Concomitant determination of pesticides in soil and drainage water over a potato cropping season reveal dissipations largely in accordance with respective models

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HIGHLIGHTS

- High frequency monitoring of pesticides in drainage water and soil
- Pesticide dissipation in soil followed in general first order kinetics
- Pesticide emission dynamics in drainage water varied substantially.
- Legacy compounds behaved fundamentally differently to freshly applied ones.
- Prospective and retrospective exposure assessments largely matched

GRAPHICAL ABSTRACT
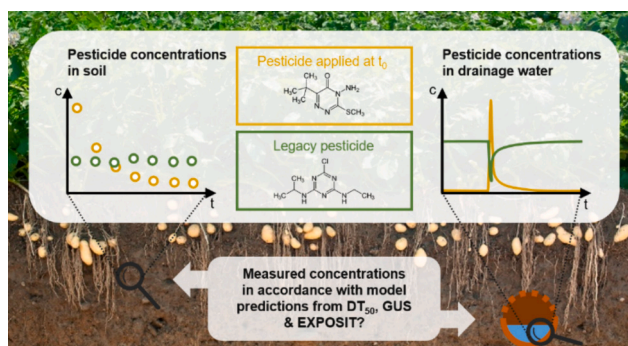
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ABSTRACT

Pesticides are widely used in agriculture where they do not only reach their targets but also distribute to other environmental compartments and negatively affect non-target organisms. To prospectively assess their environmental risk, several tools and models using pesticide persistence (DT_{50}) and leaching potential (groundwater ubiquity score (GUS), EXPOSIT) have been developed. Here, we simultaneously quantified 18 pesticides in soil and drainage water during a conventionally grown potato culture at field scale with high temporal resolution and compared our findings with predictions of the above models. Overall dissipations of all freshly applied compounds in soil were in line with published DT_{50} field values and their occurrences in drainage water were generally consistent with GUS and EXPOSIT models, respectively. In contrast, soil concentrations of the legacy pesticide atrazine and one of its transformation products (atrazine-2-hydroxy) were constant during the entire sampling campaign. Moreover, during peak discharge atrazine concentrations in drainage water were diluted whereas those of freshly applied pesticides were maximal. This difference demonstrates that the applied risk assessment tools were capable of predicting environmental concentrations and dissipation of pesticides at the short and medium time scale of a few half-lives after application, but fell short of capturing long-term trace residues.

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1. Introduction

Pesticides are used to protect plants against pests and to increase crop yields. Currently, over 3.5 million tons of these agrochemicals are used each year worldwide (FAO 2023). In Switzerland, > 2000 tons of pesticides are applied annually (BLW, 2018). Despite their benefits, pesticides can negatively affect human and ecological health. Residues in field crops for human consumption are the major contributor for human pesticide uptake and resulting health impacts (Fantke and Jolliet, 2016). Risk assessments dealing with pesticide ingestion become more demanding (Hamilton et al., 2004) and plant uptake and bioconcentration models more detailed (Li and Fantke, 2023; Xiao et al., 2021), hence an understanding of the behavior of pesticides in the environmental systems surrounding crops and target organisms is essential. Besides humans, also non-target organisms in soil and water ecosystems are affected as a considerable fraction of up to 50 % of the applied amounts ends up on the soil surface (Rodríguez-Eugenio et al., 2018) and can be spread via different transport processes, such as leaching, surface runoff and volatilization (Galon et al., 2021; Mottes et al., 2014). Consequently, agricultural soil is regularly exposed to pesticides and their residues were frequently detected in agricultural fields, even years after the last application (Froger et al., 2023; Riedo et al., 2021; Silva et al., 2019). Measured concentrations of the individual pesticides in the aforementioned studies ranged from < 1 μg/kg to several 100 μg/kg and the maximum total concentration exceeded 1000 μg/kg. Pesticide residues then adversely affected arbuscular mycorrhizal fungi, microbial biomass or earthworms (Froger et al., 2023; Riedo et al., 2021).

To assess environmental risks associated with the pesticide use, manufacturers have to provide data on persistence usually expressed as DT_{50}, i.e. the time needed for the dissipation of 50 % of the applied amount assuming pseudo-first order kinetics. This allows to predict pesticide concentrations in soil which in combination with toxicity leads to a certain risk. However, field monitoring studies often provide data for one time point long after the application and data on initial dissipation dynamics of pesticides in soil under real-world conditions are scarce.

With precipitation succeeding pesticide applications the chemicals are partly washed off from crops onto the soil from where they can be transported to surface waters (Leu et al., 2004). Receiving water bodies show widespread occurrence of pesticides (Spycher et al., 2018) negatively impacting aquatic organisms, such as insects and other macroinvertebrates (Stehle and Schulz, 2015). At catchment scale pesticide losses of 0.005–0.82 % to the receiving water bodies were reported (Doppler et al., 2014; Leu et al., 2004). Surface runoff is considered the most important pathway for rain-driven transport of pesticides to surface waters (Flury, 1996; Kladivko et al., 2001) for fields with slopes > 2 % (Gramlich et al., 2018), whereas on drained fields with a smaller slope, export occurs mainly via drainages. In Switzerland, only one study reported losses via drainage of up to 1.3 % for sugar beet seed dressings and 0.5 % for spray-applied pesticides (Wettstein et al., 2016), which agrees with studies conducted elsewhere (Brown and van Beinum, 2009; Kladivko et al., 2001). This entrance pathway into the environment recently attracted attention, as drainage systems are not always properly documented and the actual drainage area is potentially larger than previously indicated (Koch and Prasuhn, 2020).

As with persistence in soil, the leaching potential of pesticides to groundwater can be prospectively assessed using indices, such as LIX (Spadotto, 2002), LEACH.M (Papa et al., 2004), LIN (Gramatica and Di Guardo, 2002) or the groundwater ubiquity score (GUS) (Gustafson, 1989). The latter combines the half-life of a pesticide (DT_{50}) and its organic carbon-water partition coefficient ($K_{f,OC}$) to a leachability score that can then be compared with the pesticide's exported fraction (Rechsteiner et al., 2021). To finally estimate the predicted environmental concentrations and exported loads from agricultural fields, regulatory tools, such as the MACRO model for FOCUS drainage scenarios

or the EXPOSIT model can be used (Kobierska et al., 2020), taking into account additional site- and culture-specific information, such as application rate and interception.

