

Long-term Persistence of Pesticides and TPs in Archived Agricultural Soil Samples and Comparison with Pesticide Application

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Abstract

For polar and more degradable pesticides, not many data on long-term persistence in soil under
 field conditions and real application practices exist. To assess the persistence of pesticides in
 soil, a multiple-compound screening method (log K_{ow} 1.7-5.5,) was developed based on
 pressurized liquid extraction, QuEChERS and LC-HRMS. The method was applied to study 80
 polar pesticides and >90 transformation products (TPs) in archived topsoil samples from the
 Swiss Soil Monitoring Network (NABO) from 1995 to 2008 with known pesticide application
 patterns. The results reveal large variations between crop type and field sites. For the majority
 of the sites 10 to 15 pesticides were identified with a detection rate of 45% at concentration
 between 1 and 330 $\mu\text{g}/\text{kg}_{dw}$ in soil. Furthermore, TPs were detected in 47% of the cases where
 the “parent-compound” was applied. Overall, residues of about 80% of all applied pesticides
 could be detected with half of these found as TPs with a persistence of more than a decade.

Introduction

Arable soils are exposed to a large number of pesticides by direct application. In Europe several
 hundreds of pesticides are registered and approximately 300,000 tons (average between 2000

and 2008 for 20 European countries) are applied to agricultural fields per year.¹ Today, Environmental Quality Standards (EQS) exist to assess the risk of pesticides in freshwater, however, in Europe EQS for soil are absent.^{2,3} Furthermore, the potential impact for freshwater organisms has been shown on the national and international level, but the effects on soil organisms is largely unknown.⁴⁻⁶

The long-term behaviour of pesticides in soil depends on a number of factors involving chemical, photochemical and microbial transformation, volatilization, sorption, plant or organism uptake, and leaching to groundwater, with sorption and biodegradation being the most relevant.⁷⁻⁹ Systematic studies on the long-term fate and persistence of pesticides including their transformation products (TPs) have been mainly carried out under the regulatory frameworks for pesticide registration in the laboratory and in controlled field dissipation experiments, typically for one or two years for a small number of reference soils.⁹⁻¹¹ However, these limited studies cannot fully capture the large variety of different environmental scenarios and their interactions (e.g., soil types, pH, organic matter content, temperature) in agricultural practice, which can influence the degradation of pesticides to a great extent.⁹⁻¹¹ Pesticide fate can vary significantly with the number of applications, spatial and temporal variations, crop rotation and weather conditions. For example, the establishment of microflora capable of rapidly degrade triazines has been observed in soils where triazines have been applied for several years.¹² Beyond registration studies, there is also a limited number of publications addressing the long-term fate of modern pesticides in soil, mainly from lysimeter experiments and primarily addressing individual compounds or well-studied compound classes such as triazine herbicides.¹³⁻¹⁵ This outlined scarcity of data calls for a more systematic monitoring of pesticides in soils under real agricultural practice, similar to the case for surface and groundwater for decades at national and regional levels.¹⁶⁻¹⁸

Soil monitoring programs (SMP) aim to observe the soil quality of ‘real-world’ soils in order to detect possible temporal changes in soil quality. In SMP, soils are monitored in a systematic way, so as to determine soil variables and to record their temporal and spatial changes.¹⁹ Although a wide network of SMP exist in the European Union,²⁰ for historical reasons, these networks have focused mainly on the decline of soil organic matter and on soils contaminated with inorganic substances such as trace metals or highly persistent compounds like polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and highly chlorinated first-generation pesticides like DDT or hexachlorocyclohexane (HCH).²¹ In the USA, extensive monitoring is equally scarce with only few studies addressing pesticides in soils such as the National Soil Monitoring Program (NSMP) where organochlorine and

organophosphorus compounds as well as atrazine were studied in agricultural soil and mature crops from 37 different states.²² While some SMP have investigated the fate of a range of pesticides (e.g. Goncalves and Alpendurada in Portugal) over a short timeframe,²³ there is little or no information on the long-term behaviour of “modern” polar and less persistent pesticide residues at the field scale under real agricultural practices. The lack of information can partly be attributed to the absence of long-term information on land and pest management of soil monitoring sites needed for a proper sampling campaign and data interpretation.²⁴ Because of the high number of pesticides registered and their high spatial and temporal variability, it is difficult to design a proper monitoring campaign and select relevant substances to assess the exposure of agricultural soils comprehensively. Routine analysis usually focuses on just 15 – 40 analytes and analysis is mostly carried out by gas chromatography or liquid chromatography – mass spectrometry (GC/LC – MS/MS) using single or triple quadrupole instruments.^{25, 26}

Recent advances in LC – high resolution MS (LC-HRMS) allow efficient screening of a large number of substances in a single run.^{27, 28} The high mass accuracy and high mass resolution even allows a suspect screening of compounds without reference standards using exact mass information, retention time and MS/MS fragmentation. This enables also a screening of TPs for which standards are often not available or very expensive. This extensive target and suspect screening was successfully carried out in freshwater^{17, 29, 30} and recently also in sediment^{31, 32}, but not yet in soil.

The aim of this study was to make use out of the available LC-HRMS technology as well as the comprehensive Swiss archive of soil samples to study the occurrence of a wide variety of pesticides and their major TPs in soil samples of various agricultural practices. The Swiss Soil Monitoring Network (NABO) operates about 100 long-term monitoring sites throughout Switzerland and contains a comprehensive archive featuring soil samples dating back to the mid-1980s.³³ Moreover, management data including pesticide application obtained from the farmers are recorded annually. Thus, the objectives of this study were (i) to select pesticides for monitoring according to their real application on fields recorded in the monitoring program (ii) examine the suitability of LC-HRMS analysis for extraction of archived soil samples, and (iii) to compare the pattern of detected substances and their TPs in soil with the known information on applied pesticides provided by the farmers on typical agricultural cultures (crop, orchards, vineyards). As pesticide application data were available from 1995 upwards, long term persistence of a wide variety of modern pesticides could be studied for the first time.

Methods

Study design

Currently, the NABO comprises 105 observation sites across Switzerland, representing diverse geology, soil types, land use and climate conditions across the country. Monitoring sites were sampled for the first time between 1985 and 1989 and have been continuously re-sampled every five years with the same soil sampling techniques and quality assurance protocols since then.³³ Details in the collection and storage of samples are provided in Supporting Information (SI). In this study, 29 archived soil samples from 14 NABO monitoring sites were selected covering a time period between 1995 and 2008 matching the time span of the pest management data used in this study. The NABO network performed meanwhile six repeated soil surveys (1985 - 2014), but we restricted our study to 1995 – 2008 to limit number of soil samples. The sites were chosen from monitoring sites where crops received pesticides regularly considering land use and the long-term pesticide use pattern recorded as indicated by the farmers. As no constraints or recommendations are given to the farmers managing the soil monitoring sites, the pesticide management at the monitoring sites represents current agricultural practices across Switzerland. The 14 selected agricultural monitoring sites cover croplands with various crop rotations (12 soil samples from 7 sites), vineyards (8 from 3 sites), orchards (7 from 3 sites), and vegetables (2 from 1 site). Details and physicochemical soil characteristics of each sampling location are reported in Table S1.

Chemical Analysis

Details on the supplier, preparation, and storage of reference standards, reagents, and pesticide-free soil are provided in SI.

