

Trace-level Multi-residue Analysis of Pesticides in Soil: Advances, Challenges, and Future Directions

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Abstract: Pesticides are frequently applied in large quantities in agriculture, resulting in their widespread presence in agricultural areas. Additionally, processes such as drift and volatilization contribute to their dispersion far beyond treated sites. However, systematic soil monitoring remains limited. To assess pesticide exposure to soil organisms, highly sensitive, accurate, and robust multi-residue analytical methods are essential. Given the wide variety of pesticides applied, monitoring those most likely to adversely affect soil health and terrestrial ecosystems is a prerequisite. Soil is one of the most complex environmental matrices, posing significant challenges throughout the entire analytical workflow. Here, we summarize the historical evolution of pesticide analysis in soil, outline key methodological advances, and discuss major challenges that must be addressed along the whole analytical workflow to enable effective soil monitoring. Ultimately, protecting soil requires both analytical and regulatory progress, as part of a broader set of measures.

Keywords: Analytical Method · Pesticides · Soil monitoring



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1. Introduction

Soils are a finite and practically non-renewable resource. They regulate biogeochemical cycles, provide habitat for plants and animals, perform essential filtering and storage functions, and are the basis for food production. Soils are threatened by a variety and combination of factors, including climate change, physical degradation (*e.g.* erosion and compaction), loss of organic matter, and chemical contamination.^[1,2]

In agricultural areas, pesticides are among the main chemical stressors to soil. Designed to control or prevent the spread of crop pests, diseases and weeds, their ever-increasing use^[3] is a major concern for both aquatic and terrestrial ecosystems.^[4–8] Therefore, the European Union has introduced several strategies and legislative initiatives under the umbrella of the European Green Deal (COM/2019/640),^[9] aiming to protect the valuable resource of soil. The Farm to Fork strategy (COM/2020/381)^[10] seeks to reduce risks associated with pesticides, while the proposed Soil Monitoring Law (COM/2023/416),^[11] currently under provisional political agreement (as of April 2025), aims to establish a legally binding, EU-wide framework for comprehensive soil monitoring, including pesticide contamination. Similarly, national efforts such as the Swiss Action Plan for Risk Reduction and Sustainable Use of Plant Protection Products (AP PPP)^[12] pursue comparable goals through integrated risk reduction measures.

These developments highlight the growing need for systematic pesticide residue monitoring in soil and the identification of priority contaminants to assess both short- and long-term ecotoxicological risks on soil organisms. Therefore, highly sensitive, accurate, and robust multi-residue analytical methods are essential

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as the basis for monitoring studies to quantify a broad range of pesticides of emerging concern in complex soil matrices. Here, we summarize the historical evolution, highlight current challenges, and outline future perspectives in multi-residue pesticide analysis in soil.

2. Methodological Advances in Pesticide Analysis

2.1 Evolution of Extraction Techniques

Soxhlet extraction was introduced by Franz von Soxhlet in the late 19th century and was originally developed to determine the lipid content in dried foods.^[13] Over time, it became the standard technique for extracting analytes (e.g. organochlorine pesticides, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons) from solid matrices such as soils,^[14,15] and remained widely used for nearly a century. Soxhlet extraction is based on the heating of a solvent, which is continuously distilled and condensed to circulate through the sample, dissolving analytes for efficient extraction over an extended duration. This process maintains a maximum fugacity gradient of the analytes between the sample and the solvent, thereby enhancing analyte transfer. Despite continuous improvements in reducing extraction time and volume, the ability to simultaneously extract multiple samples and enhancing extraction efficiency through ultrasonic energy, this technique has been largely superseded.^[16] Nevertheless, it retains certain advantages, including its long-term availability and technical reproducibility, its independence from specific instrumentation, and its robust applicability across a wide range of sample types.

By the end of the 20th century, accelerated solvent extraction (ASE) was introduced, which mostly replaced Soxhlet extraction along with other classical techniques such as ultrasonic-assisted extraction, microwave-assisted extraction, and supercritical fluid extraction with CO₂. ASE utilizes elevated temperature and pressure, requires significantly less solvent, and achieves much faster quantitative extraction compared to Soxhlet.^[17,18] However, it remains relatively labor- and time-intensive, particularly when processing large numbers of samples, as is common in environmental monitoring. Moreover, the technique remains susceptible to technical failures, such as clogging, leakage, and cross-contamination, particularly during high-throughput applications.