Although the approach of comparing prospective and retrospective environmental risk assessments had been carried out e.g. for pharmaceuticals (Knacker et al., 2008), to our knowledge, for pesticides no comprehensive soil-drainage water monitoring at field scale, with subsequent comparison of prospective and retrospective exposure assessment endpoints (e.g. predicted environmental concentrations (PEC) vs. measured environmental concentrations (MEC)) has yet been executed. To this end, concentrations of pesticides applied during a conventional potato cultivation were measured at high temporal resolution in both matrices. As a suitable model culture, potato was chosen as it is one of the most pesticide-intensive crops grown in Switzerland. We (i) elucidate fate and temporal behavior of the applied pesticides in soil and drainage water and their losses exported via drainage, (ii) discuss these findings in the context of the physico-chemical properties of the pesticides, field characteristics and weather conditions and (iii) compare the field data with model predictions based on pesticide persistence and leachability.

2. Materials and methods

2.1. Experimental field, potato cultivation and pesticide application

Potatoes were cultivated on an experimental field at Agroscope Reckenholz (47°24′45″ N; 8°30′53″ E) that is described in detail elsewhere (Hartmann et al., 2008; Hoerger et al., 2011; Rechsteiner et al., 2021; Wettstein et al., 2016). In brief, it expands over 0.2 ha (23 m × 89 m) and has a gentle slope of 1–2°. With fractions of 30 % sand, 39 % silt and 31 % clay and an organic carbon (OC) content of 1.9 % in the upper horizon (0–29 cm) it is classified as a gleyic cambisol according to the World reference base for soil (IUSS Working Group WRB, 2015). More details on soil properties can be found in the supplementary material (SM, Table S1).

The drainage is installed 80 to 90 cm below ground. Two long and two short pipes (diameter of 15 cm) connected to a main pipe collect drainage water from the experimental field (Fig. S1). The main pipe is leading to a duct equipped with a small spillover reservoir for water sampling. While the groundwater level (100 to 125 cm) is generally below the drainage tubes (Hartmann et al., 2008), there is often excess water (i.e., amount of precipitation minus the amount of potential evapotranspiration at a given timepoint (Klaus et al., 2014)), that is partly drained, e.g., via preferential flow (Rechsteiner et al., 2021). An irrigation experiment (Wettstein et al., 2016) showed that at steady flow state approximately 50 % of the irrigated water was recorded by the discharge measurement. The authors suggested that the missing 50 % of the leaching water most likely bypassed the drainage collection tubes as groundwater flow or as lateral flow over a locally denser B-horizon. Hence, specific artefacts of the experimental field are at least partially known and are accounted for in all mass flow analyses.

A Teledyne ISCO 6712 autosampler (Lincoln, NE, USA) was installed in the field equipped with a bubbler module and connected to a V-weir in the main pipe for discharge measurement (calibrated from 0.001 to 2 L/s) and flow-proportional sampling. In total, four EnvironSCAN FDR (frequency-domain-reflectory) probes were installed (Sentek Pty Ltd., Stepney, South Australia) to measure soil moisture in several depths from 10 to 100 cm (location see Fig. S1; data presented in Fig. S5). Weather data was gathered from a meteorological station (Reckenholz, 443 m above sea level, 47°25′40″ N, 8°31′04″ E, Meteoschweiz) situated 300 m off the field.

The field was ploughed in March 2020 and harrowed on April 2. One day later the potato tubers of the variety Désirée (Cultivator HZPC, Mitselvier, Netherlands) were put into the soil ridges with a fully automated potato planting machine (34 cm distance between each tuber, 70 cm distance between the ridges, 20 cm ridge height). On April

7 the ridges were hilled up. During the growing period the field was irrigated once on July 10 with 34 mm of water (Fig. 2B). The potatoes were harvested on August 20.

Pesticide applications largely took place according to conventional agricultural practice, following application plans as suggested by regional plant protection advisory centers and commercial product vendors. The first pesticide application was conducted with a mixture of three herbicides on April 17, 2020. Until the end of July, nine additional applications took place (application time points indicated as numbers 1–10 in Figs. 1 and 2C). In total, 15 different products with 20 different chemicals were used (13 fungicides, 5 herbicides, 1 insecticide, 1 molluscicide). Most pesticides were applied once, four were applied twice, two three times and one four times. At each event, more than one pesticide was applied. The application rate ranged from 13 g/ha to 2000 g/ha depending on the product and compound. For a detailed application plan see Table S2. An overview on pesticides applied on the experimental field since 2007 can be found in Table S3.

### 2.2. Monitoring plan and procedure

Soil samples were taken according to the sampling method of the Swiss Soil Monitoring Network (Gubler et al., 2015). In brief, a 10 m × 10 m square was divided in 25 squares of 2 m × 2 m. From all sub-squares a sample was taken using a soil driller with an inner diameter of 1.8 cm. The soil was sampled to a depth of 20 cm, and the thus collected soil core separated in two parts, i.e., 0–5, and 5–20 cm,

respectively. Soil was subsequently air-dried at 40 °C for 48 h, crushed and sieved through a 2 mm sieve and then stored at room temperature and darkness. No change in concentrations of pesticides in soils were observed when stabilized and stored for several years under such conditions (Riedo et al., 2023). The first sampling was conducted on March 18, 2020, i.e., prior to the first pesticide application. Afterwards, soil samples were taken biweekly during the growing season and the application events (nine time points from mid-April until mid-August, Fig. 1A) and monthly after the harvest (in total 15 time points until January 2021).

