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Discovering complex pesticide pollution in river water irrigated soil/groundwater systems: From targeted analyses to non-targeted screening and back

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Abstract: Pesticides and their transformation products are increasingly detected in agricultural soils and surface waters, raising concerns about their persistence, mobility, and ecological impacts. Irrigation with river water contaminated by agricultural runoff represents a significant but understudied pathway contributing to soil pollution. In this study, we investigated pesticide occurrence across soils, irrigation water, and groundwater in three intensively cultivated river basins. Soil samples from vegetable-producing fields exhibited complex contamination profiles, with 12–40 co-occurring compounds and total residues frequently exceeding levels reported for European arable soils. Several pesticides, including pendimethalin, mandipropamid, and azoxystrobin, were found at notably high concentrations, with some soils surpassing 5 000 µg/kg. Comparison of detection frequencies across matrices revealed diverse transport and retention behaviour: while certain legacy compounds (e.g., atrazine metabolites) were ubiquitous in both surface and groundwater, others showed strong soil accumulation with limited mobility. Irrigation water was identified as a non-negligible contamination source, particularly for persistent and mobile substances, although direct field applications remained the dominant contributor to peak soil concentrations. By integrating targeted and non-target screening, this study provides the most comprehensive assessment to date of pesticide burdens in riverirrigated agricultural soils and highlights the need for improved monitoring strategies in systems where soil and water pollution are tightly interconnected.

Keywords: groundwater; irrigated agricultural soil; passive sampling; pesticide residues; surface water

Pesticides are indispensable in contemporary agriculture, safeguarding crops from pests, weeds, and diseases, thereby supporting global food security amid rising population demands (Sharma et al. 2019; Tudi et al. 2021). According to the Food and Agriculture Organization of the UN, global pesticide use reached

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3.73 million tons of active ingredients in 2023, with extensive application across diverse agricultural landscapes (FAO 2025). Within the European Union, nearly 500 active substances are currently authorised for use in plant protection products (European Commission 2025; Silva et al. 2019). For example, in the Czech Republic alone, 3.386 tons of pesticides were applied to agricultural fields in 2023 (ÚKZÚZ 2024).

The widespread use of pesticides has led to the pervasive presence of their residues and transformation products (TPs) in agricultural soils. Hvězdová et al. (2018), Silva et al. (2019), Sabzevari and Hofman (2022), and Knuth et al. (2024) reported that 97% of European agricultural soil samples contained at least one pesticide residue, and 88% contained mixtures of two or more compounds. This contamination is an escalating environmental concern due to the persistence and toxicity of certain pesticides to non-target organisms. Long-term accumulation in soil poses ecological risks, including crop uptake, transfer into the food chain, and potential threats to human health (Pathak et al. 2022; Wahab et al. 2022). Pesticides may also leach into groundwater (Kodešová et al. 2011), contaminating aquifers, affecting aquatic ecosystems, and contaminating drinking water supplies. Syafrudin et al. (2021) and Rein et al. (2025) further reported that pesticide pollution in river basins from agricultural runoff exceeds risk thresholds, underscoring the importance of monitoring residues and their transformation products in soils.

The selection of pesticides for soil monitoring programs should follow a structured, evidence-based approach. Target analytes are typically chosen based on regulatory priorities, usage frequency in specific agricultural settings, environmental persistence, and the availability of validated analytical standards (Brinco et al. 2023; Guo & Li 2024). Regional monitoring data provides essential insight into compounds likely to accumulate in local soils. The occurrence of pesticides in surface waters is also considered, as soil and aquatic systems often share sources and transport pathways. For example, atrazine and its transformation products are frequently detected in both compartments, highlighting their environmental interconnectedness (Guo & Li 2024).

The complexity of soil matrices (Rosch & Bucheli 2025), the diversity of pesticide chemistries, and dynamic agricultural practices, including irrigation, make residue analysis difficult. Residues from previous applications or crop rotations may persist and accumulate, leading to complex contamination profiles (European Food Safety Authority et al. 2023). Climate change-driven water scarcity has increased the importance of irrigation. While micropollutants introduced through reclaimed wastewater or groundwater are widely studied (Manasfi et al. 2021; Koumaki et al. 2025), less attention has been paid to systems irrigated with contaminated surface water.

Conventional pesticide analysis in soils has primarily relied on targeted methods, such as liquid chromatography coupled with mass spectrometry (LC–MS) (Brinco et al. 2023; Rosch & Bucheli 2025). Although highly accurate for known compounds, these approaches are limited in detecting new or unknown substances. In contrast, non-targeted screening has gained prominence by enabling the detection of a broader range of pesticides and transformation products without prior structural knowledge. Liquid chromatography hyphenated to high-resolution mass spectrometry (HRMS), particularly operated in data-independent acquisition (DIA), allows comprehensive profiling and supports the identification of emerging or previously unreported contaminants (Picó et al. 2019; Creusot et al. 2024).

Integrating targeted and non-targeted approaches provides a more comprehensive monitoring strategy. This combined methodology integrates the precision of targeted analysis with the exploratory power of non-targeted screening, thereby improving the detection of both known and emerging contaminants. Reviews of long-term soil monitoring studies have identified hundreds of pesticides and transformation products, highlighting the limitations of relying solely on targeted methods (Sabzevari & Hofman 2022).