Pressurized Liquid Extraction of Soils

Around 6 g of dried soil were homogenized with a mortar and pestle, weighed, and transferred to 11 mL stainless steel extraction cells filled with a glass fiber filter (Whatman GF/F). In addition ~1 g of diatomaceous earth was added to each extraction cell to increase solvent channeling (Hydromatrix, Restek). First, the soils were extracted with a mixture of acetone (Ac) and ethyl acetate (EtAc) at a ratio of 30:70 (% v/v) in two static extraction cycles of 5 minutes at 80°C and 130 bar using an ASE 200 (Dionex). Extraction cells were rinsed with fresh solvent (60% of cell volume) and purged with nitrogen for 120 seconds. Consequently, the soils were extracted with a mixture of Ac and 1% phosphoric acid at 120°C at a ratio of 70:30 (% v/v) in

two static extraction cycles of 5 minutes to release acidic compounds from the soil. The extracts were combined to give a final volume of about 30 mL (pH 4 - 4.5) and spiked with 10 μ L of a mixture containing 28 internal standards, resulting in an absolute amount of 100 ng of each labelled compound in the extract. The organic solvents were removed by rotary evaporation at 35°C and the remaining aqueous phase was diluted to 4 mL with HPLC grade water. Information on the overall method development is provided in SI and described in the results.

Clean-up and Enrichment of Soil Extracts

Soil matrix was removed from extracts using the “QuEChERS” approach. Briefly, 5 mL of acetonitrile (ACN) were added to 4 mL of aqueous phase and combined with 1.6 g of MgSO_4 and 0.2 g of NH_4Cl . The mixture was shaken for 2 min and centrifuged for 4 min at $1000 \times g$. After separation, the ACN phase was transferred to a centrifuge tube and combined with 800 mg of MgSO_4 , 125 mg of primary-secondary amine (PSA), 125 mg of endcapped C_{18} , and 12.5 mg of graphited carbon black (GCB) (all from Sigma-Aldrich) for d-SPE cleanup. The mixture was shaken for 1 min, centrifuged again for 5 min and the solvent phase was transferred to a graduated centrifuge tube. The d-SPE sorbent was washed with 4 mL of ACN, centrifuged again, and the ACN solvents were combined, evaporated to 50 μ L and brought to a volume of 500 μ L using methanol. The final extract was filtered into a 2 mL vial using 0.2 μ m PTFE syringe filters (BGB analytics, Boeckten).

Liquid Chromatography Tandem High Resolution Mass Spectrometric Detection

Analytes were separated on a X-bridge C_{18} column (2.1 \times 50 mm, 3.5 μ m particle size, Waters) equipped with a 2.1 \times 10 mm C_{18} security guard cartridge at 35 °C at a flow rate of 200 μ L/min similar to Kern et al.³⁴ Compounds were separated by a mobile phase consisting of water (A) and methanol (B), both containing 0.1% of formic acid (v/v). The LC program started at 95% of solvent A for 0.5 min, increasing solvent B up to 95% in 17 min, held for 4 min, returning back to 95% of solvent A in 1 min and re-equilibration for 5 min. As the extracts were in 100% methanol, 5 μ L were injected, while the flow rate was raised to 320 μ L/min for the first 0.5 min.

Detection of analytes was performed after electrospray ionization (ESI) with tandem linear ion trap-Orbitrap mass spectrometer (LTQ-Orbitrap-XL, Thermo) in positive and negative mode. Full scan accurate mass spectra were acquired from 110 to 600 Da with a nominal resolving power of 60,000 referenced to m/z 400 and a mass accuracy of ± 5 ppm. Data-dependent high-resolution product ion spectra (dd-HRMS/MS) were recorded for the five most intense ions

from a precursor ion list (calculated for the prioritized compounds) at a resolving power of 7,500 using higher energy collisional dissociation at a collision energy of 35%. Additionally, collision-induced dissociation (CID) was performed with a normalized collision energy of 35% and measured at unit resolution in the LTQ as described elsewhere.³²

Matrix-matched calibration standards (n = 9) were made with concentrations ranging from 2 ng to 500 ng/mL in vial of standard mix solution using a pristine soil extract. Full scan precursor ions were used for detection and quantification, and product ions were used for confirmation. Quality control accounted for more than 20% of the samples, which included standards, blanks and spiked samples.

Validation of the final method

The method was validated for 64 pesticides and 29 TPs. Relative recoveries were determined by using pesticide-free soil. After homogenization, this soil was distributed into different extraction cells (n=4) and spiked at the top of each cell with 50 µL of 10 mg/L standard mix solution (50 ng absolute) as illustrated in Table S2 in SI. All extracts were spiked with an internal standard mix prior to injection into the LC to calculate extraction and relative recoveries. The method limit of quantification (LOQ) was defined as the lowest point of the matrix-matched calibration curve with a S/N ratio ≥ 10 , or with the lowest visible calibration point in case no background noise was visible due to the noise cut-off algorithm used for data size reduction.

Target and suspect screening of pesticides and TPs

The selection of 80 pesticides for screening was carried out based on a list of pesticides applied to the NABO soils between 1995 and 2008 (Table S3 in SI). Inorganic substances and compounds not ionisable by ESI, based on the absence of corresponding functional groups, were excluded from this study and accounted for ~35% of the entire list of applied pesticides. Furthermore, additional information on known TPs was retrieved using literature data on the applied pesticide and from assessment reports, registration dossiers (US EPA, EU, UK, CA and AUS), the European Food Safety Authority (EFSA), and peer-reviewed publications. Overall, reference standards for 64 pesticides and 29 TPs were used for target screening. Suspect screening was performed for 16 pesticides and 62 TPs by collecting information on the molecular formula and structure. The exact mass of the expected molecular ion, $[M+H]^+$ or $[M-H]^-$ according to the assumed ionization behaviour, was extracted with a mass window of ± 5 ppm from the HR-full scan chromatogram acquired in the positive or negative mode as

described by Kern et al.³⁴ Positive detections were further substantiated by a match of observed vs. theoretical isotope patterns and the interpretation of MS/MS spectra. Beyond this analytical approach, circumstantial evidence was also used to validate positive findings, such as the simultaneous presence of parent compounds and TPs at meaningful relative retention times, the presence of compounds detected in samples after a short period of pesticide applications and their absence in samples without known application. Unequivocal confirmation was only possible if a reference standard was available. Without reference standard pesticides and TPs were tentatively identified with a level 3 of confidence as described by Schymanski et al.³⁵ Physicochemical properties of pesticides (K_{ow} and pK_a in soil) were obtained from literature data, the Pesticide Properties Database (PPDB) or estimated using the Calculator Plugins of Marvin (Chemaxon).^{36, 37}

Results and Discussion

Optimizing extraction and clean-up for pesticides and TPs by target and suspect screening

For method development, 39 target screening compounds were selected covering different compound classes and a wide range of physical-chemical properties ($\log K_{ow}$ 1.7 - 5.5, pK_a 0.1 - 10) as well as known to be persistent in soils, either due to a strong sorption, long half-life, or applied in large amount to the NABO soils as illustrated in Table S2 and S3 in the SI. In a first step, the extraction from diatomaceous earth was tested using different solvent mixtures (Ac/EtAc/H₂O 45:40:15, Ac/EtAc 30:70, Ac/H₂O 70:30) to cover different polarities. In addition, the influence of temperature (80, 100, 120 and 140°C) during PLE was investigated. All extraction setups were performed on soil samples spiked with a mixture of the mentioned pesticides.

