23] To what extent substances are further dispersed or mostly remain as residues in the soil depends on both the physicochemical properties of the pesticides and soil characteristics.[15,24] These properties are responsible for volatilization, sorption, leaching to ground-

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water, uptake by plants or organisms, and abiotic and microbial transformation, with sorption and biodegradation being the most relevant for the fate of the substances.[6,7,25] Concerning the soil characteristics, it is mainly the soil mineralogy (solid inorganic phases) and soil texture (especially clay content), the amount of soil organic matter, pH, the moisture levels, and the soil temperature that influence the behavior of pesticides over time.[24]

While earlier generations of pesticides, in particular organochlorine pesticides, were notorious for their high persistence,[26] currently used pesticides are supposedly designed to be more easily (bio-) degradable and therefore should be found less in the environment.[3] However, recent screenings of agricultural sites revealed widespread contamination of soils with various modern pesticides.[27−29] Even organically managed sites, where synthetic pesticides were not applied for multiple years, were not free of pesticides.[30−32] These findings indicate that persistence of pesticides under field conditions, including potentially cumulative contamination by repetitive applications, is underestimated so far. While several studies have looked at the distribution of pesticides in agricultural fields,[27−29] only very few assessed their occurrence in untreated sites, such as extensively managed grasslands and other, so-called ecological focus areas.[31,33] Furthermore, most studies mainly focused on neonicotinoids in untreated or off-site areas (such as field margins)[31,34] and did not conduct a comprehensive analysis over multiple substance classes. However, a more detailed knowledge about these areas would be of utmost interest as these sites represent regions that serve as ecological refuges for organisms living in and on soils[35] and are supposed to be unaffected by intense agricultural practices.

Complementary to the results from our previous study,[30] we here provide an extensive dataset with concentrations and occurrences of 46 widely applied synthetic pesticides (16 herbicides, 8 herbicide transformation products, 17 fungicides, and 7 insecticides) in 20 grassland soils. The concentrations and numbers of substances found in extensively managed grassland sites, which did not receive any pesticide treatment, were compared to the previously reported results from organically and conventionally managed vegetable fields.[30] This allowed us to study the contamination of agricultural soils along a gradient ranging from nearly untreated grassland soils, over soils with several years without pesticide treatment—after conversion from conventional to organic farming—to soils subjected to frequent pesticide treatments under conventional management. We further assessed whether the concentrations and numbers of pesticides as well as the occurrence of specific substances in the different site categories provided indications about their predominant input pathway. This includes previous on-field applications under conventional farming that would be anticipated for the organically managed fields, or diffuse contamination, such as short-range spray drift or long-range transport and atmospheric deposition. The latter was expected to lead to the presence of a given pesticide in all analyzed sites, regardless of the land use or management practice.

METHODS

Study Sites and Soil Sampling. The field sites were part of a farming network with 60 fields in eastern Switzerland, of which 20 were extensively managed grassland sites, 20 fields were under conventional vegetable production, and 20 under organic vegetable management. The grassland sites were managed extensively; therefore, farmers were not allowed to apply pesticides, fertilizers, or manure. The grass was cut at least once a year, and the cuttings were removed. Furthermore, grazing of animals was only allowed from September to November and was limited to sheep and goats. Half of the grassland sites belonged to vegetable farms which were managed conventionally (in the following termed GL_{con}), and the other half were affiliated with organically managed farms (GL_{org}). However, this allocation does not change the management of the land and the sites did not receive any pesticide or fertilizer input, regardless of which of the two vegetable farm types they belonged. The conventional vegetable fields received synthetic pesticides and mineral fertilizers and were managed according to the "Proof of Ecological Performance" as recommended by the Swiss Federal Office for Agriculture.[36] The organic vegetable fields received no chemical-synthetic pesticides and fertilizers and were managed in accordance to the guidelines of the Federation of Swiss Organic Farmers.[37] Information on each farm's management practices, such as the duration of organic farming, were collected directly from the farmers through a questionnaire. All soils were characterized as Cambisols. They did not vary significantly in parameters such as pH, texture, or organic carbon content. The sites were all located in a region with a moderate climate and precipitation that is sufficient to sustain agricultural production without additional irrigation. Therefore, pesticide contamination from irrigation or back-wash from surface waters was considered negligible. Information about the spatial distribution of the individual sites can be found in Figure S1.

Soil sampling and processing were performed as described by Yang et al.[38] The soils were sampled in December 2016; 10 soil cores (0−10 cm depth, 4 cm diameter) were randomly collected across the field at each site. Afterward, the individual soil cores were combined to obtain one composite sample per site, sieved with a 5 mm sieve and homogenized. Subsamples for pesticide analysis, microbial biomass, as well as for physicochemical soil property determination were taken and stored at −20, 4 ° C, and room temperature, respectively.

Sample Extraction and Analysis with LC−MS/MS. Pesticides were extracted and measured as described by Riedo et al.[30] Briefly, accelerated solvent extraction (Dionex ASE 350, Thermo Scientific) was used to extract pesticides from 6 g of soil. The method contained two extraction steps. In a first step, an organic mixture of acetone, methanol, and acetonitrile at a ratio of 65:10:25 (% v/v) was used. In a second, acidic step, the soils were extracted with a mixture of acetone and 1% phosphoric acid in Millipore water (Milli-Q Gradient, Merck) at a ratio of 70:30 (% v/v). The extracts were further processed by solvent evaporation under compressed air and subsequent extract dilution with 90:10 (% v/v) Millipore water and methanol. The pesticides were then analyzed by high-performance liquid chromatography coupled to a triple quadrupole tandem mass spectrometer (HPLC-MS/MS). Reversed phase HPLC with water and methanol as the mobile phase was used for separation. Detection was performed with MS/MS (QTrap 5500, Sciex), and all quantified concentrations were converted into μg per kg of dry soil. The limit of quantification ranged between 0.064 and 36 μg/kg depending on the substance. For further figures of merits and quality control/quality assurance measures, we refer to the Supporting Information (Chapter 1.2. High-performance Liquid Chroma-

