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Bee bread collected by honey bees (*Apis mellifera*) as a terrestrial pesticide biomarker to complement water studies

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Abstract

BACKGROUND: Pesticides in aquatic environments are frequently studied, yet those in terrestrial environments remain relatively unexplored. This study monitored bee bread collected from two apiaries located in a typical agricultural environment in Switzerland from March to August 2022 as a proxy for terrestrial pesticide inputs. The temporal appearance of the selected pesticides was compared to their profiles in the water of a small catchment within this area.

RESULTS: Overall, 62% (31 of 50) of the targeted pesticides were detected in bee bread, with occurrences in both apiaries largely overlapping (23 pesticides), demonstrating a similar agricultural landscape across the region. Furthermore, nine pesticides were detected in bee bread and water, two pesticides were detected only in bee bread, and two additional pesticides were detected only in water. Comparative temporal analysis revealed that pesticides with moderate-to-high movement potential [Groundwater ubiquity score (GUS) ≥ 2.19] appeared simultaneously in bee bread and water (azoxystrobin, boscalid, flufenacet and terbuthylazine). However, pesticides with low movement potential (GUS ≤ 1.86) showed different profiles in both matrices (cyprodinil, prosulfocarb, tebuconazole and thiacloprid), indicating the difficulty of predicting their fate, given that they adhere to soil particles and cannot be covered by current water monitoring programmes.

CONCLUSION: Our findings present bee bread as a viable biomarker for monitoring pesticides by complementing the conventional water monitoring, and permitting a more comprehensive assessment of the exposure of terrestrial organisms to pesticides. Bee bread allows immediate recording of the applied pesticides and promptly reflects the seasonal variation in pesticide use.

Supporting information may be found in the online version of this article.

Keywords: fate of pesticides; *Apis mellifera*; bee bread; water; GUS index; terrestrial monitoring

1 INTRODUCTION

The need to decrease the use of pesticides is widely recognized[1] to reduce the risk for pollinators and other terrestrial organisms.[2] This has been reflected in the agricultural policies of many countries and in the EU and Switzerland.[3–5] For example, in 2017, the Swiss Federal Council set out the Federal Act on reducing pesticide risks by 50% by 2027, using 2012–2015 as a reference period.[4] Therefore, having information on the occurrence of pesticides in different environmental compartments is crucial for further decision-making.

Although the Federal Office for Agriculture (FOAG) documents sales data for pesticides on a t year^{-1} basis for all, at some time point, approved active ingredients,[6] these data can only be partially correlated to application masses. The Swiss agricultural research institute Agroscope has documented that the sales volumes can be explained relatively well with the help of extrapolations for only half of these active ingredients.[7] This report does not provide any information about the seasonal variation and peak application times, and for around a third of the quantities sold in the period 2010–2020, the areas of application in which they were used remain unclear.

Globally, water monitoring is well-established.[8] In Switzerland, pesticide levels have been monitored in water bodies for more

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than 20 years by the National Groundwater Monitoring (NAQUA) and the National Monitoring of Surface Water Quality (NAWA).[9,10] The NAQUA regularly conducts pesticide measurements in groundwater at >600 monitoring sites, but only for selected pesticides.[10] However, extrapolating pesticide concentrations to the Swiss river network faces significant uncertainties owing to insufficient data on pesticide application, a limited number of substances in monitoring programmes, and an incomplete understanding of the factors contributing to loss rates in catchment areas.[11] Additionally, the extrapolation of the water concentrations to a broader spatial scale requires a local investigation into pathways (e.g. erosion, leaching) and environmental conditions (e.g. geomorphology, adsorption processes).[12]

Compared to water, pesticide monitoring in the terrestrial environment remains relatively unexplored, particularly regarding pollinators and other terrestrial organisms. Only a few studies have investigated pesticides in European soils.[13–16] The large spatial heterogeneity in soil physicochemical and microbial parameters challenges our ability to predict and model pesticide leaching from agricultural land.[17] Recognizing the importance of assessing soil quality, the Federal Office for the Environment has established the National Soil Information System (NABO) in the last few years to collect and document comprehensive information on soil types and their properties across the country.[18] However, soil heterogeneity poses challenges in achieving necessary spatial resolution.[19] Further, pesticides can persist in soils for years or decades after their last application complicating contamination assessments through soil sampling.[15] Therefore, soil sampling can provide information about the overall (chronic) contamination situation that is unspecific to the yearly, seasonal or weekly application.

Sorption, degradation, leaching and transport are the most important processes that influence the fate (persistence and mobility) in the soil.[20] Physicochemical attributes of pesticides such as sorption [carbon-water partition coefficient (K_{oc}) or expressed as organic-carbon normalized Freundlich distribution coefficient (K_{foc})], degradation [soil half-life (DT_{50})], and leaching [groundwater ubiquity score (GUS)] serve as potential indicators of pesticide behaviour in the environment and have been used in various studies.[21,22] K_{oc}/K_{foc} defines the affinity of a pesticide to soil particles compared to its solubility in water. Compounds with lower K_{oc}/K_{foc} values indicate a higher leaching potential into the waterphase.[23] Within this framework using sorption and degradation in soil, the GUS index also is utilized as an indicator that distinguishes pesticides between nonleachers (GUS < 1.8) and leachers (GUS > 2.8) into the groundwater.[24] Conventional water monitoring may not be ideal for acute exposure scenarios. Varying soil compositions complicate the prediction and comparison of pesticide emissions before entering the water phase.

Various studies previously have shown that honey bees can be used to monitor terrestrial exposure of contaminants.[25,26] Recently, Schaad *et al.*[27] showed that temporal profiles of pesticide exposure at a biweekly resolution can be obtained using honey bees. Bees usually forage within a radius of 2–3 km around their hives, sometimes even further (≤6 km), depending on the availability of good nectar and pollen sources.[28] Hence, a bee colony provides numerous randomly collected samples covering usually an area of 28 km^2, occasionally ≤113 km^2.[28,29] Thus, honey bee colonies can serve as an ideal bio-indicator reflecting changes in their environment.[30] While foraging, honey bees can be exposed to various pesticides, including insecticides, fungicides and herbicides, as shown by analysis of bees and various hive products.[31–33] Lipophilic pollutants mainly accumulate in beeswax and hydrophilic pollutants are mainly found in honey.[32] By contrast, pollen (or stored pollen as bee bred) contains a large variety of hydrophilic and lipophilic pollutants,[27] often at higher concentrations than wax or honey,[32] and should therefore preferably be used for monitoring purposes.

During the beekeeping season, a significant part of the pollen is directly consumed, and only a small part is stored as bee bread. The consumption usually is completed within a 2–3-week period.[34,35] Bee bread is a mixture of pollen pellets that have been fermented by adding saliva and other secretions of the honey bees, making it less susceptible to mould than fresh pollen.[36–38] Thus pollen reflects the exposure of the collection day, whereas bee bread represents pesticides collected during the previous days.

With >25 million registered honey bee colonies in Europe[39] and >182 000 in Switzerland[40] there is great potential to integrate bee colonies into nationwide terrestrial pesticide monitoring. Therefore, this study aimed to determine the potential benefit of using honey bees to complement conventional water monitoring programmes. We recorded temporal pesticide profiles in bee bread during an entire agricultural season. These profiles were later compared to the seasonal occurrence of pesticides in a nearby water canal. Furthermore, similarities or differences in the temporal profiles of the pesticides between the two matrices were explained based on their physicochemical properties.