The results show that a mixture of Ac/EtAc yielded higher recoveries over water-containing solvents for most compounds, as illustrated in Figure S1-S3 in the SI, with average extraction recoveries of 70%. The decrease of recoveries for phenmedipham and to a lesser extent for chloridazon, diuron, isoproturon, and bentazone with increasing temperatures suggests thermal degradation of these compounds. Recoveries of acidic substances like 2,4-D, mecoprop, sulcotrione, and the metolachlor TPs were below 40%. The results indicate that Ac/EtAc is a suitable solvent mixture for extracting uncharged and medium polar substances, but not for the most hydrophilic or charged compounds, consistent with previous studies.³² Water-containing extraction mixtures resulted in higher recoveries for acidic compounds such as 2,4-D and mecoprop, with extraction recoveries close to 80% and 60% for sulcotrione vs. $\leq 20\%$ when extracted with Ac/EtAc. However, Ac/H₂O alone was not suitable for extracting the most

hydrophobic compounds (e.g. pendimethain, chlorpyrifos). Furthermore, thermal degradation of phenylurea herbicides was higher at higher temperatures in aqueous solvents as compared to Ac/EtAc. Thus, a two-step extraction procedure was suggested, utilizing Ac/EtAc at 80°C in the first step and Ac:H₂O at 120°C in the second step, as thermolabile compounds are largely extracted with the first step.

For further optimization, a mixture of acetone with 1% phosphoric acid (70:30, v/v) was tested as second extraction step to improve the recoveries of negatively charged compounds. The results show an increased recovery of the most hydrophilic anionic compounds metolachlor OA and metolachlor ESA when using an acidified aqueous phase (Figure S4). The combination of Ac/EtAc (30:70 v/v) at 80°C, followed by Ac/1% phosphoric acid (70:30 v/v) at 120°C resulted in the best recoveries for the largest number of compounds also from spiked soil (on average 84%) and spiked soil aged for 30 days at 4°C (on average 76%, Figure S4). Low extraction recoveries of 8% were observed for the pyrethroid cypermethrin in aged soils which is consistent with the reduced bioavailability of cypermethrin due to the formation of bound residues and degradation.³⁸ Probably due to the same reason the recoveries for propachlor, dinoseb and fluazinam were $\geq 30\%$ lower in aged soils than in freshly spiked soils. Due to its short half-life and fast hydrolysis, captan could not be recovered entirely from soil.³⁹

The involved liquid-liquid extraction (QuEChERS) as a clean-up step for soil extract might be followed by an additional purification step using d-SPE, for which some studies have reported a decrease or not significant increase of recoveries.^{32, 40, 41} Therefore, recoveries of pesticides were determined for the QuEChERS extraction with and without d-SPE (combination of C18/PSA/GCB). The results show similar recoveries for both approaches with relative recoveries of 70 to 110% for most compounds as shown in Figure S5 in SI. However, for some compounds showing recoveries above 150% (likely due to different ion suppression of the analyte and the internal standards used for calibration) such as fenpropidin, isoproturon, metalaxyl and fluazinam, the recoveries moved closer to 100% after d-SPE. As no significant compound losses due to d-SPE were observed, this step was included into the method workflow also to ensure a reduction of the matrix load across samples with different organic matter content.

The final method was validated for all 93 target screening compounds (Table S2). The recoveries for soil samples spiked with 50 ng of each analyte were for 61 of the compounds between 80 and 120%, for 8 above 150%, and for 7 below 40% (mainly hydrophilic acids and hydroxy-triazines). Thus, the developed method worked well for the analysis of a wide range of compounds ($-\log K_{ow}$ -2 to 6), but it is not suitable for the analysis of highly hydrophilic due

to the liquid-liquid extraction used in QuEChERS and the LC conditions employing injection of extracts in 100% of methanol, which results in deterioration of peak shapes for early eluting compounds. Moreover, other compounds are challenging due to their low ionization efficiency in ESI (e.g., chlorothalonil, aclonifen, and most pyrethroids). Therefore, highly hydrophilic pesticides and TPs and those with low ionization efficiencies are out of the range of the analytical method. The LOQ values ranged from 0.7 ng/g_{dw} to 25 ng/g_{dw} with LOQs \leq 1.5 ng/g_{dw} for more than 80% of the pesticides (Table S2). The method performance is comparable to other studies.^{32, 40, 41} and the LOQs similar to those acquired with triple-quadrupole based methods.⁴⁰

The full scan HRMS measurement enabled to screen for suspected pesticides and TPs without reference standards by using exact mass information. This approach allowed to tentatively assign further 15 pesticides and 61 TPs, using evidence from isotopologue patterns, MS/MS spectra, and circumstantial information. Confirmation of four compounds was done retrospectively with the purchase of reference compounds whereas the finding of the others can only be reported tentatively.

This approach is illustrated in Figure 1 for the target compound fenpropidin and four suspected TPs (two hydroxylated, one N-oxide and one carboxylated TP). Their extracted ion chromatograms showed one peak of high intensity for the parent compound at 13.3 min, one peak at 9.7 min for the fenpropiden-carboxylate and five larger peaks for the hydroxy-/N-oxide TP at 9.5, 11.8, 12.5, 12.8 and 13.9 min in the soil sample of the site Vi.2 (Figure S6a). A comparison was performed between a sample from the same soil prior to fenpropidin application, soils without known fenpropidin application and a method blank. The evaluation showed that the peak at 9.5 min is related to a background contamination, while the other TP peaks were not present, substantiating that the observed peaks originate from fenpropidin. The plausibility of retention times was checked in relation to the parent compound; a carboxylation might well result in a negative retention time shift of 3.6 min, a hydroxylation in a negative retention time shift of 1-3 min. The N-oxidation could well explain the positive retention time shift of the TP at 13.9 min as compared to the parent compound as has been described in other studies.^{42, 43} Finally, MS/MS spectra of the TPs were evaluated in comparison to those of the parent compound (Figure S6b). For the peak of m/z 304.2271, no meaningful MS/MS spectrum could be obtained. For the peaks of m/z 290.2478, all MS/MS spectra showed the presence of an ion at m/z 98.0957 \pm 0.0002 (C₆H₁₂N), which could correspond to the piperidine moiety and one additional carbon atom, while for the parent compound the piperidine fragment was present (C₅H₁₂N). The peak at 13.9 min shows additionally the preservation of the *tert*-butyl-phenyl-

methylene moiety (m/z 147.1167), substantiating the tentative assignment of the N oxide. For the other three ions of the same mass (at 11.8, 12.5 and 12.8 min), no further MS/MS information was available, but the ions could possibly be assigned to three different hydroxylation products instead of the two suspected ones.

Influence of land use on Pesticide Application Pattern and Frequency of Detection

Records of applied pesticides in Swiss agriculture between 1995 and 2008 revealed large variations between crop type and field sites. The intensity of pest control was generally higher for special crops such as vineyards (Vi) and orchards (Or) with 10 to 20 compounds applied per year. Moreover, amounts of pesticide applied on vineyards were recorded to be between 12 and 17 kg ha⁻¹ yr⁻¹ and between 4 and 33 kg ha⁻¹ yr⁻¹ for orchards (Figure 2). The number of pesticides applied yearly to cropland (Cl) and vegetables (Ve) ranged from 1 to 20, but generally were below 10 pesticides per year. Typical application rates on cropland sites were below 3 kg ha⁻¹ yr⁻¹, except for potatoes which received between 6 to 15 kg ha⁻¹ yr⁻¹ of various pesticides. The numbers of pesticides applied were compared with the numbers of pesticides found in the selected 29 soil samples as illustrated in Figure 2a. For the majority of the sites, 10 to 15 pesticides were detected in the top soil. The detection frequency was in good agreement with the soil application data obtained from the farmers for special crops, but was generally higher in cropland soils. The most possible explanation is that for croplands some compounds detected in soil were applied before 1995 and thus, not reported in our farmer's records dataset. For all orchard sites the frequency of application and detection is in good agreement. The less intensive management of site Or.3, which is a traditional high-stem orchard with only 3 to 10 compounds applied per year and the high number of pesticides (average > 15) applied to the low-stem orchard sites (site Or.1 and Or.2) are well mirrored in the detection frequency. The total number of pesticides applied per site and overall years correlates with the total number of pesticides detected at each site. While the applied numbers of pesticides per site ranged between 10 and 32 (on average 17), we found between 5 and 30 (on average 12) compounds in soil per site. Notably, for 75% of the parent compounds measured in soil TPs ranged between 1 and 15 TPs per site as illustrated in Figure 2b.