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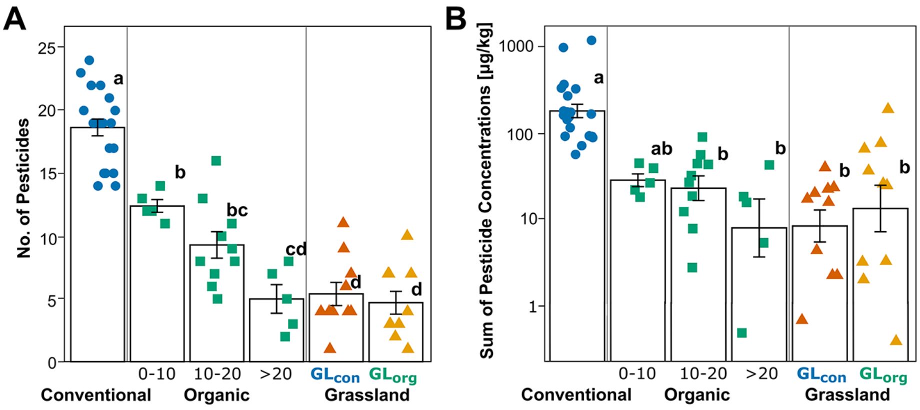

Figure 1. Number (A) and sum of the concentrations (B) of pesticides detected in soils from conventional vegetable management (blue), organic vegetable management (green), or grassland (orange). The boxes represent the mean values of each management practice with their standard errors. The organically managed sites are grouped in 10 year time intervals (0−10, 10−20, >20) since their conversion from conventional to organic management. The grassland sites are grouped in accordance with their associated conventionally (GL$_{con}$, dark orange) or organically (GL$_{org}$, light orange) managed farm. The letters indicate significant differences among individual management categories at an alpha value of 0.05.

tography coupled to Triple Quadrupole Tandem Mass Spectrometry (HPLC-MS/MS)) and Riedo et al.[30]

Persistence of Pesticide Residues from Previous Conventional Farming in Organic Sites. To gain a better understanding about the residual occurrence of pesticides due to their persistence after previous application, a relative dissipation rate constant for each detected substance at each organic site was assessed. For this, we estimated a dissipation rate constant based on the measured concentrations in soil, nominal amounts applied per area and year (maximal application rate allowed in Switzerland), time since conversion from conventional to organic farming, and pseudo-first-order dissipation kinetics. These estimated dissipation rate constants were subsequently compared with the expected dissipation rate constants reported in literature.[39] Further information about the calculation of these relative dissipation rate constants as well as a sensitivity analysis for the calculations with different assumptions (e.g., different application rates, repetitive application over several years, difference in soil properties, etc.) can be found in the Supporting Information (Chapter 1.4. Calculation of the Relative Dissipation Rate Constant in Organically Managed Vegetable Sites).

Potential Input of Pesticides through Rain (Atmospheric Deposition). To estimate the possible input of pesticides through atmospheric deposition, the loads that were expected to have entered the soil system through precipitation over the last 20 years were calculated. For this estimation, only substances for which data about loads in rainwater in Switzerland were available could be considered.[22,40] Subsequently, these values were compared with the actual measured amounts of pesticides in soil. Further information about the calculation can be found in the Supporting Information (Chapter 1.5. Calculation of the Potential Atmospheric Deposition of Pesticides).

Potential Impact of Spray Drift on the Occurrence of Pesticides in Non-treated Areas. To estimate the extent to which non-treated grassland sites might have been exposed to pesticide inputs from surrounding areas, we assessed potentially pesticide-relevant areas, meaning the agricultural land where the use of pesticides was possible or probable, in the vicinity to the sampled sites, according to Koch and Prasuhn.[41] This, in particular, includes all agricultural fields that are expected to be regularly treated with pesticides (e.g., arable land and permanent crops, such as vines, fruit and berries, vegetable crops, as well as horticultural crops). Permanent meadows and pastures as well as ecological focus areas were not counted as pesticide-relevant areas.[41] This analysis includes all agricultural land in the vicinity of the sampling sites, not just the fields sampled in this study. Using argGIS,[42] the area with potential pesticide application was estimated around each sampling site for different radial distances (1000, 500, 400, 300, 200, 100, 50, and 10 m), leading to the pesticide-relevant area for each site. This area was divided by the corresponding total circular area, leading to the approximate fraction of the pesticide-relevant area for each site. A graphical representation of this approach can be found in the Supporting Information (Chapter 1.6. Methodological Approach to Assess the Pesticide Exposure Potential from Surrounding Areas; Figure S3).

Statistical Analyses. All statistical analyses were performed using R version 4.1.2.[43] We first tested the impact of different management practices (e.g., conventional vs organic vs grasslands) on the numbers and concentrations of pesticides by analysis of variance (ANOVA) and subsequent simultaneous multiple comparison of least squares means (package "Emmeans"[44]). To gain insight into the influence of the time following the abandonment of direct pesticide application, the organically managed vegetable fields were additionally divided into 10 year intervals of the duration of organic management. Principal component analysis (PCA) was performed using the *prcomp* function of the stats package[43] to visualize the dispersion of the different sites based on the pesticide concentration. Ellipses were added to the plots, describing the 95% confidence level of the sampled sites of each group. Species scores, representing the degree of correlation between each of the original variables and the new principle components, were added for the five most influential substances responsible for the distribution of the sites along the first two principal component axes. The length of the arrows indicates the degree of importance. Due to the high dispersion of the grassland sites, we employed a hierarchically cluster analysis running UGPMA clustering from the *hclust* function to render further groupings between the grassland sites (stats package[43]). A summary of the individual pesticide concentrations was visualized by heatmaps, created using the *levelplot* function of the lattice package.[45] The difference in the