2 MATERIALS AND METHODS

2.1 Study area

The study area is representative of the farming landscape in the central Swiss Plateau. The Seeland region, encompassing the vicinity of our investigated apiaries and the Bibere Canal, is characterized by a high farmland density of similar crop cultivations (Fig. 1). The studied apiaries were 4.5 km apart from each other and situated in Witzwil (2′573′233, 1′202′938) and Bellechasse (2′577′687, 1′203′566) close to the municipalities of Ins and Sugiez in Switzerland (Fig. 1). Five colonies in 12-frame Dadant Blatt hives were included for each apiary. Their queens were of various genetic backgrounds. The colonies were regularly treated against *Varroa destructor* infestation using organic acids (e.g. formic acid in August 2021 and 2022; oxalic acid in December 2021). The bees wax used as foundation sheets in each hive was recycled wax from our own colonies.

The Bibere Canal originates in Courtepin, joins the Broye Canal, and discharges into Lake Neuchâtel. The hydraulic catchment area of the Bibere Canal spans ≈83.1 km^2. A governmental water monitoring station (2′577′790, 1′202′378) in the Bibere Canal is located ≈1.2 km from the apiary in Bellechasse and 4.6 km from the apiary in Witzwil (Fig. 1). The Bibere Canal catchment area is wider than the flight area covered by the bees of the two apiaries. However, given their exemplary character for regional agriculture, the Bibere Canal dewaters a catchment with similar agricultural practices, justifying a comparison of terrestrial bee bread monitoring with aquatic water monitoring.

2.2 Cultivated crop types around the apiaries

In order to present the agricultural crops around the studied apiaries, data were provided from the Office for Geoinformation of the Canton of Bern and Fribourg (www.geodienste.ch) and visualized using QGIS v3.28 (www.qgis.org). The prevalence of crop types exhibited notable similarities across the Witzwil and Bellechasse sampling sites, with a slight variation in the proportion of vegetables, as shown in Fig. 2.

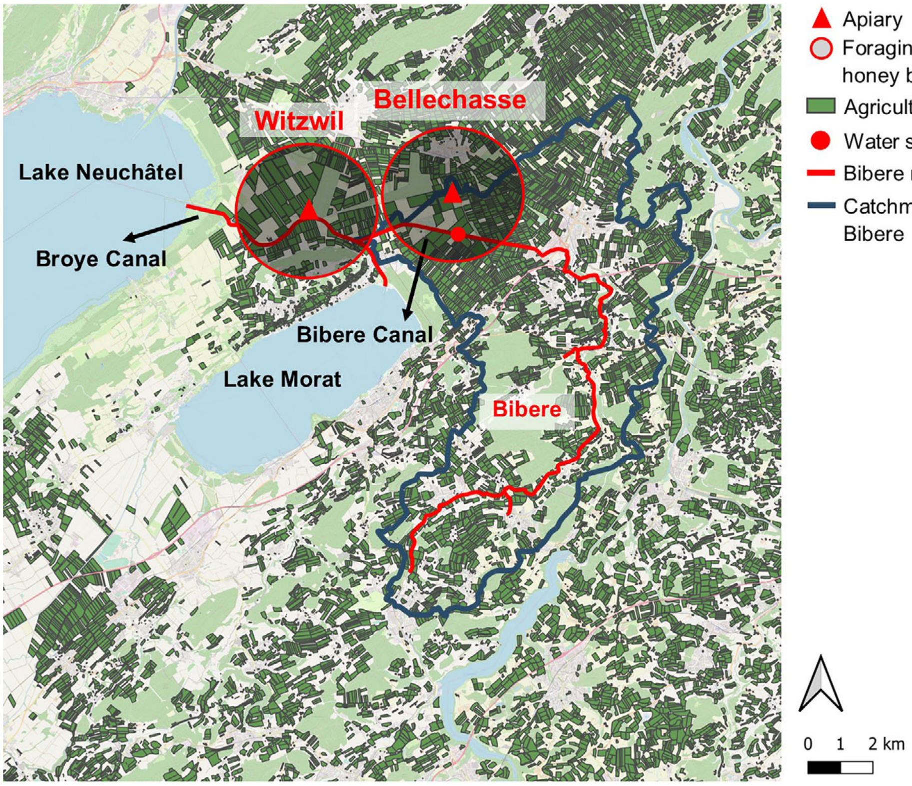

Figure 1. Location of the apiaries in the sampling area of Witzwil and Bellechasse (red triangles) surrounded by a high-density agricultural landscape (dark green). The water monitoring station in the Bibere Canal is shown as a red dot and its hydraulic catchment area as a blue line. Agricultural data were provided by the Office for Geoinformation of the Canton of Bern and Fribourg (www.geodienste.ch), and the course of the Bibere and its catchment is displayed according to the official Swiss website 'hydromaps' (www.hydromaps.ch).

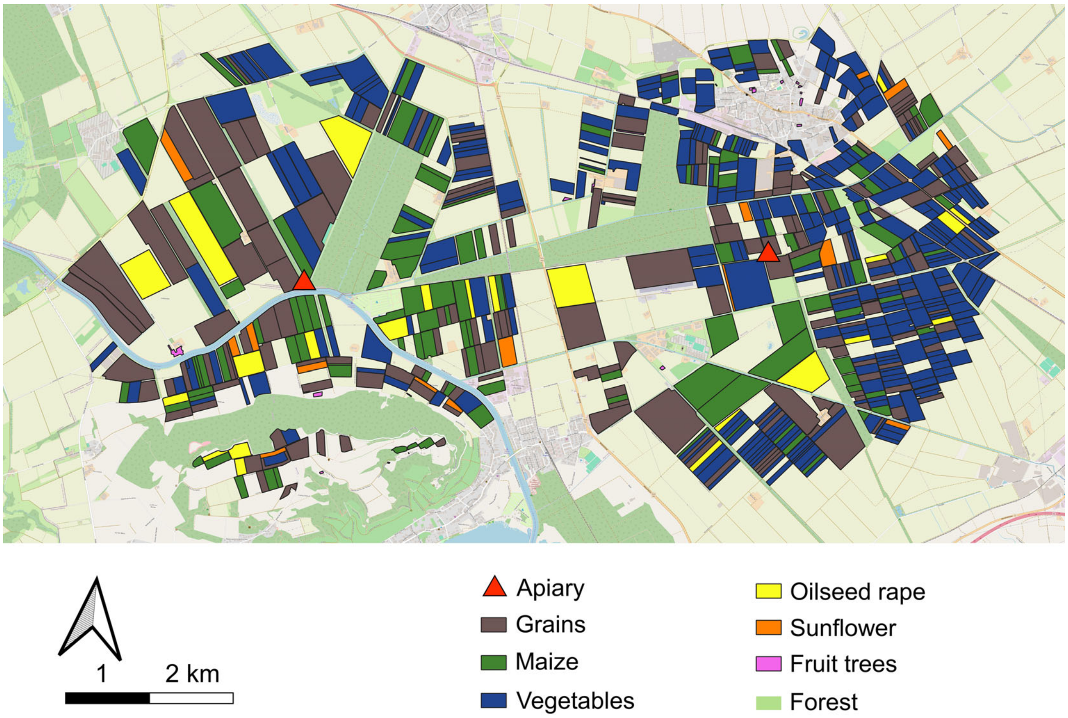

Figure 2. Cultivated crops, predominantly grains (brown), maize (green), vegetables (blue), oilseed rape (yellow), sunflower (orange) and fruit trees (pink) within a 2-km radius around the apiaries in Witzwil (left circle) and Bellechasse (right circle) sampling site in 2022. Forest areas are displayed in lighter green colour. Agricultural data was provided by the Office for Geoinformation of the Canton of Bern and Fribourg (www.geodienste.ch) and visualized by QGIS v3.28 (www.qgis.org).