Comparison of Pesticide Residues in Soil with Application Data

Application data reported by the farmers was compared with the soil chemical analysis in a qualitative manner defining four categories: (1) true-positive: pesticides detected in soil and reported as applied by farmers, (2) true-negative: compounds not detected in soil and not

applied, (3) false-positive: compounds detected in soil but not applied, and (4) false-negative: compounds not detected in soil but reported as applied. The analysis of 80 pesticides for each of the 29 soil samples at the 14 sites resulted in 2320 cases (80 x 29) within the four categories as illustrated in Figure 3a with different colors. Pesticides were reportedly applied in 421 cases. Except for the Vi and Or sites, pest management on the sites depended on the crop type cultivated and varied largely from year to year. Typically, farmers did not apply the same pesticides at these sites each year, while for Vi and Or usually the same 5 to 15 compounds were applied annually. The soil chemical analysis confirmed the presence of pesticides in 309 cases (45%), while for 112 cases (16%) the applied pesticides were not detected. The finding of 45% of the pesticides applied are rather surprising due to the relative short dissipation half-lives of these compounds (<1 year) and the relatively long periods of time between pesticide application and soil sampling, i.e., often longer than one year. Therefore, the analysis of soil samples demonstrates that although at low concentration levels, applied pesticides may be present in soils up to decades after their application. Moreover, the results revealed 260 (38%) false-positive cases in which the pesticide was not reportedly applied but were measured in soil, indicating that pesticide residues measured may result from applications prior to 1995, as has been reported in arable soils in Argentina, where some pesticides have been detected before the application period started.⁴⁴ The remarkable high numbers of false-positives (38%) was observed in particular for simazine accounting for 17 false-positive vs. 11 true-positive cases, followed by atrazine (15 vs. 10) and terbutylazine (13 vs. 5). The results are consistent with the large amounts of triazine herbicides in agriculture in the past and with the long term persistence of residues of these compounds as have been reported for atrazine (¹⁴C ring-labeled), where 50% of ¹⁴C residue was found under field condition even after nine years of application.^{13, 36, 45} Hence, the detected residues, most likely, might have originated from applications dating prior to the recorded period or impurities of other pesticides. In addition, false-positives for the fungicide carbendazim was found in 12 cases. The findings can be explained by the occurrence of carbendazim as a TP of other pesticides such as thiophanate, thiophanate-methyl, and benomyl. Furthermore, the high number of false-positives might be attributed also partly to pesticides applied at neighbouring fields (overspray) or incomplete records provided by the farmers. For example, weeds might be removed using herbicides prior to a new crop (preemergence herbicides), which might be not considered as pest control (e.g., pendimethalin and oryzalin) by the farmer and therefore, not documented as a pesticide used during the growing season. Likewise, some farmers may not have reported acaricides or might have used seeds treated with pesticides (seed coating⁴⁶) and the information was not considered

in the application data records. Such cases have been reported for imidacloprid particularly in the treatment of rapeseeds.⁴⁶ Imidacloprid leaching from sugar beet seeds to subsurface tile drains was recently observed on an experimental site.^{46, 47} False-positives for imidacloprid were in fact observed at seven cropland sites and in three orchards sites in our study.

Three herbicides of the triazine class rank in the top five most frequently found pesticides with simazine, atrazine and terbuthylazine detected in 97%, 86%, and 62% of the 29 soil samples, respectively (Table 1). The use of simazine and atrazine is not approved anymore in Switzerland (since 2012) and most EU countries since 2003, except Spain for simazine.³⁶ Furthermore, tebutam and carbendazim were detected in 79% and 72% of the samples.

Pesticide concentrations in soil samples ranged between 1 and 330 $\mu\text{g}/\text{kg}_{\text{dw}}$ as illustrated in Table 1 for the top 20 frequently detected pesticides. A full list of the measured pesticide concentrations is provided in Table S4 in the SI. The pesticide concentrations are in good agreement with other measurements of pesticides in agricultural soils. In a monitoring program of 60 soils from intensive horticulture areas in the North of Portugal, Goncalves and Alpendurata detected a large array of pesticide residues in 10% to 30% of the samples with concentrations from the low $\mu\text{g}/\text{kg}_{\text{dw}}$ up to higher than 500 $\mu\text{g}/\text{kg}_{\text{dw}}$.²³ In two Finnish arable soils, ethofumesate was found with concentrations ranging from 10 to 110 $\mu\text{g}/\text{kg}_{\text{dw}}$.⁴⁸ Additionally, in 30 soils along the Turia river in Spain, chlorpyrifos was frequently detected with concentrations up to 65 $\mu\text{g}/\text{kg}_{\text{dw}}$, while other substances were detected $< 10 \mu\text{g}/\text{kg}_{\text{dw}}$.³ Low residual amounts of terbuthylazine, metalaxyl and tebuconazole were also detected by Sanchez-Gonzales et al. in 42 soil samples across the Águeda river basin at the Spanish–Portuguese border.⁴⁹ However, different to our study, crop and pest application data were not available for most studies or only a few compounds were investigated which hampers interpretation and comparison with our results.

Transformation Products in Soils

Chemical analysis of 93 TPs resulted in the detection of TPs in 47% of the cases where the parent pesticide was reported to be applied as illustrated in Figure 3b. It should be noted that not for all pesticides given in Figure 3a ($n = 569$) TP's were analysed, hence the number of parent compounds in Figure 3b represent a subset ($n = 472$). False-positives were found in 11% of the cases where TPs were detected in soil but the parent compound was not applied within the recorded time period. In those cases the parent pesticide might be applied before the registered time period and degraded completely but residues of its TPs are still present in soil, proving evidence of the environmental exposure of these pesticides. Most of the TPs detected are

designated “major metabolites“ from registration dossiers with concentrations in soil ranging between 1 and 680 $\mu\text{g}/\text{kg}_{\text{dw}}$ as illustrated in Table 2 for the top frequently detected 20 TPs. TPs for simazine, diuron and atrazine were found at higher concentrations in soil when compared with other TPs. The isobaric TPs simazine-2-hydroxy and terbuthylazine-desethyl-2-hydroxy had the highest concentration. Furthermore, atrazine-2-hydroxy was detected in all 29 soil samples with concentrations between 2 and 220 $\mu\text{g}/\text{kg}_{\text{dw}}$. The findings are consistent with its high persistence as detected in soils after 9 and 22 years of atrazine application.^{13, 45} The complete list of TPs found in soils is provided in Table S5 in the SI.

Insights and Future Research

In this work, we have demonstrated the strength of a two-tiered approach to monitor long-term fate of pesticide residues in soil by combining consistent and reliable pest management records and a broad target and suspect screening of archived soil samples of the applied spectra of pesticides and their TPs. The analysis of soil samples demonstrates that although at low concentration levels, applied pesticides and their TPs may be present in soils for decades after their application, resulting in mixtures of typically 10-15 and up to 29 compounds. The reason for this might be a limited bioaccessibility or bioavailability of these low concentrations for further microbial degradation. Bioavailability of these low-level compound mixtures is also critical for their ecotoxicological relevance, but as we used a rather exhaustive extraction procedure, we cannot make any statements on the potential risks for soil organisms.