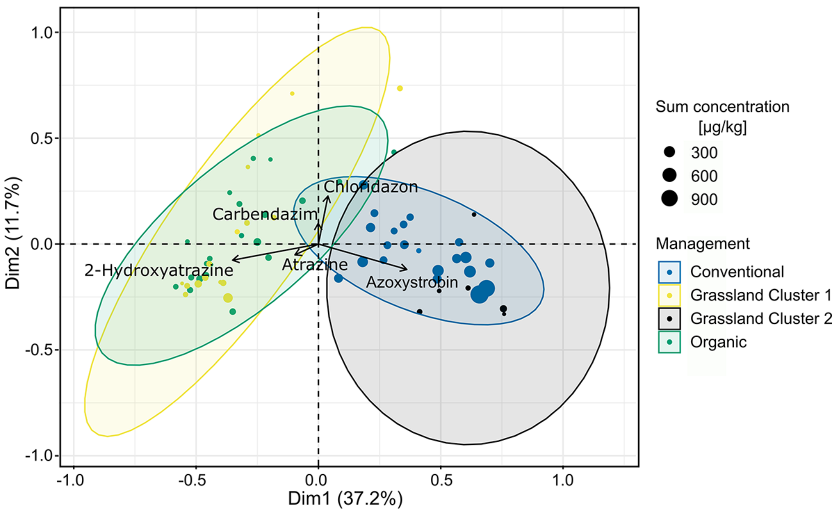

Figure 2. PCA biplots of the analyzed sites based on the concentrations of the individual pesticides. Sites close to each other contain a similar composition of substances, while sites with the biggest distance differ fundamentally in their fingerprints. The size of the points represents the sum of all pesticide concentrations of the individual site. The colors and ellipses represent the two management practices of the vegetable sites (conventional = blue, organic = green) and the two hierarchical grassland clusters (yellow and gray; for details about the hierarchical clustering, see text). The ellipses describe the 95% confidence level of the sampled sites of each group, and the arrows show the five most influential substances responsible for the distribution of the sites along the first two principal component axes.

fraction of pesticide-relevant areas for the different nominal and hierarchical clusters was analyzed with a t-test.

■ RESULTS AND DISCUSSION

Numbers and Concentrations of Pesticides in Soils under Different Management Practices. The quantification of pesticides in soils from extensively managed grasslands sites revealed that they all contained between 1 and 11 different pesticides. The number of pesticides in grassland sites (on average 5 pesticides) was about 2 times lower than in the organically managed vegetable fields, which contained between 2 and 16 individual pesticides (on average 9 pesticides), and about 4 times lower than in conventionally managed vegetable fields (on average 18 pesticides; Figure 1A). The detected sums of concentration of all analyzed pesticides in the grassland sites (median: 19 ± 42 μg/kg) were slightly lower than for the organically managed fields (median: 25 ± 21 μg/kg). The conventionally managed fields, where pesticides had still frequently been applied, contained 7−9 times higher median concentrations (median: 163 ± 286 μg/kg, almost a magnitude higher) than fields under organic management or grassland sites (Figure 1B). Furthermore, no difference in the number or concentration of pesticides was detected between the grassland sites belonging to the conventionally (GL_{con}) and organically managed (GL_{org}) farms (Figure 1A,B). In addition, no correlation was found between the number of pesticides in the grassland sites and the fields of the corresponding farms (data not shown). Furthermore, no correlation or a different trend over time for the measured soil parameters and the number of pesticide or the total pesticide concentration could be found (Figures S4 and S5). The exact concentrations of the individual substances at the 60 sites are summarized in Table S6.

We also show that the extensively managed grassland without any direct pesticide application contained considerable loads of pesticides, pointing toward a background contamination of soils with pesticides from diffuse sources. Organically managed vegetable fields only reached numbers of pesticides similar to those of grasslands sites, after having been managed organically for more than 20 years (Figure 1A), suggesting that in the first 0−20 years after conversion to organic management, there are still persistent residues, from pesticide applications during previous conventional farming, in the soils. We found further support for this decrease in the sum of the pesticide concentrations (Figure 1B). There, however, organic vegetable fields reached background concentrations of grassland sites after only 10 years already. The pattern could also be observed if the pesticides, which were not even approved at the time of conversion of a field, were excluded from the number and sum of concentrations (Figure S6, Table S7). Our previous study, which included conventionally and organically managed vegetable fields only,[30] could not clearly identify whether pesticides in organically managed fields were present as residues from former conventional applications or due to diffuse contamination, either from neighboring fields (short-range drift) or long-range transport and subsequent atmospheric deposition. The inclusion of pesticide data from grassland sites, particularly also with respect to the presence of individual pesticides, should now allow to shed further light on the relative importance of these different processes.

Pesticide Compositions in Soils with Different Management Practices. To gain a better understanding of the concentration, number, and identity of the pesticides and to later on potentially associate them with the two assessed sources—residues from past agricultural management and diffuse contamination—PCA based on the concentrations of the individual substances found in soils was carried out. The corresponding biplot, which displays the first two principal component axes and visualizes management practices, highlights distinct substance patterns between organically and conventionally managed fields (Figure S8, blue and green points and ellipses). The clear distinction is not surprising, given the marked differences in the history of pesticide use between organic and conventional farming. The grassland sites (orange points and ellipse) however did not show an equal distinctive cluster. The points of the individual grassland sites