In 2003, the QuEChERS extraction was introduced, which stands for Quick, Easy, Cheap, Effective, Rugged and Safe.^[19] Originally developed to extract pesticides from fruits and vegetables, it quickly became a widely adopted method for the extraction of various analytes from a broad range of matrices. Currently, two QuEChERS methods are commonly in use: the CEN standard method EN15662,^[20] which employs a citrate buffer, and the AOAC Official Method 2007.01^[21] using acetate buffer. Buffers are used to maintain a stable pH during extraction, which helps prevent degradation of pH-sensitive analytes and improves method robustness. QuEChERS involves a simple extraction with acetonitrile, either in its pure form or acidified, depending on the analytes of interest. For dry matrices such as soil, samples are pre-wetted with water to improve pore accessibility and facilitate analyte extraction. This is followed by a salting-out step to induce phase separation, enabling efficient partitioning of analytes into the organic phase. The extraction is commonly followed by a clean-up step to remove co-extracted matrix components, typically using dispersive solid-phase extraction with magnesium sulfate and a primary secondary amine sorbent.

Since its introduction in 2003, the use of the QuEChERS method has steadily increased. A search for ‘QuEChERS’ in Scopus, within the fields of ‘article title, abstract, and keywords’, reveals that the number of publications using QuEChERS as an extraction method rose from just a few in the early 2000s to nearly 600 in the year 2024. Even when narrowing the search to studies specifically focusing on pesticide extraction from soil (using the

terms ‘QuEChERS’, ‘soil’, and ‘pesticide’), a consistent upward trend emerges – rising from a handful of studies to around 35 publications in 2024. This trend highlights the growing relevance of QuEChERS in soil-based pesticide analysis.

Although QuEChERS is not considered to be a harsh extraction technique like ASE – as it does not operate at high temperatures and pressures – it achieves recoveries comparable to or even higher than ASE in the extraction of pesticides from soil.^[22–24] Notably, the salting-out step in QuEChERS is an exothermic reaction that shortly leads to elevated temperatures, thereby enhancing the extraction process, and making QuEChERS less mild than commonly assumed. Overall, the evolution of extraction techniques reflects a clear shift towards more sustainable, faster, and user-friendly approaches, as seen for QuEChERS.

2.2 Evolution of Instrumental Analysis

The field of instrumental analysis has similarly evolved, shifting from single-compound or compound-class-specific analytical methods to multi-residue and screening-based approaches. Starting from the 1970s, gas chromatography (GC) was predominantly used for routine pesticide residue analysis in various matrices, employing electron capture, nitrogen-phosphorous, flame photometric or flame ionization detectors.^[25] As mass spectrometry (MS) became more accessible, it gradually replaced these classical detectors due to its ability to combine simultaneous quantification and confirmation in a single run. In parallel, GC-electron impact (EI)-MS spectral databases were developed, such as the NIST library,^[26] to facilitate straightforward analyte identification. During this time, liquid chromatography (LC) methods were used less frequently because conventional UV, diode array, and fluorescence detectors typically offered lower selectivity and sensitivity compared to GC-EI-MS instruments. It was only with the commercial availability of atmospheric-pressure interfaces, such as electrospray ionization (ESI) and atmospheric-pressure chemical ionization (APCI), that the challenges of coupling LC to MS were overcome, allowing LC-MS to emerge as a viable alternative to GC-EI-MS.^[27] The use of LC-ESI-MS enables the analysis of a very broad range of analyte polarities and molecular masses, offering significantly greater universality compared to GC-EI-MS.^[28] In 2006, Alder *et al.*^[29] compared the applicability and sensitivity of 500 pesticides using either GC-EI-MS or LC-ESI-MS/MS. Only for organochlorine pesticides, GC-EI-MS performed better, while LC-ESI-MS/MS was superior for all other pesticide classes. Nowadays, tandem mass spectrometry (e.g. triple quadrupole mass analyzers) is increasingly applied in GC applications, similar to its widespread use in LC applications. In GC-EI-MS/MS, the hard ionization technique of EI results in extensive fragmentation, meaning that lower-intensity fragments often must be selected as precursor ions for further fragmentation into smaller product ions. This clearly compromises sensitivity and selectivity compared to LC-ESI-MS/MS, where soft ionization produces high-intensity molecular ions that can be used for subsequent fragmentation. Although softer ionization techniques for GC, such as chemical ionization and APCI, are available,^[30–31] they are predominantly used for specific pesticide classes in different matrices that require GC due to their high apolarity, such as organochlorine pesticides^[32] and pyrethroid insecticides^[33,34] and only a few studies have applied them for multiclass pesticide analysis.^[35] These specific pesticide classes cannot, or only with high method limits of quantification (MLOQs), be adequately analyzed by LC-ESI-MS/MS. Therefore, LC and GC techniques need to be applied complementarily in order to analyze all pesticide classes of concern at environmentally relevant concentrations.