Recent studies highlight the practical value of integrating targeted and non-targeted approaches. (Narain-Ford et al. 2022) used targeted analysis to detect pesticides in fields irrigated with treated wastewater, and (Ore et al. 2025) subsequently identified transformation products through non-targeted screening. Similarly, Rein et al. (2025) applied a combined strategy incorporating passive sampling and LC–HRMS/DIA to assess pesticide pollution at the river basin scale, proposing a workflow capable of covering a wide range of known and unknown pollutants.

In this study, we aimed to better understand the complexity of soils irrigated with polluted river water. We present a workflow that integrates targeted quantification with non-targeted screening to increase monitoring coverage. This approach enables a more holistic assessment of pesticide contamination across three surface water-irrigated areas and matrices.

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MATERIAL AND METHODS

Chemicals. A list of native pesticide standards and corresponding internal standards obtained from commercial suppliers is provided in Table S1 in Electronic Supplementary Material 1 (ESM 1). All other reagents used for extraction and instrumental analysis were of the highest available purity: acetonitrile, dichloromethane, toluene, methanol (LC-MS grade, Merck, Darmstadt, Germany), isopropanol (LiChrosolv Hypergrade, Merck, Darmstadt, Germany), and formic acid (LC-MS grade, Altium, Prague, Czech Republic). Ultrapure water produced using the MilliporeSigma™ Milli-Q™ Direct Water Purification System was used throughout the experiments.

Sampling. Soil samples were collected from agricultural fields in the Elbe and Dyje River basins in the Czech Republic (Figure 1), where irrigation by river water is routinely practised. In July 2023, soil samples were collected from 14 vegetable-producing fields. Based on the pilot study results, the following sampling was extended to 16 localities and 30 soil samples in 2024. The localities are described in detail in Table S2 in ESM 1.

At each site, topsoil (0–20 cm) was collected using a stainless-steel auger. Multiple subsamples per field were combined into composite samples. The soil was freeze-dried, homogenised, gently crushed, and sieved (2 mm) to remove coarse debris. Prepared samples were stored in clean, labelled containers at –18 °C for physicochemical characterisation and chemical analysis, minimising analyte loss and preserving integrity.

We have also added passive sampling of surface water used for irrigation and groundwater from a shallow aquifer located as close as possible to the sampled soils in 2024. A short summary is given in Table 1, and detailed information is in Table S3 in ESM 1. Passive sampling was conducted with POCIS in a pharmaceutical/HLB type configuration (Affinisep, Le Houlme, France).

Experimental workflow. The experimental workflow was designed as a multi-stage approach combining targeted and non-targeted analytical strategies

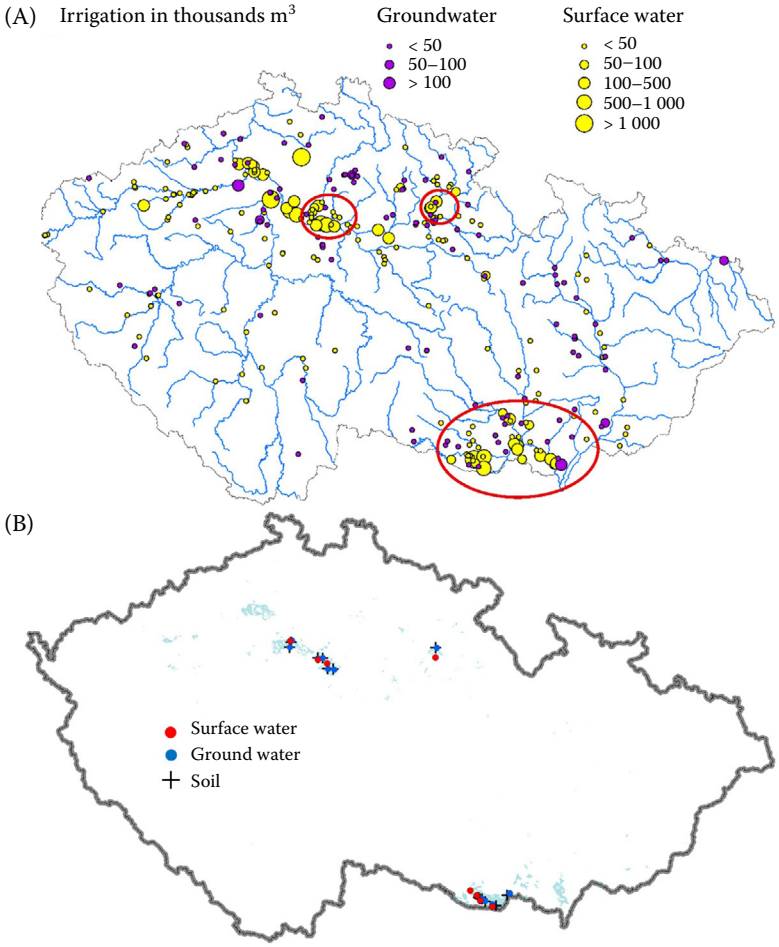

Figure 1. Location of irrigated agricultural areas along the Elbe and Dyje rivers selected for sampling (A) and site location for complex matrices sampling in 2024 (B)

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Table 1. Overview of sampled matrices and number of sites across the seasons

Basin	Summer	Autumn	Summer	Spring	Summer	Summer
			2024			2023
	SW	SW	GW	soil	soil	soil
Elbe	3	3	5	7	7	9
Jizera	1	1	1	1	2	1
Dyje	4	3	5	6	7	4

GW – groundwater; SW – surface water

to comprehensively assess pesticide residues in soil samples. The block scheme showing the consequent steps is reported in Figure 2. A targeted LC-MS/MS analysis was conducted using a predefined list of commonly monitored pesticides and their transformation products (TPs) in Czech surface and groundwater (Kodeš & Ackermanová 2023). Soil samples from 2023 were analysed using high-resolution mass spectrometry (HRMS) to detect additional pesticide-related compounds beyond the initial list. Candidate compounds were assigned tentative identifications at a confidence level according to the Schymanski et al. (2014).