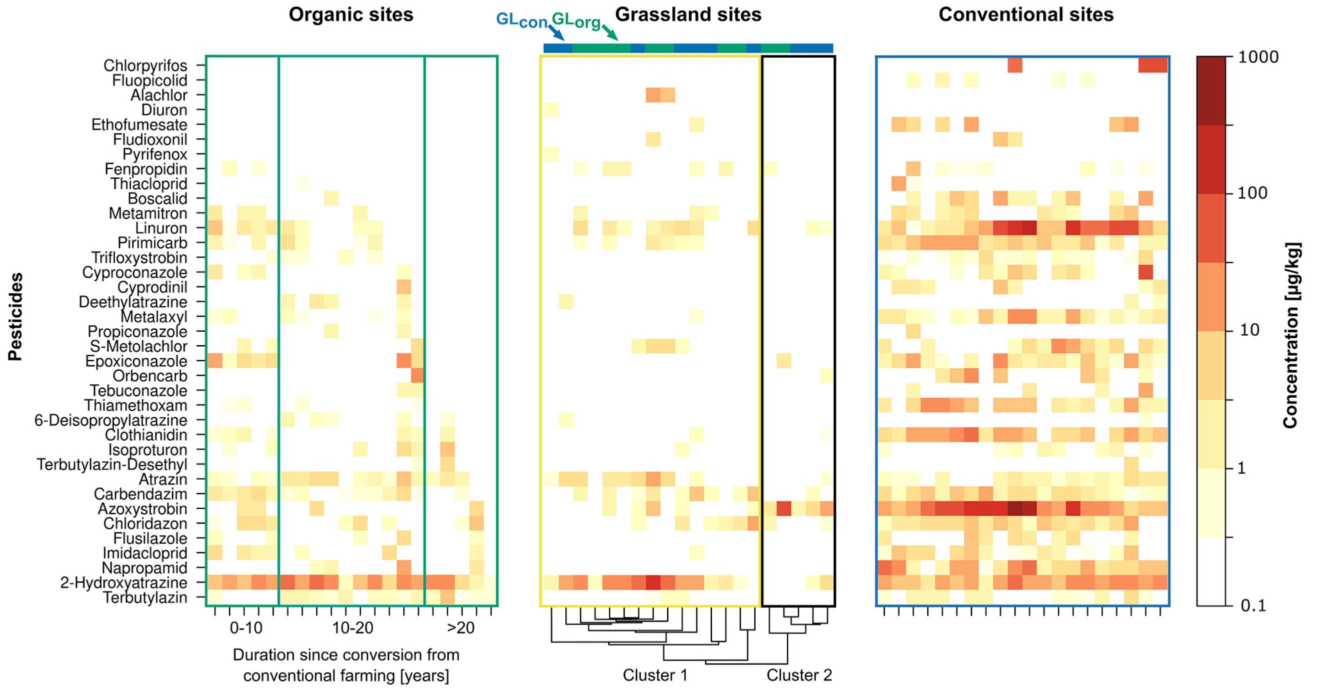

Figure 3. Heatmaps with concentrations of single pesticides in organically managed sites (left), grassland sites (middle), and conventionally managed sites (right) (partly adapted from Riedo et al.[30]). Each row represents a substance and each column one site. The organically managed sites are arranged according to their duration since conversion from conventional agriculture, and the boxes represent their division based on 10 year steps. The grassland sites are sorted in accordance with their hierarchical clustering, and the two boxes represent the two clusters. The composition of cluster 1 is closer to the one from the organic sites and the composition of cluster 2 closer to the conventional one. The green and blue boxes at the bottom represent their nominal grouping according to the corresponding farm and its management practice (blue = GL_{con}, green = GL_{org}). The conventional sites are also sorted according to their hierarchical clustered substance pattern. The substances are in order according to how long they appear in the organically managed sites. The color range represents the level of the detected concentrations, whereas empty (white) cells indicate no detects (<MLOQ).

rather segregated into two groups, which were either similar to the pattern of pesticides found under conventional or organic management. PCA was consequently repeated to visualize the sites based on the two nominal groups reflecting the corresponding farm type (GL_{con} = conventional farms, GL_{org} = organic farms). This was done to test whether this separation in farm type explained the distribution of the individual sites. However, the previously observed segregation of the grassland sites did not coincide with the management practice of the corresponding farm as the sites of the two nominal groups spread equally over those of the conventional and organic fields (Figure S9). This is potentially due to the fact that the contamination of grassland sites is related to fields other than those of the corresponding farms, which was also seen in the pattern of the general number and sum of concentrations of pesticides (Figure 1A,B). The grassland sites were thereupon hierarchically clustered to find sites with similar pesticide compositions, leading to two main clusters (see dendrogram in Figure 3), which validated the two visually recognizable clusters. Cluster 1 is largely overlapping with the organic cluster and cluster 2 with the conventional one (Figure 2). In a next step, we evaluated which substances drive the separation of the management practices and lead to these two clusters. Both the PCA scores—describing the degree of correlation between each pesticide concentration and the new principle components (arrows in Figure 2)—and the individual pesticide concentrations presented in the heatmap (Figure 3) revealed that the atrazine transformation product 2-hydroxyatrazine and the fungicide azoxystrobin were the key substances responsible for the division of the conventional versus organic vegetable fields and the two hierarchical grassland clusters. Possible reasons for the general differing pesticide pattern, partly including the occurrence of these pronounced substances, are discussed in the following sections, aiming at identifying the potential processes responsible for detected pesticides. The following discussion is focused on the organically managed fields and grassland sites, because on the conventionally managed fields, pesticides had still been applied, and this application most likely overshadowed any secondary fate processes.

Contribution of Residues from Previous Applications to the Pesticide Occurrence in Organically Managed Soils. With organically managed fields exhibiting substance numbers and concentrations between those of conventional vegetable fields and grassland sites (Figure 1A,B), it is plausible to assume that pesticides in organically managed fields are a result of both former conventional applications and contamination from diffuse sources. To isolate the former from the latter and thus to assess the contribution of pesticide residues from previous applications to the overall presence of pesticides on organically managed fields, we here separately examine pesticides that were mainly found in organically managed fields but not in grassland sites (i.e., we found trifloxystrobin, isoproturon, thiacloprid, metalaxyl, cyprodinil, thiamethoxam, tebuconazole, napropamid, propiconazole, cyproconazole, imidacloprid, boscalid, flusilazole, and epoxiconazole at no more than one grassland site; Figure 3). Thus, we assume that these substances reflect past pesticide application on the organically managed fields and do not lead to diffuse contamination to any larger extent. To assess whether these pesticides could potentially have remained as residues from earlier conventional management, we calculated the expected dissipation rate constants based on the half-lives (mean observed field values) found in literature (Table S5)[39] and compared them with the observed dissipation rate constants based on the measured concentrations in the soils (for details, see Supporting Information). The ratios of these two rate constants (Figure S10) show that only a few of these pesticides (i.e., imidacloprid and cyproconazole) dissipated in the expected range, indicating that their concentrations plausibly resulted from previous applications and can therefore be regarded as residues. For all other pesticides, we found relative rate constants clearly below zero, suggesting that persistence in the field was higher than predicted from literature (i.e., higher observed than expected concentrations). Given the fact that they are only found in organically managed fields but not in grassland sites, these substances are still most likely originating from previous applications and hence an additional input through diffuse pollution is not a plausible explanation for the higher-than-expected concentrations. That the expected concentrations are lower than observed concentrations could, on the one hand, be due to an underestimation of the applied amounts or a misjudgment of other parameters, such as plant cover, in the model. We thus conducted a sensitivity analysis of our estimations to assess how different assumptions for the input parameters (e.g., application rate, relevant depth of the soil layer, and plant cover) influence the expected concentration (for details, see Supporting Information). It was suspected that especially the inclusion of the repetitive application of pesticides over several years before the conversion to organic farming in the estimates of the dissipation calculations would have an influence on the outcome. The analysis showed the calculations to be rather robust with respect to the assumed input parameters, and the deviation of the values was not noteworthy when assuming that a pesticide was applied only in the last year before sampling or for 20 consecutive years prior to sampling. Thus, erroneous assumptions of the input parameters do not explain the slower dissipation in the field than in the laboratory, which is apparent for most of the substances. On the first sight, it seems remarkable that the discrepancy between predicted and observed dissipation was more pronounced for pesticides with a short half-life (Figure S10). However, for pesticides with a low half-life, it appears that the assumption of first-order dissipation may not be suitable for estimation over an extended period of time of more than a couple of half-lives as the discrepancy in observed and predicted dissipation was particularly striking for them. The difference between observed field dissipation and laboratory rate constants from literature could, on the other hand, also be due to the dissimilarity in partial sequestration of the pesticides,[46] which leads to their reduced availability for subsequent dissipation.[25] For literature-based data, this underestimation of the sequestration process could most likely be due to the fact that environmental factors, such as varying soil temperature and moisture contents, are not taken into account during dissipation studies for risk assessments or registration processes.[47] We also examined substance properties of the pesticides to determine if commonalities were evident among the substances that deviate strongly from expected values and if these properties could account for the greater deviation in the dissipation behavior of these substances compared to the literature values. However, no common characteristics, such as the compound class (e.g., neonicotinoids) or sorption and mobility parameters (e.g., adsorption coefficients—K_d/K_{oc}) could be found that would explain this behavior better.