In several cases, pesticides were detected in soil samples although according to the farmers' records they were never applied. Generally, these ‘false positive’ findings were related to applications apparently not recorded (e.g., seed coatings) or were applied prior to the recorded period. The outcomes demonstrate that a long-term comprehensive recording is important for results interpretation. However, this goal is hard to achieve since monitoring programs have to work with many sampling sites and reporting pesticide use by farmers is not mandatory. Based on the results of this work, we advocate further investigation on the persistence of pesticides in soil and on the ecotoxicological effects of the pesticide mixtures found in this study with up to 29 pesticides in one soil sample. Moreover, the presented work advocates complementing the required pre-registration fate studies on pesticides with soil monitoring under real agricultural practice.

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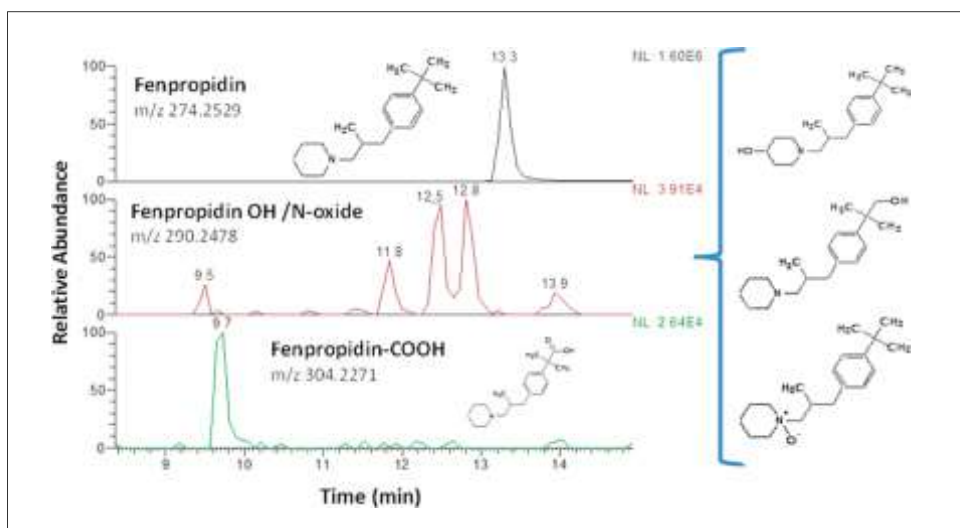


Figure 1. Extracted ion chromatogram of the target compound fenpropidin and of four of its suspected transformation products in the extract from soil sample of the site Vi.2 (NL: signal intensity at 100% of relative abundance).

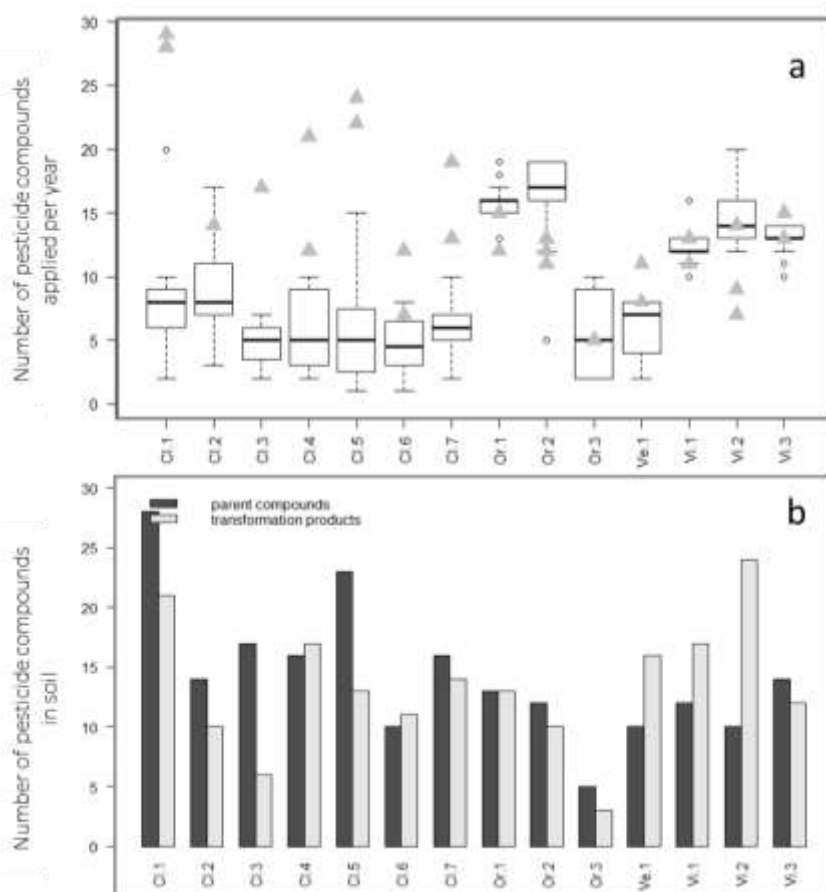


Figure 2. Applied and measured pesticides for the 14 investigated NABO soil sites (cropland sites (Cl); orchards (Or), vegetable growing (Ve), and viticulture (Vi)) between 1995 and 2008: a) number of pesticides applied per year between 1995 and 2008 (boxplot) with outliers shown

as circles outside the range of the whiskers and pesticides found in the soil samples (triangles),
b) average number of parent compounds and transformation products (TPs) measured in soil
samples.

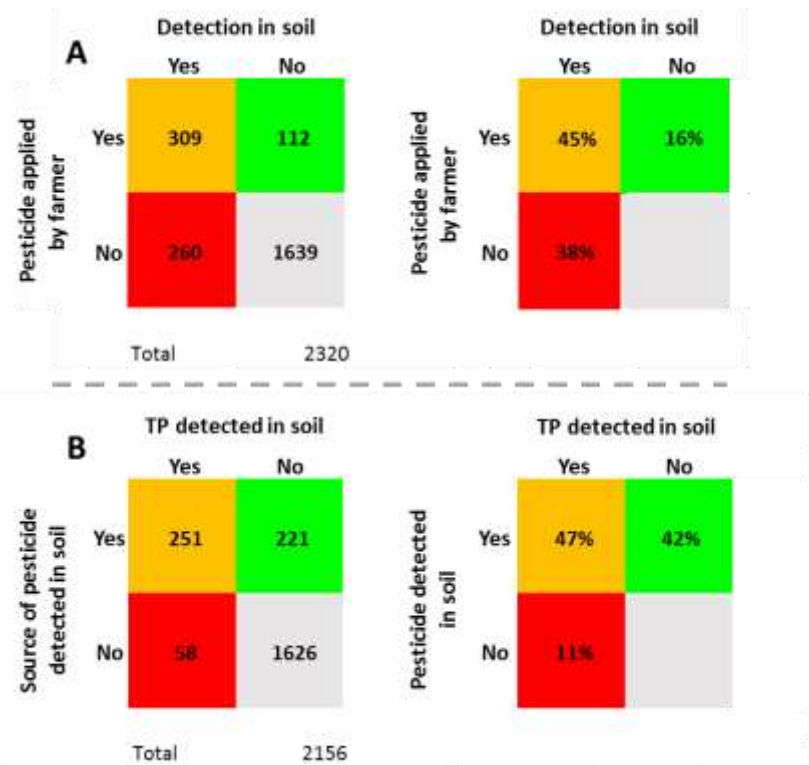


Figure 3. Qualitative analysis of applied pesticides by farmers (A) and results of the soil chemical analysis for transformation products (TPs) (B) showing (i) true-positives shown in orange (detected and applied), (ii) true-negatives shown in green(not detected and not applied) , (iii) false-positives shown in red (detected but not applied); and (iv) false-negatives shown in grey (not detected but applied). Right figure is presented in percentage of applied and detected cases.