Soft ionization techniques combined with triple quadrupole mass analyzers operating in the multiple reaction monitoring (MRM) mode – acquiring at least two ion transitions per analyte

(precursor ion → product ion) - offer high sensitivity, selectivity, as well as a broad linear range spanning several orders of magnitude. This makes them the preferred and reliable approach for analyzing environmental matrices in regulatory contexts. However, targeted triple quadrupole applications operating at unit mass resolution lack the capability to screen for suspect and non-target analytes. High resolution MS (HRMS), such as Orbitrap or time-of-flight (TOF) instruments, enable suspect and non-target screening through the use of retention time, exact mass, isotopic patterns, and MS/MS fragmentation data. This approach allows the detection and identification of compounds, such as pesticide transformation products (TPs) that may be ecotoxicologically relevant, in environmental matrices like surface water,^[36] groundwater,^[37] sediment,^[38] and soil,^[39,40] for which reference standards are often not commercially available.

2.3 Integrated Workflows for Multi-residue Pesticide Monitoring in Soil

Today, multi-residue pesticide analysis in soil is primarily conducted by combining QuEChERS extraction with LC-ESI-MS/MS (triple quadrupole) techniques.^[23,41–51] In soil monitoring studies, where a large number of samples are often analyzed, QuEChERS accelerates sample preparation without compromising method performance. LC-ESI-MS/MS in the MRM scan mode is capable of capturing a broad polarity range of modern pesticides in a sensitive and selective manner. To also detect more apolar pesticides that are not or are only marginally amenable to LC-ESI, such as legacy persistent organochlorine compounds (e.g. DDT or dieldrin) – which are still found in soil despite being banned in the European Union and Switzerland since the 1970s^[52] – and pyrethroid insecticides, some LC-based pesticide soil monitoring studies are complemented by GC methods.^[41–43,50] Additionally, there are relevant pesticides, such as glyphosate and its main TP AMPA, that are frequently applied in high amounts and require single-compound analytical methods due to their specific physico-chemical properties. Although glyphosate and AMPA are among the most frequently detected pesticides in European soils,^[42,43,50,53,54] Franco *et al.*^[50] have shown that they do not pose a significant risk to soil macro- and mesofauna.

In light of the presented wide availability of analytical methods to analyze pesticides in soil, our recently developed multi-residue analytical method^[24] offers enhanced validation and accurate quantification in the sub-ng/g range. The method covers 146 pesticide residues relevant for long-term soil monitoring (60 fungicides, 30 herbicides, 26 insecticides, 4 acaricides, 4 rodenticides, 2 plant growth regulators, 1 synergist, and 19 TPs) and is based on QuEChERS extraction followed by LC-ESI-MS/MS (triple quadrupole). Quantification was performed using matrix-matched internal standard calibration with a standard soil largely representative of Swiss agricultural soils (LUFA 2.4, Landwirtschaftliche Untersuchungs- und Forschungsanstalt, Speyer, Deutschland). Structure-identical isotopically labelled internal standards (ILIS) were available for 95 out of the 146 analytes. For analytes lacking structure-identical ILIS, suitable alternatives were chosen to maintain recoveries between 70–120% across soils with approximately 1–5% organic carbon content. Unlike conventional validation procedures, which rely exclusively on soils freshly spiked with analytes shortly prior to extraction, our method includes additional validation using a laboratory-prepared, partially aged soil containing all target analytes (hereafter referred to as ‘reference soil’), as well as real agricultural field soils with native pesticide residues.