Drainage water was sampled every 200 L of discharge whereat five of those subsamples were pooled together to one composite sample of 1000 mL. With this setting a temporal resolution of < 30 min sampling duration per composite sample during discharge peak events could be achieved. During dry weather and low flow conditions in the drainage system, intervals for drawing a complete composite sample lasted for three to five days. After the last pesticide application and at the end of the sampling campaign, the (sub-)sampling frequency was decreased to once every 500 L (August 20) and 1000 L (August 30). In total, 151 composite samples were taken from April 1 until the beginning of September. The autosampler was emptied at least twice per week, or during low flow conditions, and hence a slow sampling frequency, as soon as a sample was entirely taken. Aliquots of 60 mL were transferred to 100 mL Schott bottles and frozen at −20 °C until analysis. Analyte stability in different storage conditions was tested prior to the experiment with spiked drainage water (Fig. S2).
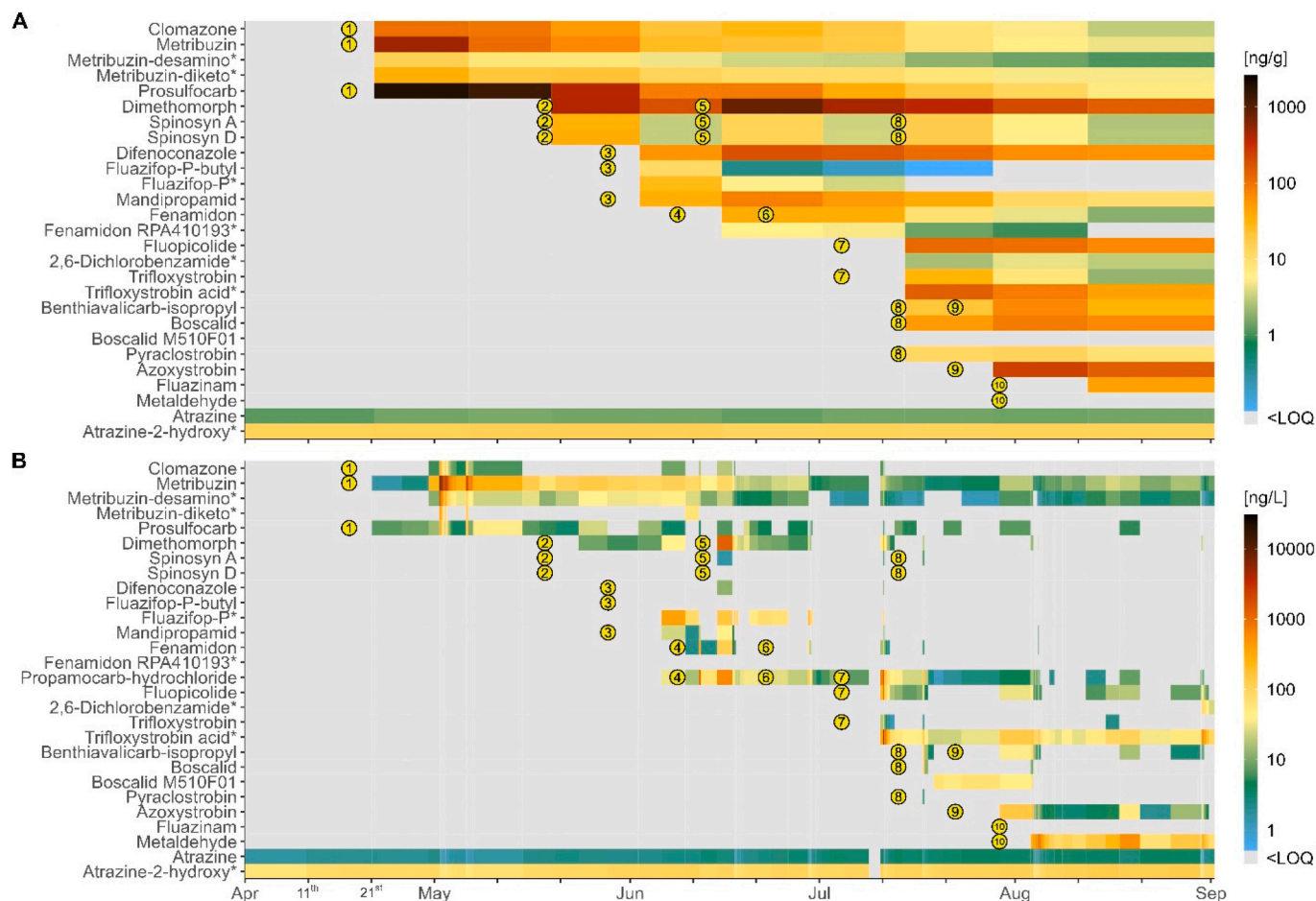
Fig. 1. Pesticide concentrations in soil 0–5 cm depth (A) and drainage water (B) from April until beginning of September 2020. Soil sampling took place at discrete timepoints and corresponding concentrations were assumed to be constant over a given interval (about two weeks). Drainage water was sampled continuously and flow-proportionally, and concentrations relate to the time period required to gather a corresponding composite sample (minutes to days; for details, see text). Numbers indicate pesticide application events (for details, see Table S2).
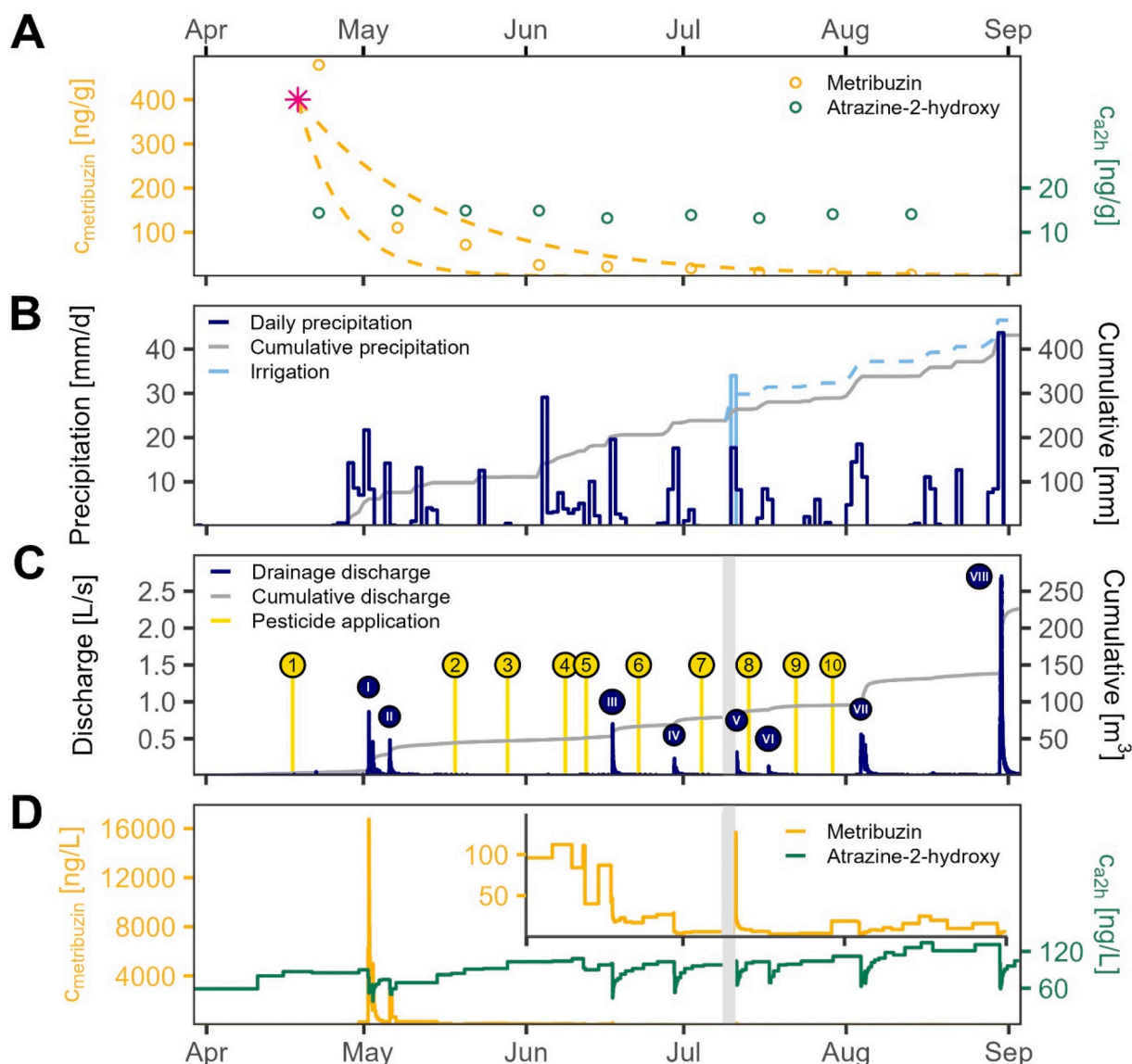
Fig. 2. Hydrological conditions and pesticide concentrations in drainage water and soil at the experimental site. A) Pesticide concentrations in soil (metribuzin & atrazine-2-hydroxy (a2h)) with theoretical applied amount for metribuzin (pink asterisk) and minimum and maximum dissipation based on field DT_{50} and lab DT_{50} (Lewis et al., 2016) (yellow dashed lines; only one field DT_{50} available). B) Daily and cumulative precipitation. C) Drainage discharge, with discharge events numbered I-VIII and pesticide application events indicated with numbers 1–10. D) Pesticide concentrations in drainage water (metribuzin & a2h). Grey bars in panel C) and D) around July 9 indicate a period of no drainage water flow, during which respective data was not available.