Compounds identified in the non-targeted analysis were then compared with those detectable by the initial targeted method to prioritise candidates for confirmation. Compounds prioritised from the initial targeted analysis are highlighted in blue in Table S1 in ESM 1. Prioritised compounds from non-targeted screening with available analytical standards are highlighted in green in Table S1 in ESM 1. Their identities were subsequently confirmed by targeted LC-MS/MS reanalysis. The developed and validated method was subsequently applied to analyse a complex irrigation water/soil/groundwater system in 2024.

Soil sample extraction. Pesticides were extracted by pressurised liquid extraction (PLE) performed on a Dionex ASE 350 according to established methods for soil micropollutants (Nováková et al. 2024). Briefly, 2.0 g of freeze-dried soil was mixed with 0.7 g of Florisil and loaded into a 5 mL stainless-steel cell with a glass-fibre filter. Samples were spiked with isotope-labelled internal standards (50 µg/kg) prior to extraction.

Extraction was performed in two static cycles at 60 °C and 1.03×10^4 kPa for a total of 24 min using a water/isopropanol/acetonitrile mixture (4 : 3 : 3, v/v/v) acidified with 0.1% formic acid. Extracts were

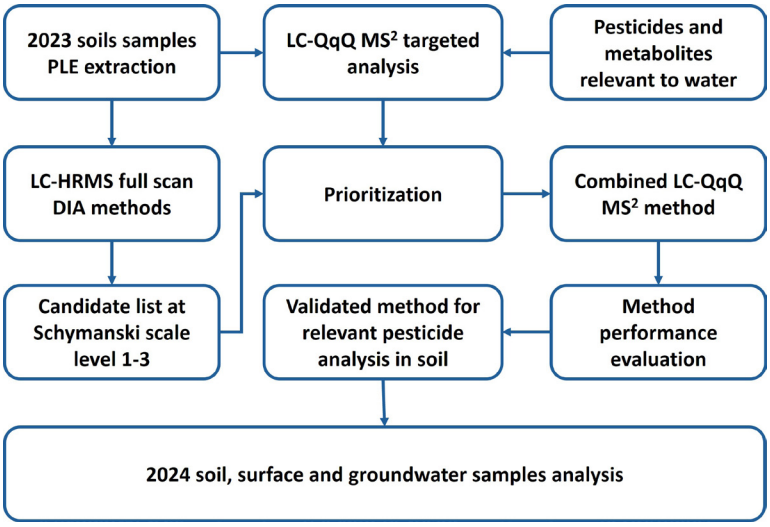

Figure 2. Experimental workflow for the identification of soil-relevant pesticides and their metabolites in the soil/water system

PLE – pressurised liquid extraction; LC-HRMS – liquid chromatography-high-resolution mass spectrometry; DIA – data-independent acquisition; LC-QqQ MS2 – liquid chromatography-triple quadrupole tandem mass spectrometry

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combined to a final volume of 10 mL. For targeted analysis, a 1 mL aliquot was filtered (0.45 µm, regenerated cellulose) and directly injected into the LC–MS system. For non-targeted analysis, the extract was concentrated tenfold under nitrogen and filtered prior to LC–MS analysis.

POCIS extraction. The passive samplers were exposed at sampling sites described in Table S3 in ESM 1 for a three-week period. POCISes were transported on ice to the laboratory and stored at –18 °C until analysis. The extraction was performed according to a standard procedure validated for a broad range of pollutants (Fialová et al. 2024). The extracts were concentrated to a final volume of 2 mL, and an aliquot of 250 µL was used for analysis.

LC-MS/MS analysis. Targeted analysis of pesticide residues in soil samples was conducted using a triple-stage quadrupole mass spectrometer (TSQ Quantiva, Thermo Fisher Scientific) coupled to a liquid chromatograph (Accela 1250, Thermo Fisher Scientific), employing internal standard calibration with matrix-matched standards. Chromatographic separation was performed on a Hypersil GOLD aQ column (2.1 × 50 mm, 5 µm particle size, Thermo Fisher Scientific) using a gradient of acetonitrile in water (acidified with 0.1% formic acid). The mass spectrometer was operated in multiple reaction monitoring (MRM) mode with electrospray ionisation. Detailed description of LC gradient and compound-specific parameters, such as precursor-product ion transitions and collision energies, are reported in Tables: Table S1 in ESM 1, Tables S1 and S2 in ESM 2.

LC-HRMS non-targeted analysis. Non-targeted analyses were performed using a QExactive HF hybrid quadrupole orbital trap mass spectrometer (Thermo Fisher Scientific) coupled to a Vanquish UHPLC system and a CTC PAL RST autosampler. Chromatographic separation was achieved on a Hypersil GOLD aQ column (2.1 × 50 mm, 5 µm) using a gradient of buffered methanol and Milli-Q water (10 mmol/L ammonium acetate) at a flow rate of 0.35–0.4 mL/min. Detailed instrumental settings and acquisition parameters have been described previously (Nováková et al. 2024). The details are provided in Tables S1 and S2 in ESM 2.