472 Table 1. Concentrations of the 20 most frequently detected pesticides in 29 soil samples (0-20 cm) from 14 NABO monitoring sites (full list is provided
 473 in Table S4).

Rank	Name	CAS No.	Type	No. of Samples Detected	% of Detected Samples	Concentration Range (µg/kg _{dw})	Median Concentration by Land use (µg/kg _{dw})				Cases (%)			
							Cl	Or	Ve	Vi	Applied-Detected	Applied-not Detected	Not Applied-Detected	Not Applied-not Detected
1	Simazine	122-34-9	Herbicide	28	97	1 - 80	1	10	1	2	38	0	59	3
2	Atrazine	1912-24-9	Herbicide	25	86	2 - 250	5	3	8	ND	34	0	52	14
3	Tebutam	35256-85-0	Herbicide	23	79	1 - 20	2	ND	ND	1	14	0	66	21
4	Carbendazim	10605-21-7	Fungicide & TP ¹	21	72	1 - 60	6	4	ND	3	31	0	41	28
5	Terbuthylazine	5915-41-3	Herbicide	18	62	1 - 9	2	2	ND	2	17	0	45	38
6	Dinoseb	88-85-7	Herbicide	17	59	2 - 320	7	5	17	4	0	0	59	41
7	Metolachlor	51218-45-2	Herbicide	16	55	2 - 25	3	ND	2	ND	34	0	21	45
8	Alachlor	15972-60-8	Herbicide	15	52	1 - 40	2	2	24	2	14	3	38	45
9	Cyprodinil	121552-61-2	Fungicide	14	48	1 - 30	1	1	ND	13	24	0	24	52
10	Diuron	330-54-1	Herbicide	14	48	2 - 330	ND	8	ND	8	31	0	17	52
11	Linuron	330-55-2	Herbicide	14	48	2 - 190	3	ND	9	185	24	0	24	52
12	Pendimethalin	40487-42-1	Herbicide	14	48	2 - 160	16	ND	2	ND	34	0	14	52
13	Chlortoluron	15545-48-9	Herbicide	12	41	3 - 6	5	ND	ND	ND	0	0	41	59
14	Ethofumesate	26225-79-6	Herbicide	12	41	2 - 80	4	ND	ND	ND	28	3	14	55
15	Fludioxonil	131341-86-1	Fungicide	12	41	2 - 330	4	2	ND	144	21	0	21	59
16	Isoproturon	34123-59-6	Herbicide	12	41	2 - 4	3	ND	ND	ND	31	0	10	59
17	Mecoprop	7085-19-0	Herbicide	11	38	4 - 20	ND	12	ND	ND	31	10	7	52
18	Metamitron	41394-05-2	Herbicide	11	38	6 - 140	12	ND	ND	ND	34	0	3	62
19	Propiconazole	60207-90-1	Fungicide	11	38	1 - 5	4	ND	ND	ND	28	3	10	59
20	Fenpropidin	67306-00-7	Fungicide	10	34	1 - 14	1	ND	ND	10	21	0	14	66

474 Land use: Cropland sites (Cl), orchards (Or), vegetable growing (Ve), and viticulture (Vi)

475 ¹Transformation product of other pesticides such as thiophanate, thiophanate-methyl, and benomyl

476 ND= Not Detectable

Table 2. Concentrations of the most frequently detected 20 transformation products (TPs) in 29 soil samples (0-20 cm) from 14 NABO monitoring sites. Note that a few TPs are formed from two parent pesticides.

Rank	Parent Compound	Type	Transformation Product (TP)	TP Type	No. Of Samples Detected	Concentration Range ($\mu\text{g}/\text{kg}_{\text{dw}}$)	Median Concentration by Land use ($\mu\text{g}/\text{kg}_{\text{dw}}$)			
							Cl	Or	Ve	Vi
1	Atrazine	Herbicide	Atrazine-2-hydroxy	Major	29	2 - 220*	23	2	10	4
2	Simazine	Herbicide	Simazine-2-hydroxy + Terbutylazine-desethyl-2-hydroxy	Major	27	2 - 680*	6	208	< LOQ	20
3	Terbutylazine	Herbicide	Terbutylazine-desethyl	Major	26	1 - 2*	1	1	< LOQ	1
4	Atrazine	Herbicide	Atrazine-desisopropyl	Major	25	1 - 9*	3	5	5	2
5	Diuron	Herbicide	Diuron-desmonomethyl	Major	22	2 - 130*	3	6	< LOQ	12
6	Chlorothalonil	Fungicide	Chlorothalonil-hydroxy	Major	19	D	D	D	D	D
7	Terbutylazine	Herbicide	Terbutylazine-hydroxy	Major	16	D	D	D	D	D
8	Chlorpyrifos	Insecticide	3,5,6-Trichloro-2-pyridinol	Major	15	6 - 70*	< LOQ	27	< LOQ	6
9	Diuron	Herbicide	Diuron-desdimethyl	Major	15	2 - 30*	< LOQ	3	5	17
10	Chlorothalonil	Fungicide	3-cyano-6-hydroxy-2,4,5-trichlorobenzamide / 3-cyano-4-hydroxy-2,5,6-trichlorobenzamide	Major	14	D	D	D	D	D
11	Terbutylazine	Herbicide	Terbutylazine-desethyl-hydroxy	Minor	14	D	D	D	D	D
12	Atrazine	Herbicide	Atrazine-desethyl	Major	12	3 - 9*	5	< LOQ	6	< LOQ
13	Carbendazim	Fungicide & TP ¹	2-Aminobenzimidazole	Major	12	2 - 3*	< LOQ	< LOQ	< LOQ	2
14	Pendimethalin	Herbicide	Pendimethalin-benzimidazole	Major	12	D	D	D	D	D
15	Metamitron	Herbicide	Metamitron-desamino	Major	11	2 - 20*	5	< LOQ	< LOQ	< LOQ
16	Isoproturon	Herbicide	Isoproturon-monodemethyl	Major	10	1 - 5*	2	< LOQ	< LOQ	< LOQ
17	Difenoconazole	Fungicide	1-[2-chloro-4-(4-chlorophenoxy)phenyl]-2-(1H-1,2,4-triazol-1-yl)ethanol	Major	9	D	D	D	D	D
18	Azoxystrobin	Fungicide	Azoxystrobin acid	Major	8	D	D	D	D	D
19	Dinoseb	Acaricide	Acetyl-dinoseb-6-amino	Unknown	8	D	D	D	D	D
20	Dinoseb	Acaricide	Dinoseb-6-amino	Unknown	8	D	D	D	D	D

Land use: Cropland sites (Cl), orchards (Or), vegetable growing (Ve), and viticulture (Vi)

¹Transformation product of other pesticides such as thiophanate, thiophanate-methyl, and benomyl