Another possible reason why these substances were only found as residues in the organic vegetable fields, but not in grassland sites, is that they were applied with a technique, such as seed treatment, that makes diffuse contamination unlikely. During sowing of treated seeds, only a very small fraction (<2%) is dispersed by drift.[48] Studies have shown that drift from seed treatment leads to very short transport pathways reaching only field edges or margins,[49,50] and more than 90% enters the soil, where the seeds coated with the pesticide had been applied.[51] Primarily substances with systemic activity (e.g., neonicotinoids) are used as seed treatment in agricultural management in Switzerland, although not all of them are exclusively applied this way.[52] However, pesticides that are used in Switzerland for seed treatment, such as clothianidin, cyproconazole, imidacloprid, and thiamethoxam, were indeed found predominantly in organic sites but hardly in grassland soils (Figure 3). This could further indicate that this difference between the two management practices (organic management and grasslands) arises from previous application rather than diffuse contamination.

Potential Pesticide Contamination from Diffuse Sources. In contrast to pesticides that were predominantly found in organically managed fields, it was assumed that substances that evenly appeared across organically managed fields as well as the grassland sites originated from diffuse sources, such as short-scale spray drift, or long-range transport and subsequent atmospheric deposition. The latter mainly takes place through dry or wet deposition, whereby the respective proportion varies depending on the pesticide.[53] Regarding wet deposition, considerable loads are deposited through rain.[54] We therefore calculated the potential input of pesticides previously found in rain in Switzerland, that is, atrazine and its transformation product 2-hydroxyatrazine, azoxystrobin, carbendazim, fenpropidin, linuron, metamitron, metylaxyl, pirimicarb, S-metolachlor, and terbuthylazine, to test whether this diffuse input pathway can explain their occurrence (Figure 3). The actual measured pesticide concentrations in the soil were then normalized to the potential input through precipitation over an assumed time period of 20 years. For metalaxyl, S-metolachlor, terbuthylazine, and pirimicarb, the corresponding log ratios were between −1 and 1 (Figure S11), indicating that their widespread contamination could potentially be explained by atmospheric deposition within a factor of 10 uncertainty. For carbendazim, azoxystrobin, linuron, and, particularly, for atrazine, such an input is less likely as their corresponding ratios of measured to calculated concentrations were orders of magnitude higher, in both the organically managed fields and the grasslands. Atrazine, which was frequently determined in rain in Switzerland as well as in remote areas in the past[22,55,56] and was banned over 10 years ago, could not be found in current precipitation samples.[40] This indicates that it currently is not deposited through rain anymore and that its widespread occurrence in grassland sites as well as the occurrence of its transformation products must either be caused be past input by precipitation and subsequent pronounced sequestration or by additional forms of diffuse contamination in the past, such as short-scale spray drift.

Therefore, in a next step, we further assessed the potential for short-scale spray drift by evaluating what fraction of the circular area around each individual grassland site was potentially exposed to pesticide applications. For this, different radial distances (10−1000 m) around the sampling site were taken into account. First, we examined the two nominal clusters from the grassland sites, GL_{con} and GL_{org}, separately. We hypothesized that GL_{con} sites generally have a higher pesticide exposure potential than the GL_{org} sites as their corresponding farm applies pesticides and they thus potentially tend to be surrounded by more conventionally managed fields. Indeed, at distances between 200 and 400 m, GL_{con} sites were statistically significantly more prone to pesticide exposure than the GL_{org} ones, and the mean percentage of the surrounding area with a potential pesticide input had a (statistically nonsignificant) tendency to be more exposed at all other distances (Figure S12A). However, since farms with different management practices tend to be located rather close to each other in Switzerland, this hypothesis and explanation must be considered with caution. Second, the pesticide exposure potential of the grassland sites was also considered for the two hierarchical clusters, which are based on actual measured pesticide patterns. Since we found a dissimilar substance composition within these two clusters, in particular pronounced concentrations of 2-hydroxyatrazine and azoxystrobin, we assumed that a difference in the extent of exposure would be evident, potentially explaining the observed patterns. However, the exposure potential of the two hierarchical clusters did not differ significantly (Figure S12B). Nevertheless, the mean percentage of the surrounding area with a potential pesticide input of the two clusters shows the tendency that cluster 1 had been more exposed to pesticide application in the surrounding areas. This cluster shows, as discussed above, a similar substance pattern to the organic sites, which mainly consists of "old" substances applied in earlier agricultural management, such as atrazine, linuron, or S-metolachlor. Therefore, it is possible that substances, such as atrazine and its transformation product 2-hydroxyatrazine, were distributed over short-scale drift during these past applications and thus occur today more in cluster 1. As currently used substances, such as azoxystrobin, which is rather a "new" substance, are designed to be less dispersed in the environment,[3] one could speculate that consequently they can be found less in this cluster. However, as the pesticide exposure potential of the different hierarchical clusters is not significantly different for any radius around the sampling sites, no strong conclusions can be drawn and the results for the individual substances have to be considered with caution.