The developed method exhibits high sensitivity (median MLOQ: 0.2 µg/kg; ≤ 0.5 µg/kg for 80% of all analytes) and surpasses the sensitivity of recently published multi-residue QuEChERS LC-ESI-MS/MS (triple quadrupole) methods by one to two orders of magnitude (see Fig. 1).^[41,42,47,48,50] Only a few methods

achieve MLOQs below 0.5 µg/kg while covering more than 100 analytes.^[45,54] The method’s intra-day and inter-day precision, based on measurements in agricultural field soils, showed a median value of approximately 4%. Trueness was assessed through multiple approaches: (i) the partially aged reference soil, in which pesticide concentrations remained stable over six months and were close to the initially spiked nominal concentration of 10 µg/kg (see section 3.1 for further discussion); (ii) relative recoveries from freshly spiked soils (median value: 103%); (iii) participation in an interlaboratory comparison (ring trial) yielding good to satisfactory results, with *z*-scores close to 1; and (iv) comparison with external reference standards (median deviation among three different analyte mix solutions: 3%). Overall, a sensitive, selective, and reliable high-throughput analytical method was developed, suitable for long-term soil monitoring and enabling the routine analysis of diverse soils with varying soil properties.

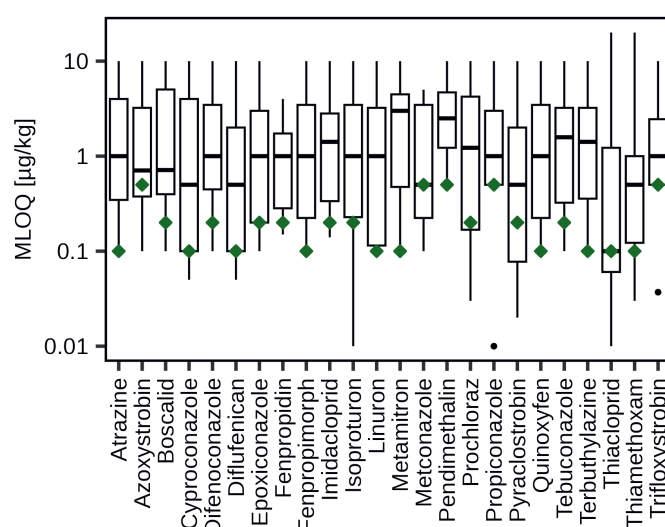


Fig. 1. Distribution of method limits of quantification (MLOQs) across nine recently published multi-residue QuEChERS LC-ESI-MS/MS (triple quadrupole) methods (Rösch *et al.*,^[24] Silva *et al.*,^[41] Knuth *et al.*,^[42] Acosta-Dacal *et al.*,^[45] Pelosi *et al.*,^[46] Hvězdová *et al.*,^[48] Franco *et al.*,^[50] Froger *et al.*,^[54] Riedo *et al.*^[55]). Only MLOQs for pesticides included in our analytical method and reported by at least six of the other methods are shown. MLOQs from our method are highlighted with green diamonds.

3. Challenges in Soil Pesticide Analysis

Pesticide analysis in soil involves multiple challenges spanning the entire analytical workflow. Fig. 2 provides an overview of these challenges, covering key steps such as soil sampling, sample pre-treatment, extraction, chemical analysis, as well as quantification and method validation. The following sections discuss some of these specific challenges in greater detail.

3.1 Challenges in Extraction, Quantification, and Assessing Method Trueness in Complex Soil Matrices

Sites included in (Swiss) soil monitoring can vary considerably in their soil properties, such as soil organic carbon, pH, and texture.^[56] These differences in soil properties influence the extent to which matrix components, such as humic substances, are co-extracted from the soil sample. For best analytical practice, quantification should be based on matrix-matched (internal standard) calibration using a soil that closely resembles the field samples in terms of key properties, and, ideally, does not contain the target analytes. Such standard soils should be available in sufficient