*Confirmed by reference standards

D Tentatively detected, but not quantified

< LOQ lower than the limit of quantification

488 References

- 489 1. EUROSTAT EUROSTAT Statistics Explained. Agri-environmental indicator -
490 consumption of pesticides. Accessed February 2017. [http://ec.europa.eu/eurostat/statistics-](http://ec.europa.eu/eurostat/statistics-explained/index.php/Agri-environmental_indicator_-_consumption_of_pesticides)
491 [explained/index.php/Agri-environmental indicator - consumption of pesticides](http://ec.europa.eu/eurostat/statistics-explained/index.php/Agri-environmental_indicator_-_consumption_of_pesticides)
- 492 2. EC., Environmental Quality Standards Directive 2008/105/EC of the European
493 Parliament and of the council of 16 December 2008 on environmental quality standards in
494 the field of water policy. European Parliament and Council. Journal European Union 348: 84–
495 97. **2008**.
- 496 3. Masiá, A.; Vásquez, K.; Campo, J.; Picó, Y., Assessment of two extraction methods to
497 determine pesticides in soils, sediments and sludges. Application to the Túria River Basin.
498 *Journal of Chromatography A* **2015**, 1378, 19-31.
- 499 4. Kuzmanović, M.; López-Doval, J. C.; De Castro-Català, N.; Guasch, H.; Petrović, M.;
500 Muñoz, I.; Ginebreda, A.; Barceló, D., Ecotoxicological risk assessment of chemical pollution
501 in four Iberian river basins and its relationship with the aquatic macroinvertebrate community
502 status. *Science of The Total Environment* **2016**, 540, 324-333.
- 503 5. Malaj, E.; von der Ohe, P. C.; Grote, M.; Kühne, R.; Mondy, C. P.; Usseglio-Polatera,
504 P.; Brack, W.; Schäfer, R. B., Organic chemicals jeopardize the health of freshwater
505 ecosystems on the continental scale. *Proceedings of the National Academy of Sciences*
506 **2014**, 111, (26), 9549-9554.
- 507 6. Munz, N. A.; Burdon, F. J.; de Zwart, D.; Junghans, M.; Melo, L.; Reyes, M.;
508 Schönenberger, U.; Singer, H. P.; Spycher, B.; Hollender, J.; Stamm, C., Pesticides drive risk
509 of micropollutants in wastewater-impacted streams during low flow conditions. *Water*
510 *Research* **2017**, 110, 366-377.
- 511 7. Bailey, G. W.; White, J. L., Factors influencing the adsorption, desorption, and
512 movement of pesticides in soil. In *Single Pesticide Volume: The Triazine Herbicides*,
513 Gunther, F. A.; Gunther, J. D., Eds. Springer New York: New York, NY, 1970; pp 29-92.
- 514 8. García-Valcárcel, A. I.; Tadeo, J. L., Influence of Soil Moisture on Sorption and
515 Degradation of Hexazinone and Simazine in Soil. *Journal of Agricultural and Food Chemistry*
516 **1999**, 47, (9), 3895-3900.
- 517 9. Gevaio, B.; Jones, K. C.; Semple, K. T.; Craven, A.; Burauel, P., Peer Reviewed:
518 Nonextractable Pesticide Residues in Soil. *Environmental Science & Technology* **2003**, 37,
519 (7), 138A-144A.
- 520 10. Boesten, J. J. T. I., Proposal for field-based definition of soil bound pesticide residues.
521 *Science of The Total Environment* **2016**, 544, 114-117.
- 522 11. Arias-Estévez, M.; López-Periago, E.; Martínez-Carballo, E.; Simal-Gándara, J.;
523 Mejuto, J.-C.; García-Río, L., The mobility and degradation of pesticides in soils and the
524 pollution of groundwater resources. *Agriculture, Ecosystems & Environment* **2008**, 123, (4),
525 247-260.
- 526 12. Krutz, L. J.; Shaner, D. L.; Zablotowicz, R. M., Enhanced Degradation and Soil Depth
527 Effects on the Fate of Atrazine and Major Metabolites in Colorado and Mississippi Soils All
528 rights reserved. No part of this periodical may be reproduced or transmitted in any form or by
529 any means, electronic or mechanical, including photocopying, recording, or any information
530 storage and retrieval system, without permission in writing from the publisher. *Journal of*
531 *Environmental Quality* **2010**, 39, (4), 1369-1377.
- 532 13. Jablonowski, N. D.; Köppchen, S.; Hofmann, D.; Schäffer, A.; Burauel, P.,
533 Persistence of 14C-labeled atrazine and its residues in a field lysimeter soil after 22 years.
534 *Environmental Pollution* **2009**, 157, (7), 2126-2131.
- 535 14. Jablonowski, N. D.; Linden, A.; Köppchen, S.; Thiele, B.; Hofmann, D.; Mittelstaedt,
536 W.; Pütz, T.; Burauel, P., Long-term persistence of various 14C-labeled pesticides in soils.
537 *Environmental Pollution* **2012**, 168, 29-36.
- 538 15. Kim, I. S.; Beaudette, L. A.; Han Shim, J.; Trevors, J. T.; Tack Suh, Y., Environmental
539 fate of the triazole fungicide propiconazole in a rice-paddy-soil lysimeter. *Plant and Soil* **2002**,
540 239, (2), 321-331.
- 541 16. Ryberg, K. R.; Gilliom, R. J., Trends in pesticide concentrations and use for major
542 rivers of the United States. *Science of The Total Environment* **2015**, 538, 431-444.