The clusters (both the nominal and the hierarchical) were also compared regarding their exposure to only vegetable fields or special crops, such as orchards, with a high pesticide input according to present farming practices (data not shown) in order to find explanations for the second cluster, containing substances such as azoxystrobin. However, no difference in exposure, explaining the discrepancy in the patterns, was apparent. Besides the exposure of the clusters, also the concentrations of single substances and the number of substances in each site were fitted against the pesticide exposure potential. No particular trend (e.g., higher exposure ∼ higher concentrations or higher exposure ∼ higher number of different substances) for any of the pesticides could be observed (Figures S13−S15). It was also further examined whether the sites from the two clusters differed regarding soil biological and chemical properties, which would explain their discrepancy, but no significant difference existed (data not shown).

Implications and Future Research. The presented study showed that pesticides are widespread in Swiss soils and are also present as background contamination at sites that reflect nearly undisturbed conditions and do not apply pesticides (extensive grassland). We further demonstrated that different management practices vary in the amount as well as concentrations of pesticides (conventional > organic > grassland). Earlier studies have already indicated the widespread distribution of pesticides in the environment. However, studies that directly compare sites under different management consequently allowing conclusions about the potential persistence of pesticides in field soils and improve differentiation of the sources of the pesticides in the different sites are rare. So far, especially the differentiation between processes contributing to pesticide occurrence in sites where pesticides had been applied in the past compared with untreated areas was missing. These results suggest that the pesticides found in grassland sites were derived from different contamination pathways. Our analyses provide indications for short-scale redistribution of pesticides to grasslands after application on close-by sites as well as for long-scale dispersion leading to offsite contamination. However, so far, our work could only partly assign the substances to the respective contamination pathways. Therefore, further investigations are needed to understand the origin of the different contaminants and to further comprehend plausible exposure processes for agricultural soils under different management practices, especially including non-treated sites. For this, monitoring studies that contain detailed records of pesticides applied to the treated fields, and also include fields from the closer vicinity of the treated field in the monitoring, are needed to directly detect the presence of residues as well as to better understand the diffuse contamination. These studies should also take into account potential contamination by irrigation of agricultural areas with the pesticide-containing surface or groundwater, if hydrodynamically relevant, or pesticide input through the application of contaminated manure, two input pathways that could not be taken into consideration with the current setup. Additional research should also take an expanded number of analytes into account, which would facilitate pesticide fingerprinting and increase the diagnostic potential of multivariate statistical analyses. In addition, high-frequency sampling and analysis that account for seasonal variability of residues should be considered to gain a comprehensive overview of the secondary fate processes of the pesticides after application, with emphasis on monitoring individual fields over a longer period of time (long-term monitoring). Such investigations are currently in progress within the Swiss Action Plan on Pesticides.[57] Moreover, future studies should also investigate the bioavailability and effects of the multitude of pesticides in these sites as their soils provide refuges for important soil organisms.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.2c02413.

Geographical location of the individual sampling sites; HPLC-MS/MS; R-code for PCA; calculation of the relative dissipation rate constant in organically managed vegetable sites; calculation of the potential atmospheric deposition of pesticides; methodological approach to assess the pesticide exposure potential from surrounding areas; pesticide concentrations for the individual sites; influence of soil properties on pesticides; numbers and concentrations of pesticides in soils of sites under different management practices corrected for not registered substances; concentrations of individual pesticides in soils of sites under different management practices; pesticide patterns according to the management practice of the sites; pesticide patterns in the nominal clusters GL_{con} and GL_{org}; expected dissipation rate of pesticides in sites under organic management; potential input of pesticides through precipitation; and pesticide exposure potential of the grassland sites (PDF)

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Author Contributions

M.v.d.H., S.B., and C.H. conceived and designed the study of the vegetable network, for which C.H. and S.B. conducted the sampling. J.R. performed the organic trace analysis and performed the data analysis. J.R. wrote the manuscript with substantial contributions from K.F., F.W., M.v.d.H., and T.D.B.; all authors edited the manuscript.

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Notes

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REFERENCES

(1) Savary, S.; Willocquet, L.; Pethybridge, S. J.; Esker, P.; McRoberts, N.; Nelson, A. The global burden of pathogens and pests on major food crops. *Nat. Ecol. Evol.* **2019**, *3*, 430−439.

(2) Sarmah, A. K.; Müller, K.; Ahmad, R. Fate and behaviour of pesticides in the agroecosystem; a review with a New Zealand perspective. *Soil Res.* **2004**, *42*, 125−154.

(3) Rodríguez-Eugenio, N.; McLaughlin, M.; Pennock, D. *Soil pollution: a hidden reality*; FAO: Rome (Italy), 2018.

(4) Mottes, C.; Lesueur-Jannoyer, M.; Le Bail, M.; Malézieux, E. Pesticide transfer models in crop and watershed systems: a review. *Agron. Sustainable Dev.* **2014**, *34*, 229−250.

(5) Galon, L.; Bragagnolo, L.; Korf, E. P.; dos Santos, J. B.; Barroso, G. M.; Ribeiro, V. H. V. Mobility and environmental monitoring of pesticides in the atmosphere—a review. *Environ. Sci. Pollut. Res.* **2021**, *28*, 32236−32255.

(6) Arias-Estévez, M.; López-Periago, E.; Martínez-Carballo, E.; Simal-Gándara, J.; Mejuto, J.-C.; García-Río, L. The mobility and degradation of pesticides in soils and the pollution of groundwater resources. *Agric. Ecosyst. Environ.* **2008**, *123*, 247−260.

(7) Fenner, K.; Canonica, S.; Wackett, L. P.; Elsner, M. Evaluating pesticide degradation in the environment: blind spots and emerging opportunities. *Science* **2013**, *341*, 752−758.

(8) Tang, F. H. M.; Lenzen, M.; McBratney, A.; Maggi, F. Risk of pesticide pollution at the global scale. *Nat. Geosci.* **2021**, *14*, 206−210.

(9) de Jong, F. M. W.; de Snoo, G. R.; van de Zande, J. C. Estimated nationwide effects of pesticide spray drift on terrestrial habitats in the Netherlands. *J. Environ. Manage.* **2008**, *86*, 721−730.

(10) International Organization for Standardization − ISO. Equipment for crop protection − Methods for field measurement of spray drift. In *ISO 22866*, 2005.