2.3. Analytics

Soil samples were analyzed in duplicates and extracted with accelerated solvent extraction (ASE, Dionex ASE 350, Thermo Scientific, Waltham, USA) prior to measurement following the method of Riedo et al. (2021). The samples (6 g) were weighed into the extractions cells and then extracted twice. For the first extraction step, an organic mixture of acetone, methanol, and acetonitrile (ACN) at a ratio of 65:10:25 (% *v/v*) was used. The second, acidic step, was performed with a mixture of acetone and 1 % phosphoric acid in Millipore water at a ratio of 70:30 (% *v/v*). Further information on extraction parameters, such as temperature and pressure are provided in the SM (Table S5). After bringing all extracts to an equal volume of 45 mL and treating them in an ultrasonic bath for homogenization, an aliquot of 100 µL was transferred to an LC vial. Isotope-labelled internal standards (ILIS, 20 µL) were added (1000 ng/L or 75 ng/g final concentration) and the aliquot evaporated to dryness under nitrogen. After dissolving it again in 1 mL of H_2O:ACN 100:7 (%, *v/v*), the sample was vortexed and

centrifuged prior to measurement.

Water samples were thawed over-night at 4 °C and brought to room temperature before sample preparation. An aliquot of 5 mL was centrifuged at 2600 *g*, 1 mL of supernatant was transferred to an LC vial and ILIS was added (1000 ng/L final concentration).

Both soil and water samples were measured with the same analytical setup consisting of liquid chromatography (LC) coupled to a triple quadrupole mass spectrometer (MS/MS). Chromatographic separation was done with an Agilent ZORBAX Eclipse Plus C18 column (rapid resolution HD, 3.0 × 50 mm, 1.8 µm) run by an Agilent 1290 binary pump together with a 1260 vial sampler and column oven. Eluents were water and ACN with 0.1 % formic acid as modifier. As detector an Agilent 6470 MS/MS was operated in dynamic Multiple Reaction Monitoring (dMRM) mode with simultaneous positive and negative electrospray ionization (ESI). More details on LC- and MS-parameters are given in SM section 2 (Tables S6-S8).

With this instrumentation, 18 of the 20 applied pesticides could be measured (all except mancozeb and diquat). In addition, the legacy

compound (atrazine) and its metabolite (atrazine-2-hydroxy) plus seven metabolites of the applied pesticides were included in the method. To compensate for matrix effects, a respective matrix-matched calibration (1–5000 ng/L or 0.075–375 ng/g) derived from soil and drainage water samples taken prior to the first application was used. Analytes showing a clear signal in the blank matrix were additionally calibrated using a solvent calibration. This was true for atrazine and atrazine-2-hydroxy. If measured concentration exceeded the calibration range, samples were tenfold diluted and remeasured. This was the case for metribuzin in eight subsequent samples.

Pesticides were quantified using the internal standard method. Around half (13) of the analytes were quantified with their structure-identical ILIS. The other analytes were quantified with one of those 13 ILIS or one of four additionally spiked pesticide ILIS (Table S9 and Table S10). Assignment for non-structure-identical ILIS was based on ionization mode and retention time.

Spinosyn A and D were only available as a combined spinosad standard in a mixture of 84:16, which was accounted for during quantification. The fungicide propamocarb-hydrochloride showed heavy interference during measurement of the soil samples and had to be excluded from quantitative soil analysis.

Limits of quantification (LOQs) ranged from 0.1 to 7.5 ng/g for soil samples (median 0.4 ng/g) and from 1 to 50 ng/L for water samples (median 1 ng/L). Relative recoveries for parent compounds obtained in both soil and water varied between 80 and 120 %. Absolute recoveries of soil extractions were obtained from freshly spiked soil samples (spiked before extraction) and the corresponding matrix matched calibration spike level (spiked after extraction) and ranged between 70 and 120 % for 89 % of the parent compounds. Calculation of recoveries and further details on the analytical method performance, such as precision, linearity of calibration and quality control measurements (e.g., external reference mix injections) are presented in section 2.4 of the SM and in Tables S9 (soil) and S10 (drainage water).

2.4. Data analysis

For the comparison of the measured data with respective models, physico-chemical properties of the investigated compounds were retrieved from the pesticide properties database (PPDB) (Lewis et al., 2016). To conduct the comparison concerning dissipation in soil, leachability (GUS) and exported fractions and maximum discharged concentrations (EXPOSIT), parameters of interest were the $K_{f,OC}$, the soil dissipation rate in the field ($DT_{50,field}$), in the lab ($DT_{50,lab}$) (all Table S4) and the GUS (Table S12). If several values were available, we used geomean values for DT_{50} and arithmetic means for $K_{f,OC}$ as the PPDB publishes the data in the same way.

Theoretical dissipation profiles were calculated as

$$c_t = c_0 \bullet e^{-k \bullet t} \tag{1}$$

where c_0 is the concentration of a given pesticide immediately after application (either measured or as a PEC), c_t is its concentration at time t after application, and k is the (pseudo-)first-order rate constant. The half-life, DT_{50}, is then obtained as

$$DT_{50} = \frac{\ln 2}{k} \tag{2}$$

A well-established index for assessing the leachability of pesticides is the GUS (Gustafson, 1989). It is calculated as

$$GUS = log_{10}(DT_{50}) \bullet \left(4 - log_{10}(K_{f,oc})\right) \tag{3}$$

where DT_{50} is the half-life of a pesticide and $K_{f,OC}$ the sorption coefficient (L/kg$_{OC}$).