Non-target data processing. HRMS data were processed using Compound Discoverer 3.1 (Thermo Fisher Scientific) according to the workflow described by Rein et al. (2025). Positive and negative ionisation data were evaluated separately with polarity-specific settings (Nováková et al. 2024; Rein et al. 2025), and duplicate detections were removed after data merging. Initial annotation was based on exact-mass database matching, followed by refinement using MS2 libraries (mzCloud, MassBank), in-house spectra, and reported pesticide fragmentation patterns. To ensure high-confidence identifications, only features meeting strict criteria were retained, including signal intensity > 10 000 counts, mass accuracy within 5 ppm (MS1) and 10 ppm (MS2), isotope pattern matching ≥ 60%, peak areas at least fivefold higher than blanks, and identification supported by at least two MS2 fragments. Detailed workflow parameters are provided in Table S3 in ESM 2.

QA/QC and method validation. To ensure the accuracy, precision, and reliability of the analytical results, a comprehensive quality assurance and quality control (QA/QC) protocol was implemented throughout the study. This included the use of internal standards, procedural blanks, solvent blanks, matrix blanks and fortified QC samples in each batch of analysis. The final quantification method was validated as described in the corresponding chapter of the ESM 2.

Statistical data evaluation. Principal component analysis (PCA) was carried out in Statistica Ver. 14.0.0.15 (©1984–2020 TIBCO Software Inc.) to identify correlations among variables and to visualise the sample.

RESULTS AND DISCUSSION

Identification of new relevant pesticide-related compounds in irrigated soils. Within the pilot study, we analysed soil samples collected in 2023 from 14 localities in agricultural areas irrigated with surface water. Non-targeted screening revealed a complex mixture of pesticide-related compounds. Using MS^2 spectral comparisons with reference databases and the Schymanski scoring (Schymanski et al. 2014), 74 compounds were identified at a confidence level of 2 (tentative candidate structures) in both ionisation modes. These corresponded mainly to pesticides, their transformation products, and several industrial chemicals (e.g., substances used in vulcanisation processes or as plasticisers in polymer production). In total, we identified 46 pesticides, 23 pesticide metabolites, and 5 industrial chemicals. Only 29 compounds were already included in the conventional targeted method. Forty-five newly identified compounds were prioritised for inclusion in the combined targeted method.

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Detailed information for all annotated compounds, including name, molecular formula, annotation score, ΔMass, isotopic pattern match, and MS^2 confirmation, is provided in Table S4 in ESM 1 for level 1 and 2 identifications.

Prioritisation of compounds for targeted method development. Despite that response (peak area) can vary by orders of magnitude across different compounds at the same concentration level, we prioritise pesticide candidates from the non-target workflow based on their maximal peak areas across the dataset. Detection frequency and accessibility of analytical standards were auxiliary criteria.

Compounds with the highest signal intensities with available reference standards were selected for confirmation analysis using a targeted method. We have combined pesticides found at high concentrations in surface water with those in soils to obtain a comprehensive set of highly relevant compounds for quantitative analysis. The complete list of prioritised pesticides is provided in Table S1 in ESM 1 – green highlighted are the newly prioritised compounds (23) and blue highlighted are conventional analytes. The list of identified pesticides and metabolites not included in the method is reported in Table S4 in ESM 1 – highlighted in yellow. Importantly, this prioritisation strategy does not aim only to maximise the number of analytes, but rather to identify a focused set of environmentally relevant compounds.

Pesticide residues in soils in the pilot study 2023. A new combined method for pesticide analysis was validated using three commonly encountered soils in the Czech Republic with contrasting physicochemical properties (Table S4 in ESM 2). The details of the validation procedure are reported in the paragraph "Method validation" and Tables S5–S10 in ESM 2, including recovery, standard deviations, limits of quantification, and matrix effects.

The results of the quantitative analysis of all soil samples from the 2023 pilot study are reported in detail in Table S5 in ESM 1. All newly prioritised compounds and conventional ones above limit of quantification (LOQ) in at least one sample were included in this table. The results summarised in Figure 3 highlight the importance of a holistic approach to pesticide monitoring. Although only 23 new pesticides were added to the combined targeted method, the number of positive pesticide detections increased in each agricultural soil by 9–14 compounds, corresponding to an average 40% increase in the total number of pesticides above the LOQ (Figure 3A). More importantly, the average total pesticide residue concentration increased by 61% (ranging from 25 to 85%) (Figure 3B).

Pesticide residues in soils across the study. The results of the analysis of pesticide residues in all soils collected during 2023 and 2024 are reported in Tables S5 and S6 in ESM 1. Soil samples (except those classified as "No crop") were collected during the main crop cultivation period. As illustrated in Figure 4, the contamination levels in all soils sampled appear to be more closely associated with the type of cultivated crop than with the river basin. Figure 4A shows the total concentrations of all detected pesticides in each soil sample. Low contamination levels were found in fields cultivated with cereals (buckwheat and maize). In contrast, soils from fields used for root crops (potato, carrot, beetroot, celery, parsley, and onion) exhibited substantially higher pesticide burdens, which is consistent with the findings of Silva et al. (2019).