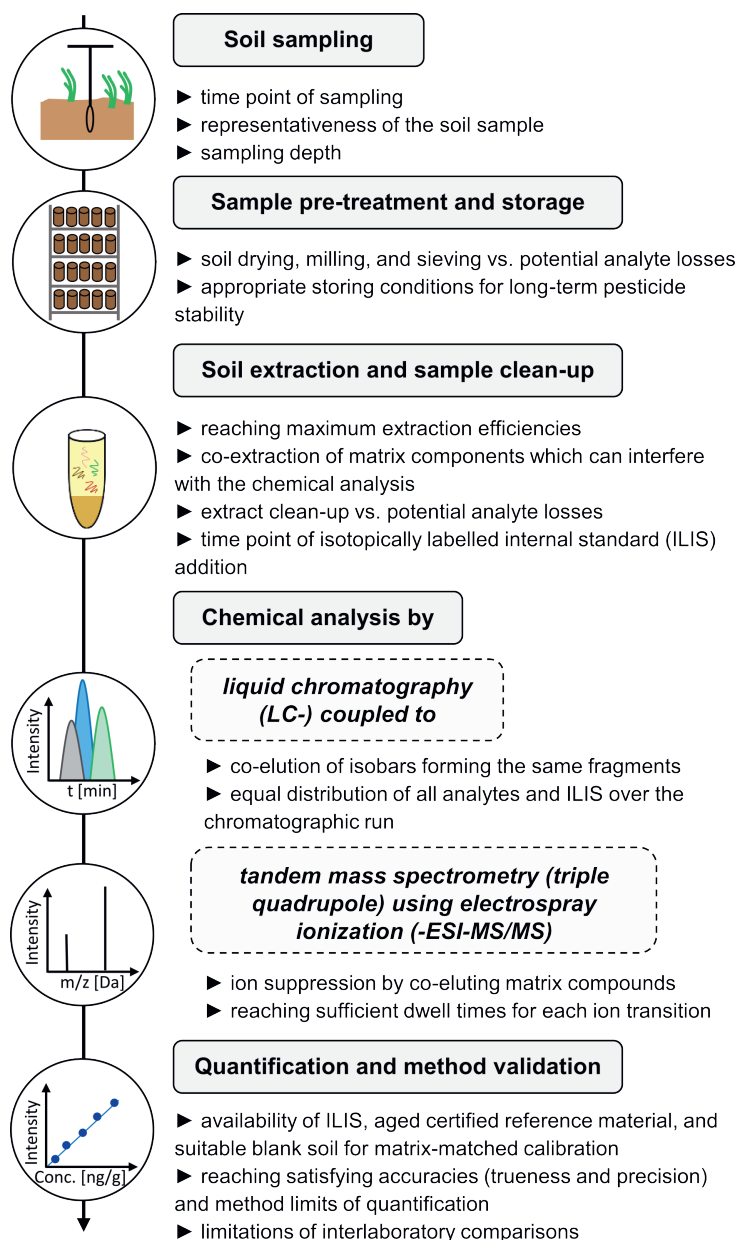


Fig. 2. Overview of key challenges encountered throughout the analytical workflow in soil pesticide monitoring and analysis.

quantities to ensure consistency and reproducibility in long-term soil monitoring programs. However, for quantification completely independent of the soil type, the use of ILIS is recommended to compensate for soil-specific matrix effects during ESI (see section 3.2), as no single standard soil can replicate the matrix effects of all analyzed field soils. When working with ILIS, solvent-based internal standard calibration can yield equally accurate quantification in LC-ESI-MS/MS – provided that structurally identical ILIS are available for the target analytes.

To compensate for matrix effects during LC-ESI-MS/MS and analyte losses throughout extraction and further sample processing, ILIS should be added as early as possible, ideally prior to extraction, to fully leverage their corrective capabilities. However, spiking ILIS before extraction has practical implications for both the volume of the extraction solvent and the achievable ILIS concentration. This is particularly relevant when aiming to maintain a simplified workflow without concentrating the final extract *via* solvent evaporation, a step that itself can introduce further analyte losses. Using large volumes of extraction solvent dilutes the ILIS concentration, and due to the high cost of ILIS, excessively high spike concentrations are often not feasible. Moreover, if analyte concentrations in the final extract exceed the linear range of the

instrument, dilution is limited, as both analytes and ILIS would be affected equally, potentially compromising accurate quantification.