Within a 2-km radius of the apiaries, a diverse range of crops was cultivated, including different grains (comprising barley, wheat and oats, among others), with maize being the predominant grain, followed by the presence of vegetables, oilseed rape, sunflower, and fruit trees. Data from the Swiss Confederation and the Cantons of Bern and Fribourg did not further distinguish the specifications regarding the types of vegetables and fruit trees. Overall, the region represents the typical agricultural landscape of the Swiss Plateau.

The flowering periods of popular foraging plants grown as crops in the vicinity of the apiaries in Witzwil and Bellechasse for the year 2022 have been reported previously by Schaad *et al.*,[27] with oilseed rape flowering ranging from 5 April to 15 May, for maize from 1 July to 1 September, and for sunflower from 1 to 25 July 2022.

2.3 Bee bread and water sampling

Different foraging behaviours of the honey bee colonies result in different pollen compositions in the bee bread samples. Thus, the type and amount of pesticides in the samples collected on the same day can vary significantly between each colony of an apiary. Previous work showed that five bee colonies are representative of an area where pesticides may be potentially problematic.[27] Thus, representative mean values for the pesticide contamination of the surroundings within the flight distance of the bees were obtained from the five sampled colonies.

Bee bread samples were collected from five colonies of the apiary located close to Witzwil. Sampling took place every second week from 28 March to 18 August 2022, resulting in 11 sampling dates covering the year's primary crop season. If possible, two combs containing fresh bee bread (dull colours) were selected for each colony. A rectangle of ≈30 cm^2 was cut off each comb, placed in a plastic bag (polyethylene) and stored at −20 °C. A specialized tool crafted by Gürle Aricilik (Nilüfer Bursa, Turkey) was employed to extract the bee bread from the comb pieces. The bee bread from the two comb pieces of the same colony gathered on the same day was combined and meticulously homogenized for 10–15 min within petri dish vials, utilizing a bespoke 3D-printed pestle.[27] For comparison, previously published data obtained from the apiary in Bellechasse[27] (same sample collection dates) were incorporated into this study. In total, 60 samples were obtained in Witzwil, which was the same sample number obtained previously in Bellechasse.[27] Samples [wet weight ($_{\text{ww}}$)] were analyzed for 50 pesticides.

Data from pesticide measurements in the surface water of the Bibere Canal at the monitoring station were provided by the Laboratory of the Office for the Environment, Canton Fribourg. Every year, the laboratory routinely monitors 83 pesticides in the Bibere Canal (2-week composite samples) from March to October. The water samples were taken for the 2-week period preceding the bee bread sampling day, thus covering a similar timespan. The start of the sampling for each time period is reported in Table S6 in the Supporting Information. The water (35 mL each) was collected time proportional every 45 min and stored in chilled glass bottles. Over a period of 2 weeks, four bottles were filled. The contents of the bottles were then mixed in the laboratory to obtain a 2-week average sample.

2.4 Quantification of pesticides in bee bread using UHPLC–MS/MS

The pesticides were extracted from bee bread using a QuEChERS procedure (quick, easy, cheap, efficient, rugged, safe), and the quantification was performed by ultra-high-performance liquid chromatography with tandem mass spectrometry (UHPLC–MS/MS), as described by Schaad *et al.*[27] Minor modifications with respect to the previously published method concerned the blank sample and the use of additional internal standards. Bee bread serving as a blank was collected in early spring 2022 from bee colonies located in Orvin (2′582′016.366, 1′222′437.894), a region located in the Jura, a predominantly grassland region of Switzerland. Nevertheless, it contained low levels of permethrin (≈ 3 $\mu\text{g kg}^{-1}$), piperonyl butoxide (≈ 0.5 $\mu\text{g kg}^{-1}$) and terbuthylazine (≈ 0.2 $\mu\text{g kg}^{-1}$). Apart from clothianidin-D3 (Cl-D3), five additional deuterated substances, namely azoxystrobin-D4 (Az-D4), fluopyram-D4 (Fl-D4), terbuthylazine-D5 (Te-D5), thiacloprid-D4 (Th-D4), clothianidin-D3 (Cl-D3) and cyproconazole-D3 (Cy-D3), were included as internal standards. The details of the extraction procedure and the chromatographic separation and quantitation of the 50 pesticides performed by UHPLC–MS/MS using a 1290 Infinity II apparatus (Agilent Technologies, Santa Clara, CA, USA) coupled with an Agilent 6495C tandem quadrupole mass spectrometer are described in Sections S1 and S2, including gradients of liquid chromatography for methods 1–3 (Table S1), ion source conditions (Table S2), and selected ion transitions for identification and quantitation (Table S3).

For quantitation, external matrix-matched calibration was used at nine concentration levels ranging from 0.05 to 1000 $\mu\text{g L}^{-1}$. Corrections were applied for azoxystrobin, clothianidin, cyproconazole, fluopyram, terbuthylazine and thiacloprid using the corresponding deuterated internal standards. Slight adaptations to the limits of detection (LOD) and quantitation (LOQ) values (e.g. owing to new blank, additional deuterated substances) were made for azoxystrobin, chlorpyrifos, coumaphos, difenoconazole, fludioxonil, flumethrin, permethrin, tebuconazole, thiacloprid, thiamethoxam and trifloxystrobin compared to values used the previous study.[27] Recovery values for these pesticides were redefined at their corresponding LOQ levels using spiked samples extracted at least eight times. In the Table S4, all of the LOD and LOQ are listed together with the recovery values at the LOQ level of each pesticide, ranging between 83% and 124% (except fenhexamid: 74%). Because the blank contained low levels of permethrin, piperonyl butoxide and terbuthylazine, the LOD and LOQ values of the three pesticides were adjusted accordingly (Table S4), but no blank subtraction was performed.

2.5 Data sources for the physicochemical parameters of pesticides

For comparative analysis of the pesticides, the physicochemical parameters (K_{foc}, DT_{50} and GUS) were taken from the Pesticides Properties Database (PPDB) of the Agriculture and Environment Research Unit (AERU) at the University of Herfordshire.[23] The Freundlich isotherm (K_{foc}) is based on a nonlinear adsorption model that describes how the concentration of a chemical in soil or sediment relates to its concentration in water at equilibrium. It is often used for systems where adsorption is not linear (K_{oc}), particularly for heterogeneous sorbents and varying chemical conditions. There are no K_{foc} values in the PPDB for thiamethoxam and iprovalicarb, so K_{foc} values were taken from the European Commission[41] and the European Food Safety Authority.[42] The Swiss sales volume for 2022 was provided by the Federal Office for Agriculture[6] of the identified pesticides (given as active substances).