Fields sampled in early spring, prior to active irrigation and before the crop type could be confidently identified – or where crops had not yet been planted – are marked as No crop in Figure 4A. Overall, pesticide concentrations in these early spring samples were lower, both for individual compounds and total residues, compared to soils collected during the main crop cultivation period, reflecting seasonal differences in pesticide application timing. No crop category displayed the largest variability in contamination levels: concentrations ranged from 42 µg/kg in a field in Skalička (Elbe basin), where carrots were later cultivated, to 5 250 µg/kg in a field in Hrádek (Dyje basin), where onions were subsequently grown. In the latter case, contamination was dominated by pendimethalin (5 200 µg/kg). This high level indicates that pendimethalin had been applied just prior to sampling, representing an exception to this seasonal trend. Our finding of exceptionally high pendimethalin concentrations is consistent with previous evidence demonstrating that this herbicide is strongly retained in the topsoil and exhibits relatively slow dissipation, with half-lives of 43–45 days, while its sorption can be substantially enhanced under certain application conditions (e.g., in the presence of adjuvants), thereby reducing mobility and promoting accumulation in surface soil layers (Kočárek et al. 2018).

The number of co-occurring compounds in a single soil ranged from 12 to 40, most of which were present at concentrations close to the LOQ or did not exceed 50 µg/kg. Such detection frequency is substantially higher than the literature data for arable soils in the Czech Republic or Europe (Silva et al. 2019; Kosub-

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ová et al. 2020), where the most frequent numbers of residues were two to seven and two to five for CZ or Europe, respectively. Also, the frequency of exceedance of the 1 000 µg/kg level for pesticide residues is higher than reported across Europe (Silva et al. 2019). Seven pesticides were found at levels exceeding 500 µg/kg, pendimethalin (6 soils), azoxystrobin, cyprodinil, mandipropamid (2), chlorotoluron, linuron and metobromuron. The levels exceed the maximum levels reported for individual pesticides in extensive studies conducted specifically in the Czech Republic (Hvězdová et al. 2018; Kosubová et al. 2020). Comparing our findings with regions worldwide pendimethalin concentrations up to 6 906 µg/kg have been observed in agricultural soils in Portugal, while levels around 1 980 µg/kg were reported in Korea (Sabzevari & Hofman 2022). For azoxystrobin, concentrations up to 250 µg/kg have been reported in European agricultural soils (Silva et al. 2019), whereas higher levels (up to 460 µg/kg) have been observed in other regions, such as Jordan (Sabzevari & Hofman 2022). Similarly, cyprodinil concentrations of approximately 460 µg/kg have been reported in Spain (Sabzevari & Hofman 2022). Banned linuron reached in a carrot field near Věkoše, consistent with Swiss findings (Riedo et al. 2021; 2023), even in organically managed fields.

All the above-mentioned findings can be attributed either to our non-targeted prioritisation

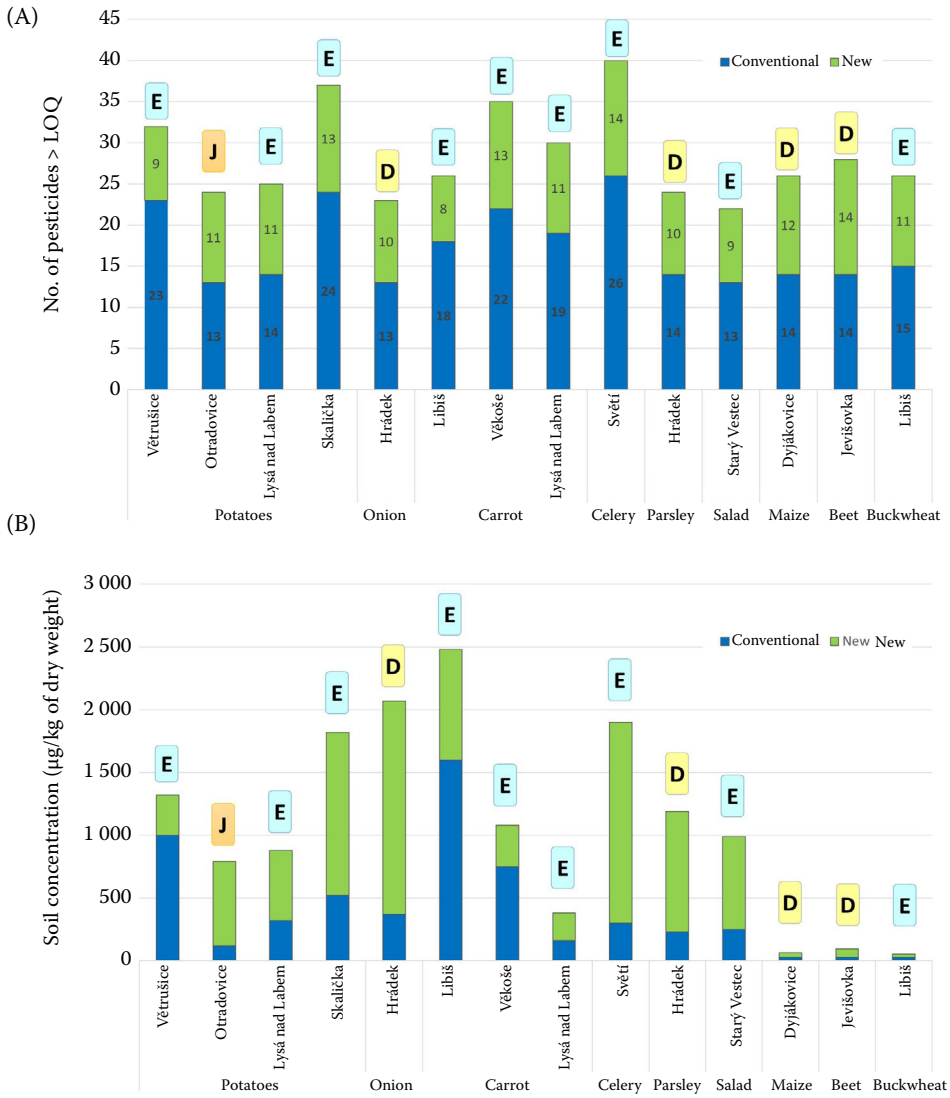

Figure 3. Summary of the number of quantified compounds (A), and sums of pesticide concentrations (B) in soil samples collected in 2023