(11) Løfstrøm, P.; Bruus, M.; Andersen, H. V.; Kjær, C.; Nuyttens, D.; Astrup, P. The OML-SprayDrift model for predicting pesticide drift and deposition from ground boom sprayers. *J. Pestic. Sci.* **2013**, *38*, 129−138.

(12) Rautmann, D.; Streloke, M.; Winkler, R. New basic drift values in the authorization procedure for plant protection products. In *Workshop on risk management and risk mitigation measures in the context of authorization of plant protection products*, 1999; pp 133−141.

(13) Nuyttens, D.; De Schampheleire, M.; Baetens, K.; Brusselman, E.; Dekeyser, D.; Verboven, P. Drift from field crop sprayers using an integrated approach: results of a five-year study. *Trans. ASABE* **2011**, *54*, 403−408.

(14) Baetens, K.; Nuyttens, D.; Verboven, P.; De Schampheleire, M.; Nicolaï, B.; Ramon, H. Predicting drift from field spraying by means of a 3D computational fluid dynamics model. *Comput. Electron. Agric.* **2007**, *56*, 161−173.

(15) Tuduri, L.; Harner, T.; Blanchard, P.; Li, Y.-F.; Poissant, L.; Waite, D. T.; Murphy, C.; Belzer, W. A review of currently used pesticides (CUPs) in Canadian air and precipitation. Part 2: Regional information and perspectives. *Atmos. Environ.* **2006**, *40*, 1579−1589.

(16) Vorkamp, K.; Rigét, F. F. A review of new and current-use contaminants in the Arctic environment: Evidence of long-range transport and indications of bioaccumulation. *Chemosphere* **2014**, *111*, 379−395.

(17) Cotham, W. E.; Bidleman, T. F. Estimating the atmospheric deposition of organochlorine contaminants to the Arctic. *Chemosphere* **1991**, *22*, 165−188.

(18) Muir, D. C. G.; Teixeira, C.; Wania, F. Empirical and modeling evidence of regional atmospheric transport of current-use pesticides. *Environ. Toxicol. Chem.* **2004**, *23*, 2421−2432.

(19) Daly, G. L.; Lei, Y. D.; Teixeira, C.; Muir, D. C. G.; Castillo, L. E.; Wania, F. Accumulation of Current-Use Pesticides in Neotropical Montane Forests. *Environ. Sci. Technol.* **2007**, *41*, 1118−1123.

(20) Guida, Y. d. S.; Meire, R. O.; Torres, J. P. M.; Malm, O. Air contamination by legacy and current-use pesticides in Brazilian mountains: An overview of national regulations by monitoring pollutant presence in pristine areas. *Environ. Pollut.* **2018**, *242*, 19−30.

(21) Majewski, M. S.; Coupe, R. H.; Foreman, W. T.; Capel, P. D. Pesticides in Mississippi air and rain: A comparison between 1995 and 2007. *Environ. Toxicol. Chem.* **2014**, *33*, 1283−1293.

(22) Bucheli, T. D.; Müller, S. R.; Heberle, S.; Schwarzenbach, R. P. Occurrence and behavior of pesticides in rainwater, roof runoff, and artificial stormwater infiltration. *Environ. Sci. Technol.* **1998**, *32*, 3457−3464.

(23) Zhang, X.; Meyer, T.; Muir, D. C. G.; Teixeira, C.; Wang, X.; Wania, F. Atmospheric deposition of current use pesticides in the Arctic: Snow core records from the Devon Island Ice Cap, Nunavut, Canada. *Environ. Sci.: Processes Impacts* **2013**, *15*, 2304−2311.

(24) Gevao, B.; Semple, K. T.; Jones, K. C. Bound pesticide residues in soils: a review. *Environ. Pollut.* **2000**, *108*, 3−14.

(25) Ortega-Calvo, J. J.; Parsons, J. R. *Bioavailability of Organic Chemicals in Soil and Sediment*; Springer, 2020; pp 243−265.

(26) Hilber, I.; Mäder, P.; Schulin, R.; Wyss, G. S. Survey of organochlorine pesticides in horticultural soils and there grown Cucurbitaceae. *Chemosphere* **2008**, *73*, 954−961.

(27) Silva, V.; Mol, H. G.; Zomer, P.; Tienstra, M.; Ritsema, C. J.; Geissen, V. Pesticide residues in European agricultural soils−a hidden reality unfolded. *Sci. Total Environ.* **2019**, *653*, 1532−1545.

(28) Hvězdová, M.; Kosubová, P.; Košíková, M.; Scherr, K. E.; Šimek, Z.; Brodský, L.; Šudoma, M.; Škulcová, L.; Sáňka, M.; Svobodová, M.; Krkošková, L.; Vašíčková, J.; Neuwirthová, N.; Bielská, L.; Hofman, J. Currently and recently used pesticides in Central European arable soils. *Sci. Total Environ.* **2018**, *613*, 361−370.

(29) Chiaia-Hernandez, A. C.; Keller, A.; Wachter, D.; Steinlin, C.; Camenzuli, L.; Hollender, J.; Krauss, M. Long-term persistence of pesticides and TPs in archived agricultural soil samples and comparison with pesticide application. *Environ. Sci. Technol.* **2017**, *51*, 10642−10651.

(30) Riedo, J.; Wettstein, F. E.; Rösch, A.; Herzog, C.; Banerjee, S.; Büchi, L.; Charles, R.; Wächter, D.; Martin-Laurent, F.; Bucheli, T. D.; Walder, F.; van der Heijden, M. G. A. Widespread occurrence of pesticides in organically managed agricultural soils—the ghost of a conventional agricultural past? *Environ. Sci. Technol.* **2021**, *55*, 2919−2928.

(31) Humann-Guilleminot, S.; Binkowski, Ł. J.; Jenni, L.; Hilke, G.; Glauser, G.; Helfenstein, F. A nation-wide survey of neonicotinoid insecticides in agricultural land with implications for agri-environment schemes. *J. Appl. Ecol.* **2019**, *56*, 1502−1514.

(32) Geissen, V.; Silva, V.; Lwanga, E. H.; Beriot, N.; Oostindie, K.; Bin, Z.; Pyne, E.; Busink, S.; Zomer, P.; Mol, H.; Ritsema, C. J. Cocktails of pesticide residues in conventional and organic farming systems in Europe − Legacy of the past and turning point for the future. *Environ. Pollut.* **2021**, *278*, 116827.