3 RESULTS

3.1 Prevalence of pesticides in bee bread and sales figures

The prevalence of the pesticides in bee bread collected in Witzwil and Bellechasse was compared to the total amount of pesticides sold in Switzerland in 2022 (Fig. 3). Of 50 pesticides tested, 28 (56%) pesticides were quantitated above the LOQ in at least one sample. In addition, three pesticides were detected but were below the quantification limit (>LOD < LOQ).

The types of pesticides in bee bread from both apiaries largely overlapped, demonstrating a similar agricultural landscape across the Seeland region. Of 31 detected pesticides, 23 pesticides (74%) were present at both sites. Additionally, seven pesticides were detected only in bee bread from Bellechasse and one only in Witzwil (Fig. 3). The herbicide prosulfocarb, the insecticide acetamiprid, and the fungicides difenoconazole, cyprodinil, azoxystrobin, fluopyram, trifloxystrobin, pyraclostrobin and desthio-prothioconazole (transformation product of prothioconazole) were detected in >50% of the samples from at least one of two apiaries. The prevalence of the herbicide terbuthylazine, the fungicides mandipropamid and fludioxonil, and the insecticides thiacloprid and indoxacarb were between 30 and 50% (Fig. 3). The fungicides (boscalid, tebuconazole, mepanipyrim, metconazole, iprovalicarb, fenhexamid, cyproconazole and dimoxystrobin), the insecticides (permethrin, spinosad, dimethoate, chlorpyrifos and lambda-cyhalothrin), the herbicides (aclonifen and flufenacet), the acaricide (E)-fenpyroximate and the synergist piperonyl butoxide showed a prevalence of <30%.

In general, herbicides are sold at higher volumes (values given in t active ingredients, a.i) [e.g. prosulfocarb 26.6, aclonifen 20.7, terbuthylazine 11.9 and flufenacet 10.9], followed by fungicides (e.g., difenoconazole 10.0, azoxystrobin 7.9 and mandipropamid 8.2), whereas insecticides are sold at lower volumes (e.g. acetamiprid 2.7 and spinosad 3.1). Pesticides with high sales volumes were more prevalent than those sold at lower volumes, given the especially high prevalence of herbicides and fungicides in our apiaries (Fig. 3). However, the detection of specific pesticides in bee bread samples also could be linked to their different analytical LOD values (Table S4), as illustrated by the prevalence of aclonifen (30%; LOD = 4 $\mu g\ kg_{ww}^{-1}$) *versus* prosulfocarb (88%; LOD = 0.4 $\mu g\ kg_{ww}^{-1}$), although both pesticides have high sales volumes (26.6 t *versus* 20.7 t).

The neonicotinoid insecticide thiacloprid, as well as three additional insecticides (permethrin, dimethoate and chlorpyrifos) and one fungicide (dimoxystrobin) were detected in bee bread, even though their approval as a plant protection product was revoked before 2022, and their application deadline had expired (Fig. 3; sales volume = 0). Two neonicotinoid insecticides, imidacloprid and thiamethoxam, detected in water (Table 1) had no valid application status in the open field in 2022 (authorized in glasshouses from 2019 to mid-2022).[43] In 2022, acetamiprid was the only neonicotinoid insecticide that was still approved (sales volume 2.7 t). Clothianidin, imidacloprid, thiamethoxam, azoxystrobin, cyproconazole, fipronil, tebuconazole and thiacloprid also could have been used as biocides (Tables 1 and S7).[45]

3.2 Temporal profiles of pesticides in bee bread

The herbicides were the earliest quantified pesticides in the bee bread samples, occurring at the end of March. They included flufenacet [Fig. 4(A)], terbuthylazine [Fig. 4(B)] and prosulfocarb [Fig. 4(E)]. Prosulfocarb remained quantifiable in bee bread throughout the season until mid-August, reaching peak levels of 24.3 $\mu g\ kg_{ww}^{-1}$ in May. Terbuthylazine and flufenacet

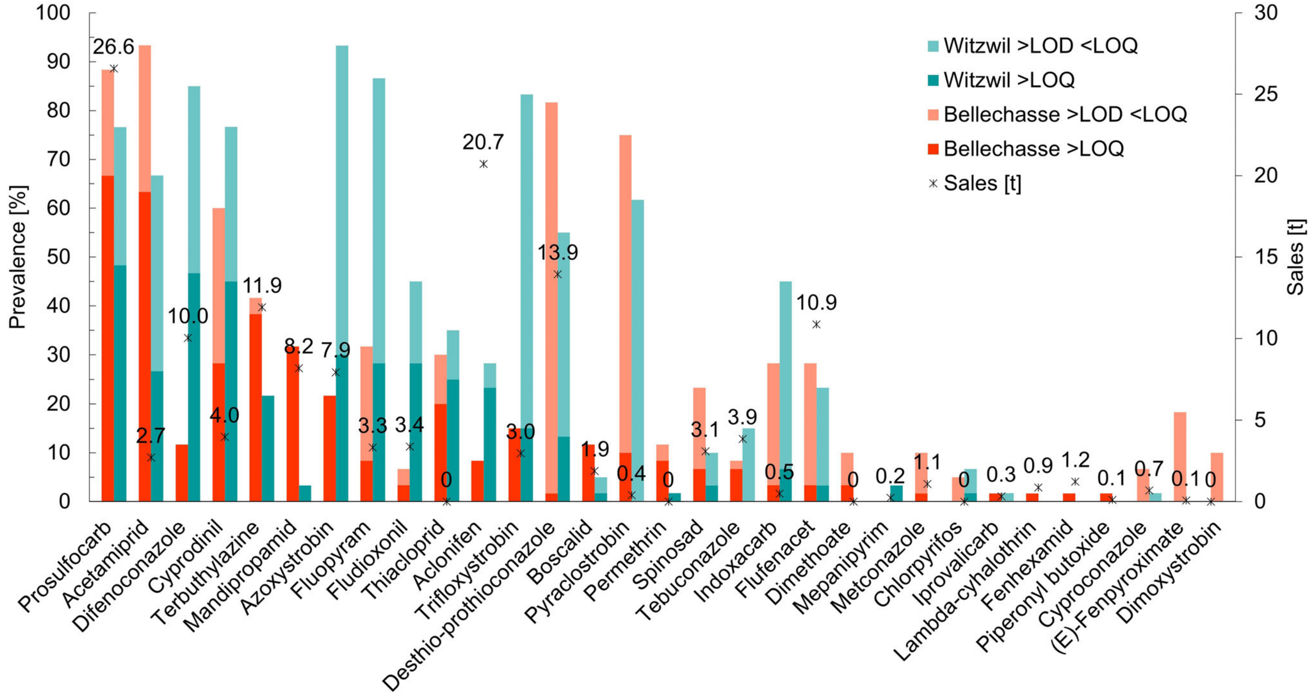

Figure 3. Prevalence (%) of pesticides in bee bread samples from Witzwil (turquoise) and Bellechasse (red) compared to the total amount (marked as ⁎) of the corresponding pesticide (active ingredient) sold in Switzerland during the year 2022. Values >LOQ are represented by dark turquoise and bright red bars, whereas light turquoise and light red represent the values between limits of detection (LOD) and limits of quantitation (LOQ). The pesticides are listed in order of the prevalence priority (>LOQ).