LOQ – limit of quantification;The corresponding irrigation water basins are labelled as E (Elbe), J (Jizera) (Elbe tributary), and D (Dyje) above the columns

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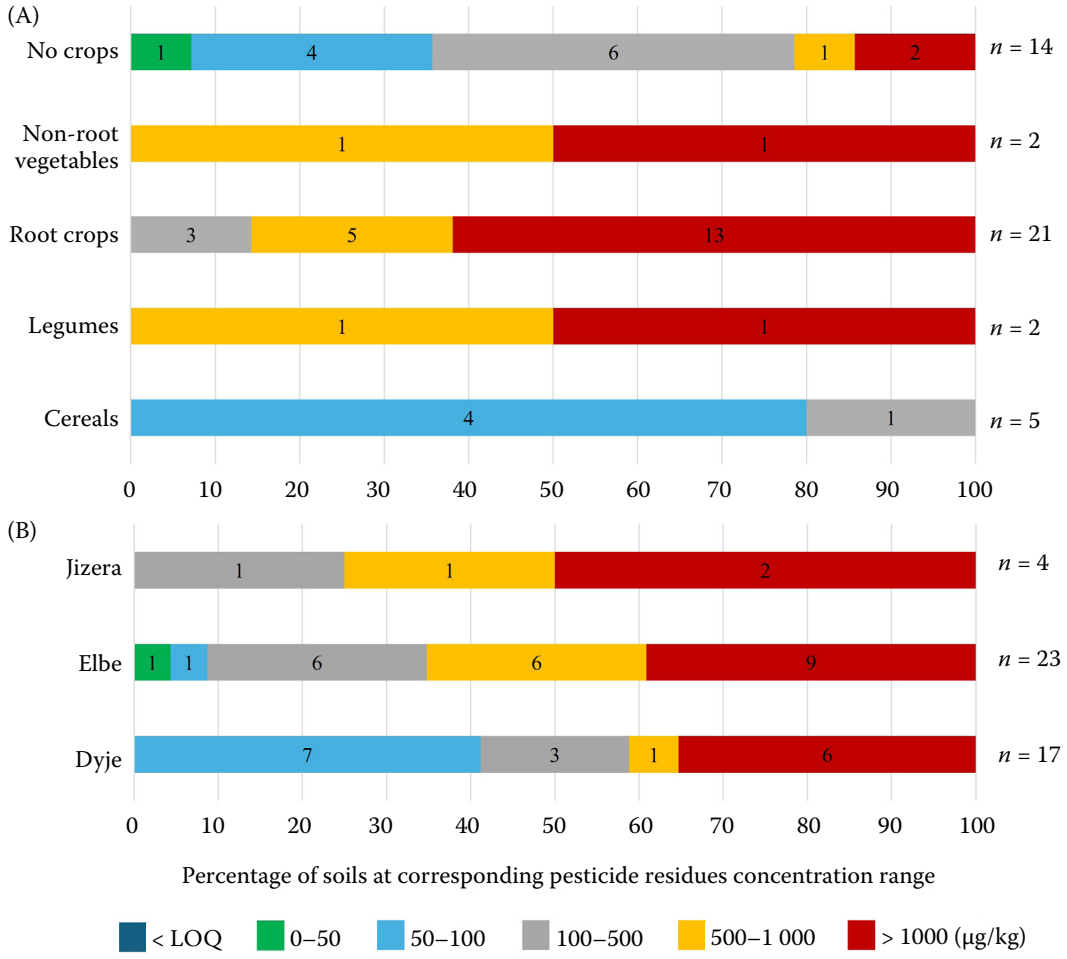

Figure 4. Summary of total pesticide residues in 2023 and 2024 soil samples according to the crop planted (A) or the corresponding irrigation water basin (B)
LOQ – limit of quantification

workflow, which does not rely on farmers' reports and official statistics, or to differences in agricultural practices in irrigated areas, such as irrigation and faster crop rotation.

Pesticide residues in soils, surface, and groundwater in 2024. The 2024 experiment was conducted to investigate the relationships between irrigation water, irrigated soil, and groundwater. Results from passive sampler analyses are reported in Tables S7 and S8 in ESM 1. Hypothesising contamination transfer from surface water used for irrigation and/or leaching pesticides and metabolites into groundwater, we calculated detection frequency (DF) for analysed compounds across sampled matrices. The results are reported in Table S9 in ESM 1. PCA analysis of this data is presented in Figure 5. This figure shows that PC1 explains about 62% of the variation and is negatively correlated with detection frequency across all matrices. PC2 then positively correlates with DF in soils. The green circle in Figure 5 represents ubiquitous compounds: the pesticides pendimethalin and azoxystrobin, together with legacy or recent pesticide metabolites 2-hydroxy atrazine, hydroxy propazine, and 2-hydroxy terbuthylazine.