The EXPOSIT 3.02 model is a tool for predicting different pathways (e.g., run-off and drainage) of pesticides in surface waters and is used in the Swiss and German pesticide approval process (BVL, 2023). It applies

a set of rules to determine exported loads and maximum concentrations expected in the environment. More specifically, one part of the model deals with pesticide export via drainage and hence represents the situation on our test field well. Mobility of pesticides is divided in two mobility classes only ($K_{f,OC} >> 500$ L/kg$_{OC}$ and < 500 L/kg$_{OC}$). As worst-case scenario a rain event takes place three days after application (20 mm/24 h, thereof 9 mm precipitating during 15 min, simulating a heavy rain event). During the three days between application and precipitation parent compounds are dissipating with the single first-order kinetics model (DT_{50}). The last necessary input value is the interception, which describes what percentage of the applied pesticide is retained by the plant canopy.

A part of the remaining mass is exported via drainage depending on their mobility (0.01 % for $K_{f,OC} >> 500$ L/kg$_{OC}$ and 0.2 % for $K_{f,OC} < 500$ L/kg$_{OC}$). Peak concentrations are based on a fix percentage (12.5 %) of the total export and a duration of 24 h and a drainage discharge of 5 % of the precipitation amount (10 m^3). For the final environmental concentration an eight-fold dilution of the drainage water is assumed.

EXPOSIT is applied as an Excel Workbook. As input data physico-chemical properties of the pesticides obtained from the PPDB and actual application rates were taken. Screenshots of the input and output sheets concerning drainage are shown in SM section 4.5 (Fig. S11).

3. Results and discussion

3.1. Pesticides in soil samples

All of the applied and measured pesticides and metabolites except metaldehyde and the boscalid metabolite M510F01 were detected in soil samples, as shown for the top layer (0–5 cm, Fig. 1A). The majority of the analytes was detected in both depths (0–5 cm and 5–20 cm; Fig. S6), with concentrations being generally lower by a factor of 10–30 in the subsurface (Fig. S7). Fluazifop-P-butyl and its metabolite fluazifop-P were detected in the top soil only. Maximum concentrations found shortly after applications ranged from 6 ng/g (spinosyn D) to 1900 ng/g (prosulfocarb) which matched the expected concentrations in the top soil (Table S11, Fig. S7) considering the application rate, a soil bulk density of 1.5 g/cm^3, and corresponding soil depths for two-thirds of all compounds (moderately persistent to persistent pesticides) within a factor of two. An increasing concentration from the first to the second sampling without an additional application was observed for boscalid, difenoconazole, mandipropamid and pyraclostrobin (applied on May 18 or July 13, respectively). In these cases, the first soil sampling took place directly or shortly (1 day) after the application with no rainfall between the application and the first sampling. Plant growth at those time points was already advanced and the application spray was partly retained by the plant canopy (also called interception (Linders et al., 2000)). We assume that the pesticides were then washed off to the soil surface with rain between the first and second sampling following the pesticide application.

Most compounds were detectable in soil during the entire study from April 2020 to January 2021, i.e., 6.5 to 9 months, depending on their application date. For only a few compounds (mainly metabolites) the concentration decreased below LOQ earlier (Fig. S6, Table S11). Residue concentrations at the last sampling (January 13, 2021) ranged from < LOQ for easily degradable ($DT_{50} < 30$ days, e.g., trifloxystrobin) over < 1 ng/g for moderately persistent compounds ($DT_{50} = 30$–100 days, e.g., pyraclostrobin) to approximately 10 ng/g for persistent compounds ($DT_{50} = 100$–365 days, e.g., fluopicolide). These residues correspond to < 0.1 % to 5 % of the originally applied amount which is consistent with previous studies (Chiaia-Hernandez et al., 2017; Kosubova et al., 2020; Riedo et al., 2021, 2023), although a direct comparison is partly limited by methodological differences.

The measured pesticide concentrations (expressed as concentrations relative to the initial/maximum one) in top soil generally decreased in agreement with the single first-order dissipation model (Fig. 3).

Dissipation rates were in most cases within the range of field-derived DT_{50} ($DT_{50,field}$; obtained from the pesticide properties database (PPDB) (Lewis et al., 2016)), as illustrated for metribuzin (Fig. 2A) and all other pesticides (Fig. S7). Specifically, at our experimental site, concentrations of persistent pesticides tended to decrease faster than predicted by the model using laboratory DT_{50} values ($DT_{50,lab}$; i.e., prospective risk assessment), while those of non-persistent ones (e.g., trifloxystrobin and fluazifop-P-butyl) decreased less rapidly (Fig. S8). However, this pattern was somewhat less pronounced when the available $DT_{50,field}$ values were used (Fig. 3). Contrary to laboratory studies performed under defined and stable conditions, pesticide dissipation in the field is influenced by seasonal variations in weather conditions (e.g., temperature, solar irradiation, precipitation) and soil properties, such as water holding capacity or growth and activity of microbial degraders (Arbeli and Fuentes, 2007; Yale et al., 2017). Also, repeated applications of the same pesticide or another with a similar chemical structure accelerate its dissipation in soil, as shown at field scale for atrazine (Zablotowicz et al., 2007) and metribuzin (Mutua et al., 2016). Other factors, such as increased or more frequent precipitation, may also facilitate pesticide biodegradation and affect leachability by increasing pesticide mobility through the soil horizon (Carpio et al., 2020).

Furthermore, the observed DT_{50} values derived from our field experiment (Table S4) were compared with the corresponding DT_{50} values published in the PPDB (Fig. S9) demonstrating that persistent ($DT_{50} = 30$–100 days) and very persistent ($DT_{50} > 100$ days) pesticides dissipated more quickly than previously recorded, whereas nonpersistent compounds ($DT_{50} < 30$ days) were scattered around the 1:1 line. In general, the observed field-derived DT_{50} were usually in the range of reported min- and max-values from the PPDB and corresponded in some cases well with the presented geomean values (e.g., metribuzin, clomazone). Overall, the observed field-derived values match in almost all cases better with the field- than the lab-derived values from the PPDB, respectively (Table S4).