Table 1. Pesticides included in both analytical methods (bee bread and water) grouped according to their level of the GUS value, their chemical properties, and their approval status as plant protection products or biocides

Pesticide[†]	Class[‡]	Log DT-50 field[§]	Log K_{foc}[¶]	GUS[¥]	Bee bread	Water	Approval status as PPP 2022[□]	Crop applications	Biocide[Ψ]
Clothianidin	I[23]	2.08[23]	2.20[23]	3.74 H[23]	<LOD	<LOD	UD (2021)[43]	Maize, oilseed rape, grains, beet[44]	M[45]
Imidacloprid	I[23]	2.24[23]	2.35[23]	3.69 H[23]	<LOD	>LOD; <LOQ	G UD (June 2022)[43]	Maize, oilseed rape, grains, beet[44]	M[45]
Thiamethoxam	I[23]	1.59[23]	1.73[41]	3.58 H[23]	<LOD	>LOQ	G UD (July 2022)[43]	Maize, oilseed rape, grains, beet[44]	M[45]
Azoxystrobin	F[23]	2.26[23]	2.63[23]	3.10 H[23]	>LOQ	>LOQ	A[46]	Maize, oilseed rape, sunflowers, potatoes, grains[46]	M[45]
Cyproconazole	F[23]	2.11[23]	2.56[23]	3.04 H[23]	>LOD; <LOQ	>LOD; <LOQ	A[47]	Grains[47]	M[45]
Methoxyfenozide	I[23]	1.83[23]	2.36[23]	3.00 H[23]	<LOD	<LOD	A[46]	Fruit trees, vineyards[46]	-
Boscalid	F[23]	2.40[23]	2.89[23]	2.68 T[23]	>LOQ	>LOQ	A[46]	Fruit trees, oilseed rape[46]	-
Flufenacet	H[23]	1.59[23]	2.44[23]	2.49 H[23]	>LOQ	>LOQ	A[46]	Maize, potatoes, grains[46]	-
Iprovalicarb	F[23]	1.19[23]	2.03[42]	2.35 T[23]	>LOQ	<LOD	A[46]	Vineyards[46]	-
Terbuthylazine	H[23]	1.34[23]	2.36[23]	2.19 T[23]	>LOQ	>LOQ	A[46]	Maize[46]	-
Dimethoate	I[23]	0.86[23]	1.45[23]	2.18 T[23]	>LOQ	>LOD; <LOQ	A[47]	Cherry trees[48]	-
Fipronil	I[23]	1.81[23]	2.86[23]	2.06 T[23]	<LOD	<LOD	UD (2014)[49]	Maize, grains, beet, oilseed rape[50]	M[45]
Tebuconazole	F[23]	1.67[23]	2.89[23]	1.86 T[23]	>LOQ	>LOQ	A[46]	Oilseed rape, grains, fruit trees[46]	M[45]
Thiacloprid	I[23]	0.91[23]	2.79[23]	1.10 L[23]	>LOQ	<LOD	UD (2021)[51]	Oilseed rape[52]	M[45]
Cyprodinil	F[23]	1.65[23]	3.36[23]	1.06 L[23]	>LOQ	>LOQ	A[46]	Fruit trees, vegetables[46]	-
Prosulfocarb	H[23]	0.99[23]	3.23[23]	0.76 L[23]	>LOQ	>LOQ	A[46]	Fruit trees, oilseed rape[46]	-

Abbreviations: LOD, limits of detection; LOQ, limits of quantitation; GUS, groundwater ubiquity score.

[†] Pesticide: Detected in both matrices (green); detected in bee bread only (red); detected in water only (blue); not detected in bread and not in water (grey).

[‡] Class of pesticides: Insecticides (I), fungicides (F), herbicides (H).

[§] Log soil half-life (DT_{50}): nonpersistent (<1.5); moderately persistent (>1.5 < 2.0); persistent (>2.0 < 2.6); very persistent (>2.6).

[¶] Log organic-carbon normalized Freundlich distribution coefficient (Log K_{foc}): very mobile (<1.2); mobile (>1.2, <1.9); moderately mobile (>1.9 < 2.7); slightly mobile (>2.7 < 3.6); nonmobile (>3.6).

[¥] Groundwater GUS: L-low (GUS <1.8), T-transition state (GUS 1.8–2.8), H-high (GUS >2.8).

[□] Approval status as a plant protection product (PPP) in Switzerland 2022: Authorized in glasshouses (G); authorized in open land (A); utilization deadline (UD).

[Ψ] Products as a biocide on the Swiss market in 2022: Products on the market (M), for details see Table S7; no products on the market (–).

were detected until July and reached peak values of 8.1 and 1.7 μg/kg$_{ww}^{-1}$, respectively, in June at the apiary in Bellechasse.

The insecticide thiacloprid [Fig. 4(G)] was detected from the end of March until July (excluding 23 June), with the highest average concentrations recorded in April at both apiaries (Witzwil 3.4 μg kg$_{ww}^{-1}$ and Bellechasse 14.6 μg kg$_{ww}^{-1}$), even though it was not sold that year. The fungicide azoxystrobin [Fig. 4(C)] was detectable throughout the sampling period in Witzwil and reached the highest peak concentrations in August, at 22.5 μg kg$_{ww}^{-1}$ in Bellechasse. The highest concentrations were measured for the fungicide cyprodinil [Fig. 4(F)], reaching peak levels of 480.7 μg kg$_{ww}^{-1}$ in April (Table S5) at the apiary in Bellechasse. The fungicides boscalid [Fig. 4(D)] and tebuconazole [Fig. 4(H)] were present from July to August, with peak levels in July of 14.8 and 4.0 μg kg$_{ww}^{-1}$, respectively, both at the apiary in Bellechasse.

3.3 Comparison of residues in bee bread to pesticides detected in surface water

Of the target pesticides in the surface water, 16 pesticides overlapped with our analysis of bee bread,[27] which included six fungicides (azoxystrobin, boscalid, cyproconazole, cyprodinil, iprovalicarb and tebuconazole), three herbicides (flufenacet, prosulfocarb and terbuthylazine), and seven insecticides (clothianidin, dimethoate, fipronil, imidacloprid, methoxyfenozide, thiacloprid and thiamethoxam). The 16 shared pesticides are listed in Table 1. Of these pesticides, azoxystrobin, boscalid, cyprodinil, cyproconazole, dimethoate, flufenacet, prosulfocarb, tebuconazole and terbuthylazine were detected in bee bread and water (nine pesticides). Iprovalicarb and thiacloprid were detected solely in bee bread, whereas imidacloprid and thiamethoxam were detected only in water, as illustrated in Table 1. The representative mean concentrations of the quantitated pesticides (>LOQ) are listed in Table S5 (bee bread; 10 pesticides), and the concentrations of the 2-week composite samples (>LOQ) of the Bibere Canal in Table S6 (water; eight pesticides).