The blue circle marks compounds commonly present in surface and ground water with DF > 80% but are negligibly (< 25%) present in soils. The long-time banned pesticides atrazine and chloridazone belong to this cluster, together with the recently used pesticides terbuthylazine and tetraconazole (maximum concentrations in soils: 0.74, 5.3, 27, and 8.7 µg/kg, respectively), and the metabolites metazachlor ESA and metolachlor ESA. Notably, atrazine and chloridazone were detected in organically managed fields up to ~20 years after conversion (Riedo et al. 2021).

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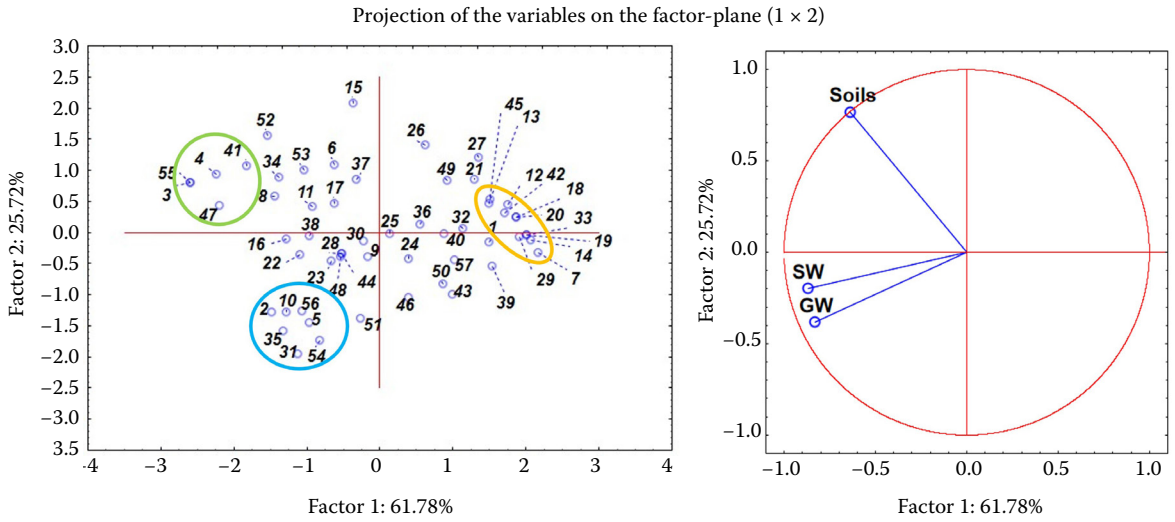

Figure 5. Results of principal component analysis (PCA) of detection frequency (DF) across the matrices sampled in 2024
Data points are labelled with numerical identifiers corresponding to compounds listed in Table S9 in ESM 1; SW – surface water; GW – groundwater; green circle groups compounds with DF > 80% in all matrices, blue circle groups compounds with DF > 80% in ground and surface water, and orange ones highlight pesticides with DF < 30% in soils and < 10% in water

A high number of investigated compounds were found in low frequency, mainly in soils (orange eclipse): clothianidine, cyprodinil, cyantraniliprole, fenpropidin, fenpropimorph, fluazinam, metamitron, metobromuron, monuron, prochloraz, and propamocarb. However, metabolites of some compounds were detected by non-targeted screening but not prioritised for the targeted method, e.g., prochloraz metabolites BTS 40348 and BTS 44595 (Table S4 in ESM 1).

By focusing on highly detected compounds in soils, we can identify highly diverse patterns of their co-occurrence in surface water used for irrigation in given areas and in groundwater (Figure 6). The absence of some pesticides in irrigation water and groundwater indicates low mobility in soils and/or rapid transformation into metabolites and consequently excludes irrigation as the source. This pattern was observed only with mandipropamid, particularly with linuron.

All other frequently observed pesticides in soil were detected in most surface water, suggesting that irrigation cannot be excluded as a contributor to soil contamination. The sources of some compounds in irrigation water are highly variable, as shown in Figure 7 and Table S10 in ESM 1 for three parent pesticides and their metabolites.

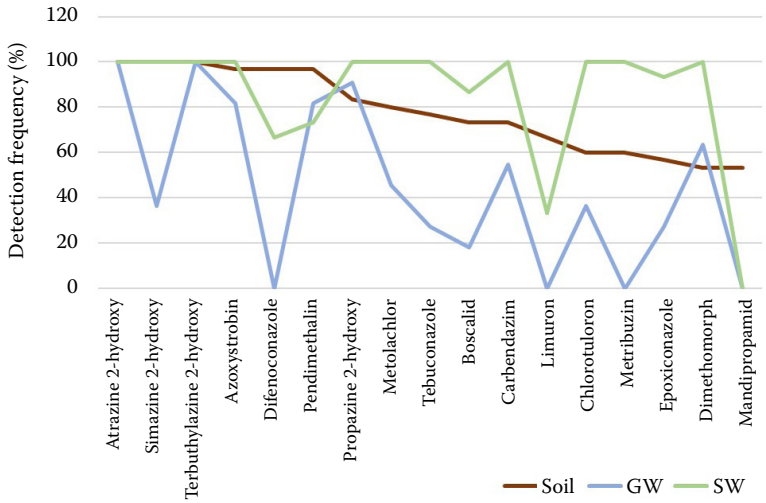

Figure 6. Compounds found with detection frequency (DF) > 50% in soils related to water matrices collected in 2024
GW – groundwater; SW – surface water

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It is anticipated that the legacy pesticide atrazine is present primarily as a metabolite. Although atrazine has been banned in the EU since 2004, legacy reservoirs in agricultural soils and connected groundwaters can retain the parent compound for more than two decades. Its transformation products, such as desethyl- and hydroxy-atrazine, often persist even longer due to greater mobility, sorption into non-extractable fractions, and slower subsequent degradation (Gallego et al. 2024). Separately, the atrazine metabolite 2-hydroxyatrazine was observed at organic sites with zero on-farm applications for ~15–75 years (Riedo et al. 2023). However, there is an obvious low transformation of atrazine in the springtime in the Elbe basin, indicating some conserved source in the basin or perhaps its illegal application.