In contrast to all freshly applied pesticides, for atrazine (last application in 2009, Table S3) and its metabolite atrazine-2-hydroxy very

constant concentrations of approximately 1.5 and 14 ng/g, respectively, were measured throughout the entire sampling period and both sampling depths (Fig. 1, Fig. S6, Table S11). Atrazine and its metabolites are known to persist in soil for decades (Jablonowski et al., 2011) which contrasts with available $DT_{50,field}$ values (6–108 days) (Lewis et al., 2016), assuming single first-order kinetics. Atrazine residues measured in our study confirmed the high persistence of this legacy pesticide: even eleven years after its last application (i.e., 37 to 669 times the $DT_{50,field}$), the investigated experimental field contained approximately 900 mg of atrazine in the upper 20 cm, assuming the soil bulk density of 1.5 g/cm^3 (corresponding to 4.5 g/ha atrazine). The total atrazine pool is presumably larger, as traces of atrazine are probably also present in deeper soil layers. Indeed, dissipation kinetics of atrazine seem to vary with time and were better predicted with biphasic decay models already at a time scale of around 150 days (Sarmah and Close, 2009). This apparent discrepancy between the initial and long-term dissipation rates of atrazine in the environment calls for further monitoring of aged atrazine residues to improve the accuracy of dissipation models as well as risk assessment. Apart from atrazine, also other pesticides, such as, for instance, pirimicarb or S-metolachlor, may form stable residues detectable at concentrations substantially higher than those suggested by the single first-order kinetics (Riedo et al., 2023) and that accumulated over time while in use (Gabbert and Hilber, 2016). The formation of those residues is time- and compound-specific and it is also proportional to the soil organic matter content (Abdelhafid et al., 2000). This process decreases immediate pesticide availability by stabilizing the total pesticide pool in soil. However, on a longer term, the aged pesticide residues may be a source of chronical soil contamination characterized by a slow pesticide release (Barriuso et al., 2008).

A comprehensive review on pesticide monitoring studies in soil was published recently (Sabzevari and Hofman, 2022), covering a broad spectrum of compounds and regional and climatological differences. However, within 82 included publications only a few discussed temporal variations of pesticides at field scale. For instance, multiannual monitoring campaigns with annual resolution were executed in Germany
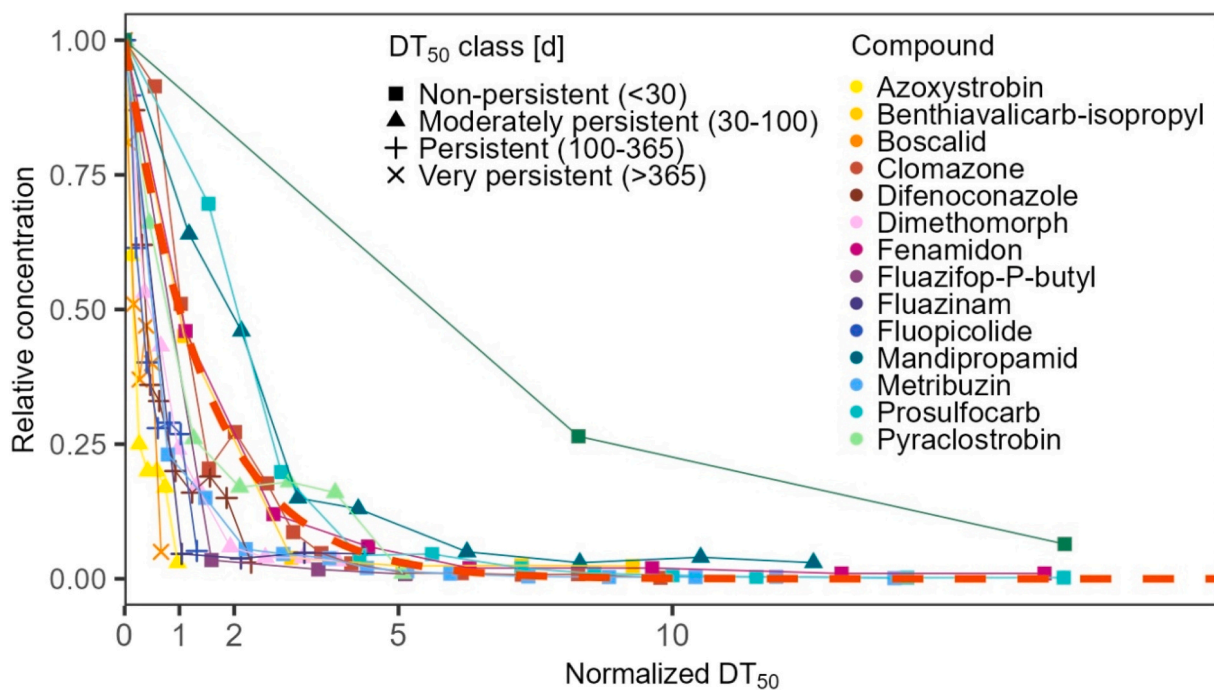

Fig. 3. Pesticide dissipation in soil, expressed as concentrations over time divided by initial concentrations right after application. Time after application is normalized for all investigated compounds to their respective field DT_{50}, which were retrieved from the PPDB (Lewis et al., 2016). The red dashed line represents the generic pseudo-first order dissipation model. In case of increasing concentrations in the initial phase after application due to interception (e.g. difenoconazole) or a second application, only the decaying phase is shown.

(Kramer et al., 2001), Spain (Padilla-Sanchez et al., 2015) and the Czech Republic (Kosubova et al., 2020). Studies at higher temporal resolution are scarce and include selected individual compound only, such as atrazine (Kramer et al., 2001) and acetochlor (Sun et al., 2011). Hence, the here presented data obtained biweekly during the growing phase of potatoes and monthly after harvest, which is quite unique among pesticide monitoring studies in soil, revealed a good picture of fate and behavior of the applied chemicals in soil under real agro-environmental conditions.

3.2. Pesticides in drainage water samples and exported fractions

A total precipitation of 431 mm was recorded during the study (April until beginning of September 2020) (Fig. 2B) which was 17 % less than the average precipitation of the same period in the years 1981–2010 (for more details on weather and precipitation data see SM section 3). These rainfalls induced major drainage events at eight time points (numbered I-VIII in Fig. 2C) with discharge peaks from 0.1 to > 2 L/s. The events were relatively evenly distributed among the pesticide applications.

Almost all applied pesticides and their measured metabolites were detected in the drainage water (Fig. 1B) except for fluazifop-P-butyl, spinosyn D and the fenamidon metabolite RPA410193. Concentrations and temporal occurrence of identified compounds varied considerably. For instance, after its first appearance in the drainage water the herbicide metribuzin was detectable throughout the entire sampling period (~140 d) at a maximum concentration of 17,000 ng/L (Table S12). In contrast, trifloxystrobin with a similar application rate was detectable only during three days at a maximum concentration of approximately 200-times lower than that of metribuzin (85 ng/L), and fluazinam was found in one sample only at a concentration of 5 ng/L (August 3; Fig. 1B, Table S12). In general, pesticides were detected in the earliest drainage event after application, and peak values of both pesticide concentrations and drainage discharge coincided (Fig. 2C discharge peak I and Fig. 2D metribuzin concentration in drainage water) indicating preferential flow (Flury et al., 1994; Weiler, 2017). A similar "first flush" leaching behavior from this experimental field was observed before for pesticides, estrogens, phyto- and mycotoxins (Hartmann et al., 2008; Rechsteiner et al., 2021; Schenzel et al., 2012; Wettstein et al., 2016). This was also true for most of the metabolites, except for 2,6-dichlorobenzamide, which only appeared more than one month and four drainage events after the application of its parent compound fluopicolide. With decreasing discharge, the pesticide concentrations diminished simultaneously. In some cases, concentrations rapidly fell below the LOQ after several hours or days (trifloxystrobin, pyraclostrobin, Table S12). Other compounds were still detectable in a second drainage event after a single application (e.g., clomazone, prosulfocarb, fluopicolide, metribuzin, metaldehyde, trifloxystrobin acid).