Eight of these pesticides were quantified at higher levels. The comparative analysis between these pesticides in bee bread and water revealed an overlapping temporal distribution pattern for flufenacet, terbuthylazine, azoxystrobin and boscalid (Fig. 4). Peak levels of these pesticides appeared in bee bread and water at

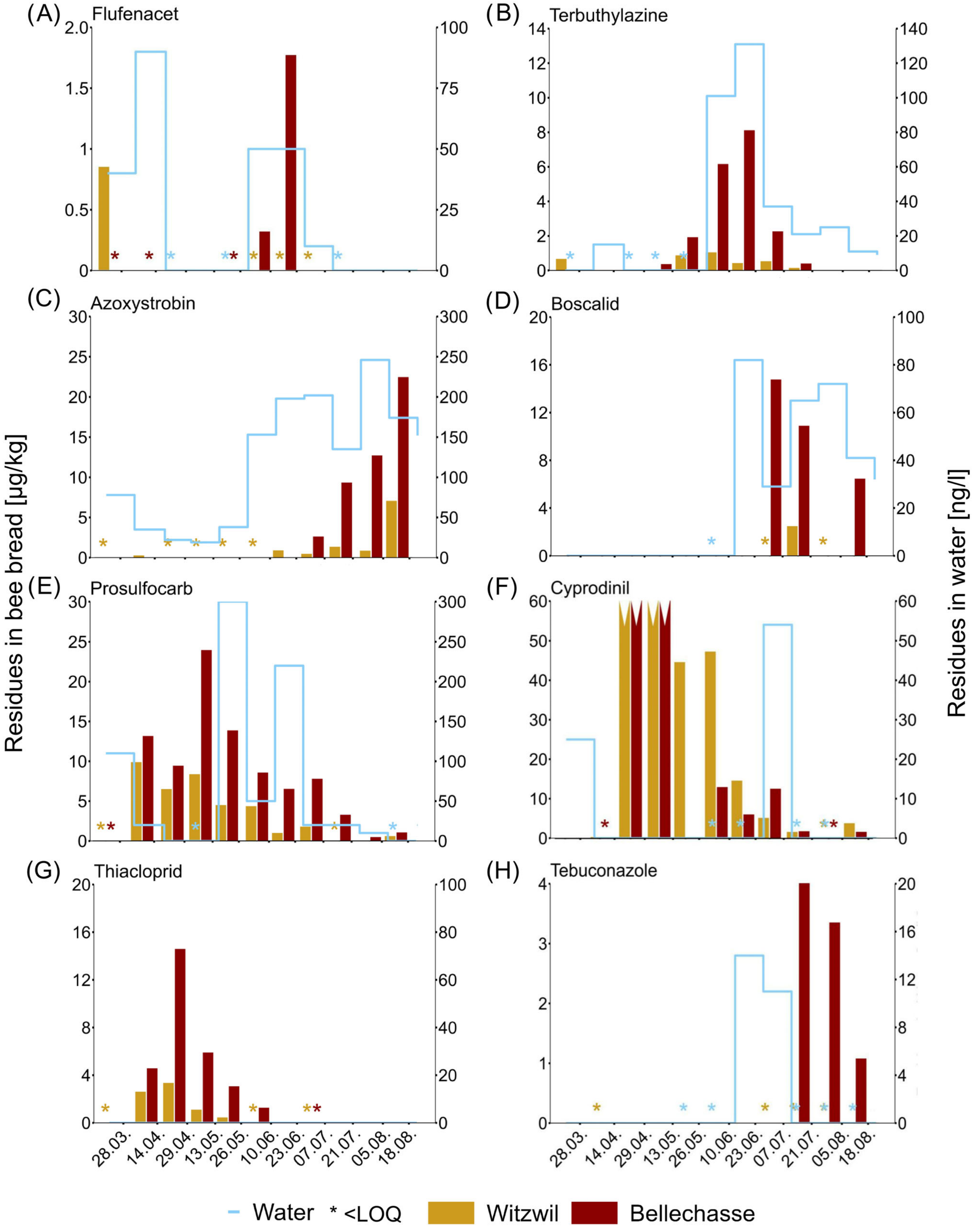

Figure 4. Comparison of pesticide levels in bee bread from Witzwil (representative mean values from five colonies shown as yellow histogram bars) and Bellechasse (representative mean values shown as dark red histogram bars) and residue levels in the Bibere Canal (composite biweekly samples shown as blue lines). Asterisks represent values above limits of detection (LOD) but below limits of quantitation (LOQ). The x-axes show the sampling dates for bee bread in 2022. Within the categories, pesticides are ordered according to their temporal occurrences in the season. As shown with jagged tips, the four histogram bars of cyprodinil (yellow and red on 29 April and 13 May) extend beyond the applied scale (Witzwil: 386.4 and 86.5 µg $\mathrm{kg_{ww}}^{-1}$; Bellechasse: 480.7 and 85.2 µg $\mathrm{kg_{ww}}^{-1}$).

similar time points during the agricultural season [Fig. 4(A)–(D)]. Notably, flufenacet [Fig. 4(A)] and terbuthylazine [Fig. 4(B)] displayed dual peaks in both matrices at the end of March/beginning of April and June. In spring, flufenacet and terbuthylazine were detected at the same time, whereas maximal levels in water of 90 ng L^{-1} (flufenacet) and 15 ng L^{-1} (terbuthylazine) were recorded 2 weeks later in April. For flufenacet, a second peak in bee bread and water was observed from late May to early June, with maximal levels of 50 ng L^{-1} in the water. Terbuthylazine emerged simultaneously in both matrices between mid-May and early August, reaching the highest peak level of 131 ng L−1 in the water in June.

Azoxystrobin [Fig. 4(C)] was quantifiable in water throughout April and May, with three peaks in water at the end of March, the end of June and the beginning of August. In late May and early June, a significant increase in azoxystrobin was observed in water, followed by an increase in bee bread in early July. Maximum values of 246 ng L^{-1} in water and 22.5 μg $kg_{ww}{}^{-1}$ in bee bread (apiary in Bellechasse) were recorded in August. Only trace levels were detected in bee bread during the early period. Boscalid [Fig. 4(D)] exhibited two peaks in water at the end of June (maximum of 82 ng L^{-1}) and at the end of July. In bee bread, only one peak encompassing this period was observed.

Prosulfocarb, cyprodinil, thiacloprid and tebuconazole [Fig. 4 (E)–(H)] exhibited distinctive behavioural patterns in water compared to bee bread. The water analysis of prosulfocarb revealed three peak concentrations at the end of March, the end of May and the end of June, with the highest concentration of 300 ng L^{-1} at the end of May. Cyprodinil was present at high concentration levels in bee bread throughout the season from April to August, although it was not quantifiable on 5 August. By contrast, cyprodinil was quantified in water, with peak levels of 25 ng L^{-1} in March and 54 ng L^{-1} in July. Thiacloprid [Fig. 4(G)] could not be detected in the water throughout the season. Conversely, although bee bread exhibited maximal tebuconazole [Fig. 4(H)] values in late July, water samples displayed earlier tebuconazole peak levels of 14 ng L^{-1} during June and July.