For the other two recently used pesticides, the pattern corresponds to an application contribution in spring and the prevalence of metabolites in autumn, independently of the basin.

The detection frequency of parent compounds in soils was low (30, 3, and 3% for atrazine, simazine, and terbuthylazine), with very low residue concentrations exceeding 10 µg/kg observed only at the maize field for terbuthylazine. The ratio of metabolite/parent was near 1 in this soil, suggesting that application was likely the source in this case. However, irrigation could be a source of trace amounts of both parent and metabolites for the mentioned triazine herbicides, at other localities.

Ground water appear to reflect the retention and transformation of both parent and metabolites, as seen in Figure 7B, where legacy atrazine shows a ratio mostly above 5, whereas recently used terbuthylazine shows a ratio in the range 1–6. The picture is distorted by very low sampling levels in some groundwater (labelled in Figure 7B), and there is obvious contamination from the application of terbuthylazine to maize (only positive soil sample

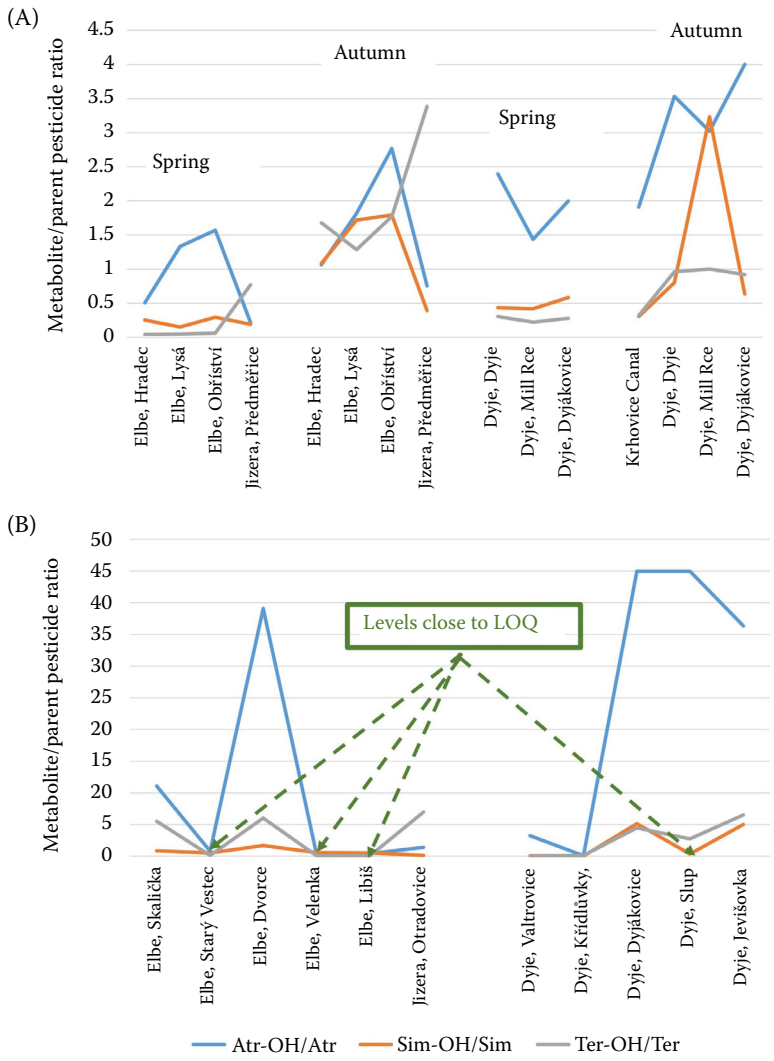

Figure 7. Ratio of metabolite/parent in surface water (A) and ground water (B) sampled in 2024

Atr – atrazine; Atr-OH – atrazine 2-hydroxy; Sim– simazine; Sim-OH – simazine 2-hydroxy; Ter – terbuthylazine; Ter-OH – terbuthylazine 2-hydroxy; LOQ – limit of quantification

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at site Dyje-Valtrovice), with a groundwater level of 790 ng/POCIS.

CONCLUSION

We have applied a workflow consisting of non-targeted data acquisition and suspect screening to obtain more comprehensive information on complex pesticide pollution in irrigated soils. The resulting targeted method extended the analysis coverage, leading to a greater number of pesticide residues detected and higher total concentrations found. The investigation of the soil/water systems in three irrigated areas across three river basins showed elevated co-occurrence of pesticide residues as well as higher total and individual contamination levels compared to agricultural soils across Europe and the Czech Republic. Those findings can be attributed either to our non-targeted prioritisation workflow, which does not rely on farmers' reports and official statistics, or to differences in agricultural practices in the investigated areas, such as irrigation and faster crop rotation. Irrigation with river water could contribute to soil contamination, especially legacy pesticides. However, the highest soil values observed can be directly attributed to pesticide application to the crop, as the irrigation techniques and intensity in the Czech Republic do not reach levels common in southern countries.

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