17. Moschet, C.; Wittmer, I.; Simovic, J.; Junghans, M.; Piazzoli, A.; Singer, H.; Stamm, C.; Leu, C.; Hollender, J., How a Complete Pesticide Screening Changes the Assessment of Surface Water Quality. *Environmental Science & Technology* **2014**, *48*, (10), 5423-5432.
18. Kern, S.; Singer, H.; Hollender, J.; Schwarzenbach, R. P.; Fenner, K., Assessing Exposure to Transformation Products of Soil-Applied Organic Contaminants in Surface Water: Comparison of Model Predictions and Field Data. *Environmental Science & Technology* **2011**, *45*, (7), 2833-2841.
19. EC. *Proposal for a Directive of the European Parliament and of the Council establishing a Framework for the Protection of Soil and Amending Directive 2004/35/EC - European Community. (COM(2006)232 final)*; 2006.
20. Morvan, X.; Saby, N. P. A.; Arrouays, D.; Le Bas, C.; Jones, R. J. A.; Verheijen, F. G. A.; Bellamy, P. H.; Stephens, M.; Kibblewhite, M. G., Soil monitoring in Europe: A review of existing systems and requirements for harmonisation. *Science of The Total Environment* **2008**, *391*, (1), 1-12.
21. Saby, N. P. A.; Bellamy, P. H.; Morvan, X.; Arrouays, D.; Jones, R. J. A.; Verheijen, F. G. A.; Kibblewhite, M. G.; Verdoodt, A. N. N.; Uvéges, J. B.; Freudenschuß, A.; Simota, C., Will European soil-monitoring networks be able to detect changes in topsoil organic carbon content? *Global Change Biology* **2008**, *14*, (10), 2432-2442.
22. Carey, A. E.; Gowen, J. A.; Tai, H.; Mitchell, W. G.; Wiersma, G. B., Pesticide residue levels in soils and crops from 37 states, 1972--National Soils Monitoring Program (IV). *Pestic Monit J* **1979**, *12*, (4), 209-229.
23. Gonçalves, C.; Alpendurada, M. F., Assessment of pesticide contamination in soil samples from an intensive horticulture area, using ultrasonic extraction and gas chromatography–mass spectrometry. *Talanta* **2005**, *65*, (5), 1179-1189.
24. Kibblewhite, M. G.; Jones, R. J. A.; Montanarella, L.; Baritz, R.; Huber, S.; Arrouays, D.; Micheli, E.; Stephens, M., *Environmental Assessment of Soil for Monitoring Volume VI: Soil Monitoring System for Europe*. 2008.
25. Fisher, J. A.; Scarlett, M. J.; Stott, A. D., Accelerated Solvent Extraction: An Evaluation for Screening of Soils for Selected U.S. EPA Semivolatile Organic Priority Pollutants. *Environmental Science & Technology* **1997**, *31*, (4), 1120-1127.
26. Richter, P.; Sepúlveda, B.; Oliva, R.; Calderón, K.; Seguel, R., Screening and determination of pesticides in soil using continuous subcritical water extraction and gas chromatography–mass spectrometry. *Journal of Chromatography A* **2003**, *994*, (1–2), 169-177.
27. Krauss, M.; Singer, H.; Hollender, J., LC–high resolution MS in environmental analysis: from target screening to the identification of unknowns. *Anal Bioanal Chem* **2010**, *397*, (3), 943-951.
28. Moschet, C.; Piazzoli, A.; Singer, H.; Hollender, J., Alleviating the Reference Standard Dilemma Using a Systematic Exact Mass Suspect Screening Approach with Liquid Chromatography-High Resolution Mass Spectrometry. *Analytical Chemistry* **2013**, *85*, (21), 10312-10320.
29. Ruff, M.; Mueller, M. S.; Loos, M.; Singer, H. P., Quantitative target and systematic non-target analysis of polar organic micro-pollutants along the river Rhine using high-resolution mass-spectrometry – Identification of unknown sources and compounds. *Water Research* **2015**, *87*, 145-154.
30. Sjerps, R. M. A.; Vughs, D.; van Leerdam, J. A.; ter Laak, T. L.; van Wezel, A. P., Data-driven prioritization of chemicals for various water types using suspect screening LC-HRMS. *Water Research* **2016**, *93*, 254-264.
31. Chiaia-Hernandez, A.; Schymanski, E.; Kumar, P.; Singer, H.; Hollender, J., Suspect and nontarget screening approaches to identify organic contaminant records in lake sediments. *Anal Bioanal Chem* **2014**, *406*, (28), 7323-7335.
32. Chiaia-Hernandez, A. C.; Krauss, M.; Hollender, J., Screening of Lake Sediments for Emerging Contaminants by Liquid Chromatography Atmospheric Pressure Photoionization and Electrospray Ionization Coupled to High Resolution Mass Spectrometry. *Environmental Science & Technology* **2013**, *47*, (2), 976-986.

33. Gubler, A.; Wachter, D.; Blum, F.; Bucheli, T. D., Remarkably constant PAH concentrations in Swiss soils over the last 30 years. *Environmental Science: Processes & Impacts* **2015**, 17, (10), 1816-1828.
34. Kern, S.; Fenner, K.; Singer, H. P.; Schwarzenbach, R. P.; Hollender, J., Identification of Transformation Products of Organic Contaminants in Natural Waters by Computer-Aided Prediction and High-Resolution Mass Spectrometry. *Environmental Science & Technology* **2009**, 43, (18), 7039-7046.
35. Schymanski, E. L.; Jeon, J.; Gulde, R.; Fenner, K.; Ruff, M.; Singer, H. P.; Hollender, J., Identifying Small Molecules via High Resolution Mass Spectrometry: Communicating Confidence. *Environmental Science & Technology* **2014**, 48, (4), 2097-2098.
36. Lewis, K. A.; Tzilivakis, J.; Warner, D. J.; Green, A., An international database for pesticide risk assessments and management. *Human and Ecological Risk Assessment: An International Journal* **2016**, 22, (4), 1050-1064.
37. JChem, ChemAxon software. Version 16.10.300 <https://www.chemaxon.com>. **2016**.
38. Fenlon, K. A.; Andreou, K.; Jones, K. C.; Semple, K. T., The extractability and mineralisation of cypermethrin aged in four UK soils. *Chemosphere* **2011**, 82, (2), 187-192.
39. Wolfe, N. L.; Zepp, R. G.; Doster, J. C.; Hollis, R. C., Captan hydrolysis. *Journal of Agricultural and Food Chemistry* **1976**, 24, (5), 1041-1045.
40. Caldas, S. S.; Bolzan, C. M.; Cerqueira, M. B.; Tomasini, D.; Furlong, E. B.; Fagundes, C.; Primel, E. G., Evaluation of a Modified QuEChERS Extraction of Multiple Classes of Pesticides from a Rice Paddy Soil by LC-APCI-MS/MS. *Journal of Agricultural and Food Chemistry* **2011**, 59, (22), 11918-11926.
41. Salvia, M.-V.; Vulliet, E.; Wiest, L.; Baudot, R.; Cren-Olivé, C., Development of a multi-residue method using acetonitrile-based extraction followed by liquid chromatography–tandem mass spectrometry for the analysis of steroids and veterinary and human drugs at trace levels in soil. *Journal of Chromatography A* **2012**, 1245, 122-133.
42. Gulde, R.; Meier, U.; Schymanski, E. L.; Kohler, H.-P. E.; Helbling, D. E.; Derrer, S.; Rentsch, D.; Fenner, K., Systematic Exploration of Biotransformation Reactions of Amine-Containing Micropollutants in Activated Sludge. *Environmental Science & Technology* **2016**, 50, (6), 2908-2920.
43. Merel, S.; Lege, S.; Yanez Heras, J. E.; Zwiener, C., Assessment of N-Oxide Formation during Wastewater Ozonation. *Environmental Science & Technology* **2017**, 51, (1), 410-417.
44. Loewy, R. M.; Monza, L. B.; Kirs, V. E.; Savini, M. C., Pesticide distribution in an agricultural environment in Argentina. *Journal of Environmental Science and Health, Part B* **2011**, 46, (8), 662-670.
45. Capriel, P.; Haisch, A.; Khan, S. U., Distribution and nature of bound (nonextractable) residues of atrazine in a mineral soil nine years after the herbicide application. *Journal of Agricultural and Food Chemistry* **1985**, 33, (4), 567-569.
46. Bayer 2016 , Imidacloprid - A genuine game-changer. Website: <http://www.seedgrowth.bayer.com/explore/100%20years%20of%20innovation/imidacloprid> visited: 03.08.2016 13 :29.
47. Wettstein, F. E.; Kasteel, R.; Garcia Delgado, M. F.; Hanke, I.; Huntscha, S.; Balmer, M. E.; Poiger, T.; Bucheli, T. D., Leaching of the Neonicotinoids Thiamethoxam and Imidacloprid from Sugar Beet Seed Dressings to Subsurface Tile Drains. *Journal of Agricultural and Food Chemistry* **2016**, 64, (33), 6407-6415.
48. Laitinen, P.; Siimes, K.; Eronen, L.; Rämö, S.; Welling, L.; Oinonen, S.; Mattsoff, L.; Ruohonen-Lehto, M., Fate of the herbicides glyphosate, glufosinate-ammonium, phenmedipham, ethofumesate and metamitron in two Finnish arable soils. *Pest Management Science* **2006**, 62, (6), 473-491.
49. Sánchez-González, S.; Pose-Juan, E.; Herrero-Hernández, E.; Álvarez-Martín, A.; Sánchez-Martín, M. J.; Rodríguez-Cruz, S., Pesticide residues in groundwaters and soils of agricultural areas in the Águeda River Basin from Spain and Portugal. *International Journal of Environmental Analytical Chemistry* **2013**, 93, (15), 1585-1601.

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