3.4 Leaching potential of pesticides

The comparison of physicochemical parameters, such as log DT_{50} soil with log K_{foc} in conjunction with the GUS index, showed different characteristics for the 12 pesticides (of the overlapping 16 pesticides) quantitated in at least one of the two matrices bee bread and water (Fig. 5; Table 1). According to Lewis *et al.*,[23] nonpersistent pesticides, such as terbuthylazine, iprovalicarb, prosulfocarb, thiacloprid and dimethoate, degrade rapidly in soil ($DT_{50} < 30$ days or log $DT_{50} < 1.5$). The moderately persistent pesticides tebuconazole, thiamethoxam, cyprodinil and flufenacet have DT_{50} values between 30 and 100 days, and persistent pesticides have values above 100 days (log $DT_{50} \geq 2$; boscalid, imidacloprid and azoxystrobin).[23] Pesticides with log K_{foc} values below 1.9 are considered mobile (e.g. thiamethoxam), and those between 2.7 and 3.6 are considered slightly mobile (e.g. cyprodinil).[23]

Pesticides with a GUS index >2.8, such as azoxystrobin (GUS = 3.10),[23] tend to leach easily into the groundwater. By contrast, pesticides with GUS < 1.8, such as cyprodinil, prosulfocarb and thiacloprid (Table 1; Fig. 5), remain in the soil for a longer time, which is in line with our observations. Similar temporal profiles in bee bread and water were observed for azoxystrobin, a groundwater leacher according to its GUS index, whereas the nonleachers cyprodinil and prosulfocarb showed different temporal profiles, as shown in Fig. 4. On the transition state between leachers and nonleachers (1.8< GUS < 2.8) were terbuthylazine, iprovalicarb, flufenacet and boscalid, with higher GUS indices (between 2.19 and 2.68) than tebuconazole (GUS = 1.86) (Table 1; Fig. 5). Accordingly, the temporal profiles of terbuthylazine, flufenacet and boscalid in bee bread and water were similar, whereas the profile of tebuconazole did not overlap (Table 1; Fig. 4). The open field application in Switzerland was revoked for imidacloprid and thiamethoxam in 2018, and the thiacloprid utilization deadline expired in 2021.[43,51]

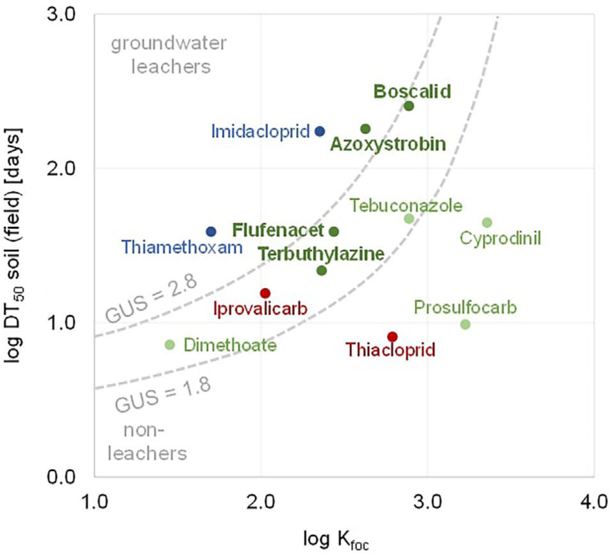

Figure 5. Comparison of the log DT_{50} of soil to the log K_{foc} incorporating the groundwater ubiquity score (GUS) index shown for the pesticides that were detected in bee bread and water. Pesticides detected in both matrices are highlighted in green. Those with similar temporal profiles in bee bread and water are shaded dark green, whereas those with dissimilar patterns are light green. Pesticides detected solely in bee bread are marked in red, and those only in water in blue. DT_{50} of soil and K_{foc} values were taken from PPDB,[23] ECHA[41] (K_{foc} thiamethoxam) and EFSA[42] (K_{foc} iprovalicarb). GUS lines were incorporated according to Arp & Hale.[53]

4 DISCUSSION

Our study revealed that bee bread can serve as a viable biomarker for monitoring pesticides by complementing the conventional practice of water monitoring and permitting a more comprehensive assessment of the exposure of terrestrial organisms to potential pesticide exposure. The study encompassed 2-week systematic collections of bee bread and composite water samples throughout the season, allowing temporal profiling of the appearance of pesticides in a terrestrial environment and a direct comparison of their appearances in the water phase. The patterns of appearance differ particularly for pesticides that degrade relatively rapidly in soil and are moderately mobile. They are less prone to leach from soils into water. Pesticides with a GUS index <1.8 were recorded promptly in bee bread, whereas they did not appear in water (e.g. thiacloprid) or exhibited a delayed emergence in the surface water (e.g. cyprodinil or prosulfocarb). Hence, our study suggests that bee bread may be a more sensitive indicator for terrestrial organisms, as it allows for a near-time recording of the terrestrial exposure risk.

4.1 Complementing conventional water surveys with terrestrial monitoring

Monitoring pesticides in water is well-established, as long-term historical data archives exist in Switzerland for selected pesticides (NAWA, NAQUA).[9,10] As our study reports, this monitoring focused on water organisms and consumer safety only partially captures pesticide exposure for terrestrial organisms. Therefore, monitoring studies using bee bread may complement such water monitoring, as it allows the detection of not only pesticides assigned to groundwater leachers, but also pesticides belonging to the nonleachers, which could be missed or delayed in water monitoring (e.g. thiacloprid, prosulfocarb or cyprodinil). Hence, a near-time recording of the applied pesticides is possible, whereas conventional water monitoring is less suitable for an acute exposure scenario, because the adherence of pesticides to soil particles results in a lag time for entering the water phase. Furthermore, monitoring pesticides with bee bread promptly reflects seasonal variations in pesticide use. Although water samples can have a greater catchment of the environment, the allocation of the pesticide concentrations found is more difficult, as pesticide concentrations may enter the water phase through different pathways, such as volatilization, runoffs from agricultural or urban uses, and areal application through spray drift or leaching processes of the soils.[54] For example, a study on prosulfocarb showed that the risk of surface water contamination through runoff increases when applied as a pre-emergent herbicide on bare soil.[55] Furthermore, Fabre *et al*.[11] found that high precipitation or runoff significantly decreases pesticide concentrations. By contrast, Lewan *et al*.[56] stated that high pesticide inputs into surface waters are mainly related to precipitation events. Therefore, the influence of precipitation on pesticide concentrations in surface waters discussed in the literature is controversial, as precipitation may dilute or enrich pesticide concentrations in water systems.

4.2 Influence of soil types on the leaching behaviour of pesticides

Previous research has shown that the GUS index-related distinction becomes oversimplified when macropore flow becomes important.[57] Further studies with additional pesticides with a broad range of GUS values would confirm our observed trends. Factors such as prevailing climatic conditions, soil biotic characteristics and other environmental variables may significantly influence the fate and behaviour of pesticides.[58] For example, the pH value, the soil organic carbon, the soil organic matter and the cationic exchange capacity can vary between soil types, affecting leaching potentials.[59–61] A previous study by Rosenbom *et al*.[62] showed that clay till soils result in higher leaching potentials for azoxystrobin and terbuthylazine compared to sandy soils. By contrast, dimethoate and prosulfocarb were found to have low leaching potentials in both soil types, and thiacloprid was not detected in groundwater from either soil.