Similar to their occurrence in soil, atrazine and its metabolite were detectable in the drainage water during the entire sampling period (Fig. 1B) with a slight increase in concentration from April until August (Fig. 2D), probably due to higher temperature and increased solubility. Contrary to all freshly applied pesticides, their concentrations were inversely correlated with drainage discharge flow (Fig. 2D). Apparently, under stagnant dry weather conditions, a fraction of the atrazine (and its metabolite) soil pool desorbed and re-equilibrated with local pore water which was then exchanged and diluted with freshly percolating water during a rain event. As (de)sorption kinetics are comparably slow and a new equilibrium is often reached not until hours or even days (Delle Site, 2001), and because desorption can be slower than sorption, particularly with increased incubation time (Ma et al., 1993), these processes could not replenish solutes at the speed they were exported. Interestingly, metribuzin changed its initial "first flush" behavior (events I, and II) shortly after application to this inverse, dilution driven "atrazine behavior" (events III, IV, VI-VIII) over the season (Fig. 2D). Discharge event V constitutes a special case: presumably, artificial irrigation initially caused pore water saturation and metribuzin desorption. A

subsequent rain event then flushed away that readily available fraction.

For the detected pesticides, exported fractions calculated based on application data, drainage relevant area, measured concentration and drainage water discharge were mostly < 0.1 % and ranged from < 0.001 % (0.00002 %) to 0.43 % (Table S12). Metribuzin showed the highest exported fraction (0.43 %) followed by metaldehyde (0.20 %). With quantified metabolites included, the exported fractions were 0.51, 0.48, 0.20 and 0.15 % for metribuzin, trifloxystrobin, metaldehyde and fluopicolide, respectively.

Two comprehensive reviews on pesticide losses via drainage covering numerous studies conducted in North America (Kladivko et al., 2001) and Europe (Brown and van Beinum, 2009) contain data for 60 pesticides, including four compounds and their metabolites examined in our study: Metribuzin, clomazone, atrazine and fluazifop-butyl. However, fluazifop-butyl and clomazone were analyzed, but not detected in the respective study (Baker and Melvin, 1994) and atrazine was freshly applied in an number of studies, but is only a legacy compound in our case. This leaves us with metribuzin as the sole pesticide for literature comparison. The most comprehensive study on metribuzin was conducted on an 18 ha sized field where it was repeatedly applied in the years 1991, 1993 and 1995 with the same application rate as in this study, i.e. 400 g/ha (Moorman et al., 1999). Maximum metribuzin concentrations in the drainage water during the entire monitoring period did not exceed 2 μg/L and losses ranged from 0.00 to 0.30 %. While overall in the same range, these somewhat lower values compared to our study (17 μg/L and 0.43 %) could be explained by a lower sampling frequency likely missing the maximum concentration and/or by a higher soil OC content (3–4 %) which might have caused more retardation.

The GUS for the substances monitored in this study ranged from 0.05 to 3.2 (Table S12) implying a highly variable leaching potential from "leachers" (GUS > 2.8) to "non-leachers" (GUS < 1.8). The wide range of exported fractions reported above positively correlated with the GUS suggesting that leachability was at least partially influenced by physico-chemical properties of pesticides (red dots in Figs. S10A and S10B). Other leaching indices like the VI (vulnerability index) include not only compound-specific but also site-specific data, such as organic matter content or bulk soil density (Schlosser, 2002). However, a comparison of multiple indices including different sets of accounting parameters showed only minor changes in the leachability rankings for single pesticides if more parameters were used in addition to DT_{50} and $K_{f,OC}$ (Demir et al., 2019).

Pesticides with a similar GUS range applied in an earlier study on the same field showed comparable exported fractions (orange data points in Fig. S10) (Wettstein et al., 2016). The insecticides thiametoxam and imidacloprid were applied as seed dressings and had the highest exported fraction (1.2 and 0.48 %), probably because of reduced sorption due to their locally elevated concentrations and as they did not have to pass the organic rich upper soil layer. However, despite imidacloprid exhibiting a higher GUS (3.69) and being applied as seed dressing in the soil, it showed an identical exported fraction (0.48 %) as metribuzin in our study with a GUS of 2.96. Such discrepancies might be explained by the different crop (sugar beets vs. potato), crop cultivation and different weather conditions during the individual field studies (Kobierska et al., 2020). The three other (spray-applied) pesticides S-metolachlor, epoxiconazole and kresoxym-methyl (0.00 < GUS < 2.32) showed fractions of well below 0.1 % (Wettstein et al., 2016) and hence were in the range of exported fractions in this study. Overall, the exported fractions reported here are qualitatively explainable by GUS, match with earlier results of other pesticides investigated on the very same field, and are also in line with corresponding data from a literature review (Kordel et al., 2008) (blue dots in Fig. S10A). However, slight deviations on both ends of the correlation can be observed: the exported fraction of metaldehyde (0.2 %; Table S12) was higher than suggested by the GUS (1.5) but it was the only compound applied as solid grains and hence could not sorb to surfaces between application and the first rain. Also, a very

low export of difenoconazole (< 0.0001 %) contrasted with a medium GUS (0.83). This substance was detected above LOQ in three water samples and additional export below LOQ was maybe missed. Emitted fractions of other types of micropollutants investigated earlier on the same field did not correlate with GUS, likely because both the occurrence pattern and the pathway by which they were introduced in the environment (e.g., natural estrogens via manure, mycotoxins via fungi metabolism, pesticides via spray application etc.) affected their leachability (Rechsteiner et al., 2021) (Fig. S10B).