(33) Pelosi, C.; Bertrand, C.; Daniele, G.; Coeurdassier, M.; Benoit, P.; Nélieu, S.; Lafay, F.; Bretagnolle, V.; Gaba, S.; Vulliet, E.; Fritsch, C. Residues of currently used pesticides in soils and earthworms: A silent threat? *Agric. Ecosyst. Environ.* **2021**, *305*, 107167.

(34) Botías, C.; David, A.; Horwood, J.; Abdul-Sada, A.; Nicholls, E.; Hill, E.; Goulson, D. Neonicotinoid residues in wildflowers, a potential route of chronic exposure for bees. *Environ. Sci. Technol.* **2015**, *49*, 12731−12740.

(35) EFSA Scientific Committee. Recovery in environmental risk assessments at EFSA. *EFSA J.* **2016**, *14*, 4313.

(36) FOAG, Federal Office for Agriculture. *Ökologischer Leistungsnachweis*. https://www.blw.admin.ch/blw/de/home/instrumente/direktzahlungen/oekologischer-leistungsnachweis.html (accessed July 2, 2019).

(37) BioSuisse. *Richtlinien und Weisungen*. https://www.bio-suisse.ch/de/richtlinienweisungen.php (accessed July 2, 2019).

(38) Yang, B.; Banerjee, S.; Herzog, C.; Ramírez, A. C.; Dahlin, P.; van der Heijden, M. G. A. Impact of land use type and organic farming on the abundance, diversity, community composition and functional properties of soil nematode communities in vegetable farming. *Agric. Ecosyst. Environ.* **2021**, *318*, 107488.

(39) Agriculture & Environment Research Unit. *The Pesticide Properties Database (FOOTPRINT PPDB)*; University of Hertfordshire. https://sitem.herts.ac.uk/aeru/ppdb/ (accessed December 17, 2021).

(40) Schläpfer, K.; Farronato, N.; Zoller, N.; Tiefenbacher, A.; Winter, F.; Mazacek, J.; Ruppe, S.; Joss, M.K.; Kappeler, R.; Roth, Z.; Fuhrimann, S.; Probst-Hensch, N. *Pilot-Messungen von Pflanzenschutzmitteln in Luft und Regen in der Schweiz*; Basel, 2021.

(41) Koch, U.; Prasuhn, V. Risikokarten für den Eintrag von Pflanzenschutzmitteln in Oberflächengewässer auf Einzugsgebietsebene. *Agroscope Sci.* **2021**, *126*, 1−185.

(42) *ArcGIS [GIS software]. Version 10.0*; Environmental Systems Research Institute, Inc.: Redlands, CA, 2010.

(43) R Core Team. A language and environment for statistical computing; R Foundation for Statistical Computing. https://www.R-project.org/ (accessed March 22, 2022).

(44) Lenth, R. lsmeans: Least-Squares Means. https://cran.r-project.org/web/packages/lsmeans/index.html (accessed April 24, 2020).

(45) Sarkar, D.; Andrews, F.; Wright, K.; Klepeis, N.; Murrell, P. lattice: Trellis graphics for R. https://cran.r-project.org/web/packages/lattice/index.html (accessed April 24, 2020).

(46) Barriuso, E.; Benoit, P.; Dubus, I. G. Formation of pesticide nonextractable (bound) residues in soil: magnitude, controlling factors and reversibility. *Environ. Sci. Technol.* **2008**, *42*, 1845−1854.

(47) European Food Safety Authority. EFSA Guidance Document for evaluating laboratory and field dissipation studies to obtain DegT50 values of active substances of plant protection products and transformation products of these active substances in soil. *EFSA J.* **2014**, *12*, 3662.

(48) Tapparo, A.; Marton, D.; Giorio, C.; Zanella, A.; Soldà, L.; Marzaro, M.; Vivan, L.; Girolami, V. Assessment of the environmental exposure of honeybees to particulate matter containing neonicotinoid insecticides coming from corn coated seeds. *Environ. Sci. Technol.* **2012**, *46*, 2592−2599.

(49) Main, A. R.; Webb, E. B.; Goyne, K. W.; Mengel, D. Reduced species richness of native bees in field margins associated with neonicotinoid concentrations in non-target soils. *Agric. Ecosyst. Environ.* **2020**, *287*, 106693.

(50) Jones, A.; Harrington, P.; Turnbull, G. Neonicotinoid concentrations in arable soils after seed treatment applications in preceding years. *Pest Manage. Sci.* **2014**, *70*, 1780−1784.

(51) Goulson, D. Review: An overview of the environmental risks posed by neonicotinoid insecticides. *J. Appl. Ecol.* **2013**, *50*, 977−987.

(52) Wettstein, F. E.; Kasteel, R.; Garcia Delgado, M. F.; Hanke, I.; Huntscha, S.; Balmer, M. E.; Poiger, T.; Bucheli, T. D. Leaching of the neonicotinoids thiamethoxam and imidacloprid from sugar beet seed dressings to subsurface tile drains. *J. Agric. Food Chem.* **2016**, *64*, 6407−6415.

(53) Sauret, N.; Wortham, H.; Strekowski, R.; Herckès, P.; Nieto, L. I. Comparison of annual dry and wet deposition fluxes of selected pesticides in Strasbourg, France. *Environ. Pollut.* **2009**, *157*, 303−312.

(54) Casas, G.; Martinez-Varela, A.; Vila-Costa, M.; Jiménez, B.; Dachs, J. Rain amplification of persistent organic pollutants. *Environ. Sci. Technol.* **2021**, *55*, 12961−12972.

(55) Buser, H. R. Atrazine and other s-triazine herbicides in lakes and in rain in Switzerland. *Environ. Sci. Technol.* **1990**, *24*, 1049−1058.

(56) Thurman, E. M.; Cromwell, A. E. Atmospheric transport, deposition, and fate of triazine herbicides and their metabolites in

pristine areas at Isle Royale National Park. *Environ. Sci. Technol.* **2000**, *34*, 3079−3085.

(57) Bundesrat der Schweizerischen Eidgenossenschaft. *Aktionsplan zur Risikoreduktion und nachhaltigen Anwendung von Pflanzenschutzmitteln*; Bern, Switzerland, 2017.

https://doi.org/10.1021/acs.est.2c02413
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