Furthermore, old emissions from the soil are possibly responsible for some pesticides that were applied years ago. Examples in our study are the insecticides imidacloprid and thiamethoxam, which were detected in water. The use of these two neonicotinoids in 2022 is unlikely, because their authorization for open land use expired several years ago.[43] Likewise, a Swedish study reported that the persistent and mobile groundwater leacher azoxystrobin was stored in clay soils for >10 years and later leached into water in batches.[21]

4.3 Detection of a pesticide in water in relation to its sales volume

The sales reported for the pesticides in our study reflect the volume sold in Switzerland in 2022. They approximately estimated the rate at which the pesticides might have been applied at our study sites. The quantity of a pesticide applied may influence the level to which a pesticide appears in the water. Within the scope of this study, the herbicide prosulfocarb was the pesticide with the highest sales volume in 2022 (26.6 t).[6] This is reflected in its appearance in water [Fig. S1(A)]. Although prosulfocarb belongs to the nonleachers owing to its low persistence and moderate mobility (GUS = 0.76),[23] it was found in high concentrations in water in addition to bee bread. High levels of prosulfocarb in groundwater as a consequence of a high application rate also were found by Troldborg *et al*.[63] By contrast, thiacloprid was not sold in 2022, because its authorization expired in 2021.[51] However, in our study, thiacloprid was detected in bee bread, possibly owing to unauthorized use on some oilseed rape fields. Such a punctual application in the field and its nonleaching characteristics, might explain why thiacloprid was not detected in the water. Thiacloprid also might have been diluted to concentrations below LOD as a consequence of the large hydraulic catchment area of the Bibere Canal. Furthermore, the distance of the pesticide application to the water source also plays an important role, which was not explicitly analyzed in this study. Pesticides can leach from soils in water with a lag time of several years, as shown for thiamethoxam or imidacloprid (whose authorization for open fields has ceased since 2019[43]).

Furthermore, in 2022 thiacloprid may have been applied as a biocide in wood protection. Products as biocides containing thiacloprid might still have been on the market in 2022, even though its notified authorization expired 2019 (Tables 1 and S7). After expiration, products can remain on the market for a few years and can be used until the expiration date of the products. Another possibility could be that the detection of thiacloprid in 2022 could be to the consequence of agricultural applications in previous years. Because the dissipation rate (RL_{50}) of thiacloprid on plant matrix is 8.8 days [Fig. S1(B)],[23] it is probably unlikely to find high levels in bee bread in the subsequent year.

4.4 Crop application

The herbicides flufenacet, terbuthylazine and prosulfocarb were detected in bee bread and water as early as March in the season of 2022. Flufenacet can be applied on cereals up to the main shoot growth stage (BBCH 00 to BBCH 32) until mid-April.[46] Later, flufenacet can be used until the end of June on maize and potatoes at the seedling stage (BBCH 00 to 07). The time point of the occurrence indicates the possible application of flufenacet on the mentioned crops [Fig. 4(A)]. Prosulfocarb is used for weed control in various grain and vegetable crops,[46] which is reflected in its presence in bee bread and water throughout the season. Terbuthylazine is registered mainly for application on maize (BBCH 00 to 16), and can be applied until the end of June.[46] This time frame agrees with the occurrence of terbuthylazine in bee bread and water at the end of June [Fig. 4(B)].

The insecticide thiacloprid was detected in early spring. Thiacloprid was previously registered as a plant protection product for oilseed rape against the canola gloss beetle in Switzerland.[52] Despite its utilization deadline in September 2021,[51] thiacloprid appeared in the bee bread of both apiaries during the flowering period of oilseed rape from mid-April to late May [Fig. 4(G)]. Its occurrence in bee bread might be related to unauthorized use or, less likely, to applications in previous years.

Fungicides were detected in early spring (cyprodinil) or later in August (azoxystrobin, boscalid, cyprodinil and tebuconazole). For example, azoxystrobin is primarily used on oilseed rape, cereals and sunflower,[46] but is also registered for application to seed dressing in maize.[46] In springtime, azoxystrobin was quantifiable in water, whereas only traces were detectable in bee bread [Fig. 4(C)]. A possible explanation for the low residue levels in bee bread could be related to climatic factors, which can influence the foraging behaviour of honey bees. During the sampling period from 1 to 14 April, maximum temperatures remained below 12 ° C, accompanied by several days of precipitation[65] (Fig. S2). However, honey bees rarely forage for pollen below 10 °C.[66,67] The fungicide boscalid can be applied during various stages of oilseed rape growth (BBCH 20 to 32; BBCH 61 to 65), on potatoes or to fruit trees post-flowering,[46] whereas cyprodinil is authorized for the use on wheat (BBCH 31 to 32) and for fruit trees until the end of the flowering period (BBCH 69) and at fruit development stages (BBCH 71 to 72; BBCH 77 to 79). Flowering periods of fruit trees typically occur between March and May in Switzerland.[68]

In our study, high cyprodinil levels were detected in bee bread collected at the end of April, which may have been related to such use. Furthermore, cyprodinil also can be applied on lawns,[46] which indicates urban use with potential discharges into surface waters. In agricultural practices, the fungicide tebuconazole is approved for use on oilseed rape (on seedlings in autumn), grains (until summer) and fruit trees (summer).[46] In addition to its agricultural use, tebuconazole is also used as a biocide (Tables 1 and S7) in urban areas for the surface treatment of wood, walls and facades, from where it can enter surface water.[69,70] Tauchnitz *et al.*[71] showed that tebuconazole was one of the most frequently detected pesticides in surface waters from 53 nonagricultural uses.

4.5 Outlook

Switzerland's large number of beehives holds great potential for nationwide pesticide monitoring across different regions with varying agricultural, rural or urban characteristics. In the future, these beehives could enable testing for other contaminants, such as heavy metals and micropollutants, to expand our understanding of how pesticides and other pollutants can reach nontarget organisms, such as honey bees and other pollinators. Further studies spanning several years and assessing weather variability may provide a better understanding of bee exposure and the cycle of pesticides in the environment.

5 CONCLUSION

Studies on terrestrial environments are under-represented in comparison to monitoring studies on aquatic environments, such as rivers and creeks, where the allocation to the catchment area is sometimes difficult and the levels of contaminants might be amplified by peak values, or underestimated owing to dilutions through rain events. Pesticides, which sorb to soil particles or with low stability (GUS indices <1.8) can be promptly detected in bee bread, whereas they may not appear in water or occur at a much later time point. This study demonstrated that bee bread is a suitable bio-marker complementing water surveys, given that it allows the monitoring of acute, season-specific and application-specific scenarios of pesticide contamination for a terrestrial environment.

AUTHOR CONTRIBUTIONS

CK and AC: Conceptualization, project administration, and funding. SS: Investigation, validation; MF and CK: Supervision of analytics; BD: Beekeeping; MF, SS, BD: Sample collection; SS, CK, AK, and AC: Data interpretation; SS: Writing of original draft; CK, AK, and AC: Review/editing of the manuscript. All of the authors read and approved the final manuscript.

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CONFLICT OF INTEREST

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

DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in the supplementary material of this article.

SUPPORTING INFORMATION

Supporting information may be found in the online version of this article.

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