To not only consider leachability but actual loads into, and concentrations in the aquatic environment, we compared our field findings with the EXPOSIT 3.02 model predictions (BVL, 2023) (Fig. 4). The emitted fractions were estimated conservatively for the majority of compounds, i.e., the actual emitted amounts were a factor of up to 30 (for fluazinam > 200) lower than predicted. However, total loads during the field experiment exceeded calculated values by a factor of 2–3 for metribuzin and metaldehyde and by a factor of 1.5 for fluopicolide and trifloxystrobin (Fig. 4A). Those four substances cover "leachers" and "non-leachers" exhibiting a GUS range from 0.15 to 3.2. A similar pattern was found for the 24 h averaged peak concentration (Fig. 4B). Most compounds showed lower than predicted 24 h peak concentrations to a degree similar to the total emitted amounts. The actual measured peak concentrations though exceeded predicted ones for the above-mentioned pesticides (except metaldehyde) by a factor of up to 6 (empty dots, Fig. 4B). Those results are particularly remarkable as EXPOSIT was designed to represent a hydrodynamic worst-case scenario, which was not the case during our field study (precipitation during the growing season was at the lower end of the long-term average). In 2021 during the same period, for example, the amount of precipitation was 50 % higher inducing a three times larger drainage discharge (Fig. S4). The EXPOSIT model discharge (10 m^3 during 24 h) was largely exceeded several times presumably resulting in higher exported fractions of pesticides.

4. Environmental relevance

Being aware of limitations and gaps in the presented data set concerning a full mass balance, we nevertheless gathered temporal high-resolution data for pesticides in two environmental compartments, addressing major distribution and fate processes under agricultural practice. The pesticide concentrations in soil measured shortly after application matched the expected concentrations by a factor of two for moderately persistent and persistent compounds. Up to 0.43 % (or 0.48 % if metabolites are included) were exported via drainage. Most remaining pesticides dissipated according to first order kinetics to < 0.1 % to 10 % of the applied amount during a period of 169–271 days. In contrast, > 60 % of the originally applied amount of boscalid (a persistent fungicide with DT$_{50,field}$ of 254 days) remained in the top 20 cm of soil after nine months.

With this study we gained insight into the highly dynamic fate of pesticides during the initial stage shortly after application not only in soil but also in drainage water. Pesticide concentrations and their exported fractions were consistent with previously published data, but additionally, we could demonstrate how emission dynamics shift from "first flush" to desorption-limited dilution, as freshly applied pesticides increasingly interact with the soil matrix over time. The presence of residual pesticides in soil, which do not dissipate as predicted by the DT$_{50}$ values, raises a question about the underlying sorption and sequestration mechanisms and how they differ from freshly applied compounds.

Most pesticides were largely within an expectable range under real world conditions when compared retrospectively with DT$_{50}$ (for soil), GUS and EXPOSIT (both for water). Observed deviations between field data and EXPOSIT reflect the differences between real and model weather conditions leading to underestimated environmental concentrations and loads to surface water bodies for a few substances. The corresponding model parameters should ideally be adapted to the local hydrological conditions.

Pesticide fate and behavior studies allow for a retrospective exposure
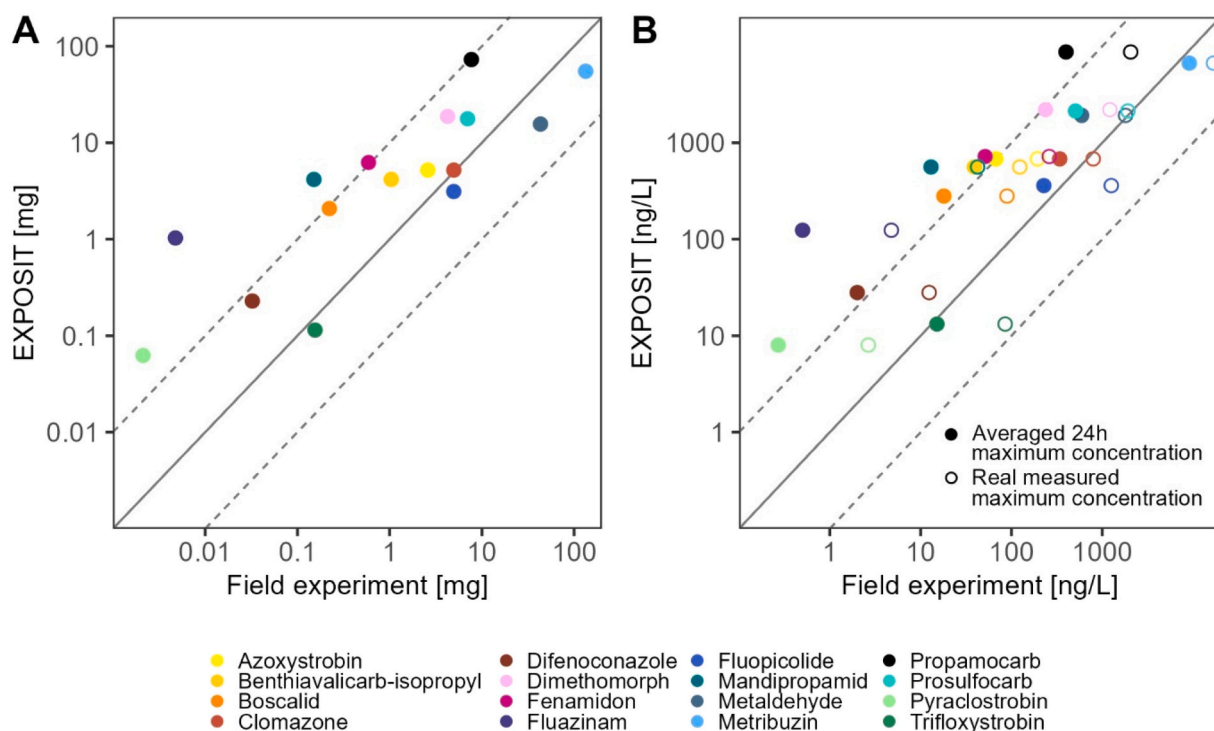
Fig. 4. Comparison of experimental and EXPOSIT model data for total exported load (A) and maximum peak concentration (B). Solid dots in B) represent a direct comparison with maximum field concentrations averaged to a 24 h peak concentration as it results from the model. Empty dots represent a comparison with real maximum concentrations measured for sampling events lasting from 32 min to almost 10 h.

and risk assessment, but are, at this scale, laborious and therefore relatively scarce. Conversely, the level of realism is high and corresponding results directly representative for environmental conditions. We therefore suggest expanding such field experiments to other soil types, crops, and climatic regions. Parameters varying at one location over time, such as different cultivations under a multi-year crop rotation or meteorology – and here mainly precipitation – are important to study as well (Kobierska et al., 2020). Corresponding data validate and improve dissipation and leachability models such that pesticides fate and behavior can be better prospectively assessed in future.

CRediT authorship contribution statement

Simon Mangold: Writing – review & editing, Writing – original draft, Methodology, Formal analysis, Data curation, Conceptualization. **Karel Hornák:** Writing – review & editing, Writing – original draft. **Nora Bartolomé:** Data curation. **Isabel Hilber:** Writing – review & editing, Data curation. **Thomas D. Bucheli:** Writing – review & editing, Project administration, Methodology, Funding acquisition.

Declaration of competing interest

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

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.173971.

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