Soil is one of the most complex environmental matrices, and pesticide interactions occur with it through a range of mechanisms, including ionic, hydrogen, and covalent bonding, charge transfer, Van der Waals forces, ligand exchange, and hydrophobic bonding and partitioning.^[57,58] Due to the absence of certified reference materials containing aged residues of a broad range of currently used pesticides, it is standard practice during method validation to use soils that are spiked with target analytes just prior to extraction. However, such spiked soils do not replicate the time-dependent binding processes that occur under field conditions. Only aged soils reflect the realistic interactions between pesticides and the soil matrix, as found in field soils, which intensify over time. Consequently, extraction efficiencies determined using freshly spiked soils are notably higher, as they lack the strong pesticide binding observed to aged soils. Therefore, we decided to prepare a reference soil, which is considered to be partially aged. All target pesticides were allowed to interact and equilibrate with the soil matrix over a period of seven days, during which the soil-water suspension was mixed at 5 °C. After freeze-drying and sieving (≤ 2 mm), the soil was stored in an amber glass bottle at -20 °C

in the dark. Initial measurements indicated stable pesticide concentrations in the reference soil over six months (median inter-day precision of 6%, see section 2.3). However, continued monitoring over two years revealed concentration changes, with a median absolute change of 9% – exceeding the inter-day method precision for 80% of the monitored pesticides (see Fig. 3). Therefore, extended time-series analyses are needed to assess the long-term stability of pesticides in stored soil samples and to determine whether the averaged individual pesticide concentrations in the reference soil can serve as target values for evaluating accuracy – regarding both trueness and precision – in ongoing pesticide soil monitoring using the partially aged reference soil. The observed decrease in concentrations also prompts further consideration of sample storage conditions, especially since the dried reference soil was stored at -20°C in the dark. This stands in contrast to storage practices, *e.g.* in the Swiss soil monitoring network (NABO),^[59] where samples are kept in the dark at ambient or moderately cooled temperatures.

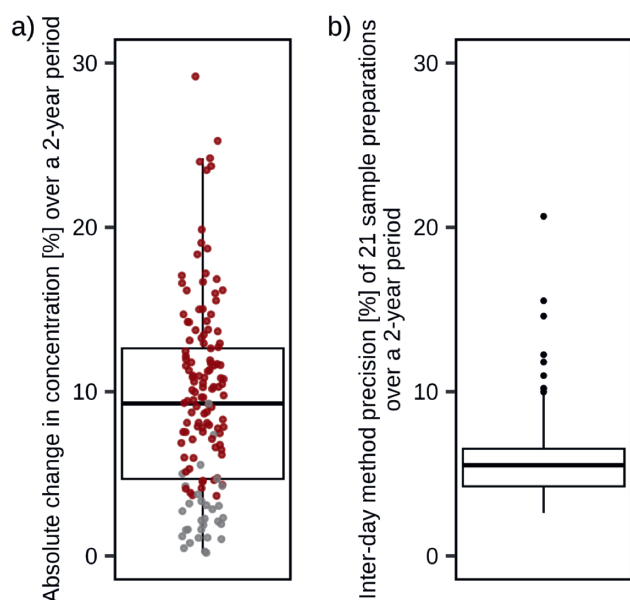


Fig 3. (a) Absolute change in the concentration of each pesticide in the reference soil over a 2-year period, comparing the concentrations from the first and last sample preparation (total number of sample preparations: $n = 21$). Red points indicate cases where the absolute change exceeds the inter-day method precision, while grey points represent changes within inter-day method precision. (b) Inter-day method precision for each pesticide, calculated from 21 sample preparations of the reference soil, each conducted in duplicate over the 2-year period.

3.2 Instrumental Challenges

ESI is strongly influenced by co-extracted soil matrix components, which can alter the ionization efficiencies of target analytes and, consequently, affect their instrumental sensitivity. This phenomenon, known as matrix effects, can lead to either ion enhancement or ion suppression. In our study, matrix effects – observed as ion suppression – increased with rising matrix complexity, as indicated by higher soil organic carbon content (see Fig. 4). ILIS can compensate for matrix effects and thus enable accurate quantification of pesticides in soil. However, as structure-identical ILIS are not available for all target analytes, non-structure-identical ILIS must be selected for the remaining analytes. Ideally, the chosen non-structure-identical ILIS should effectively compensate for matrix effects of each analyte across diverse soil matrices. This was ensured by a systematic evaluation of relative recoveries,

aiming to achieve values between 70% and 120% across five test soils with organic carbon contents ranging from approximately 1% to 5%.

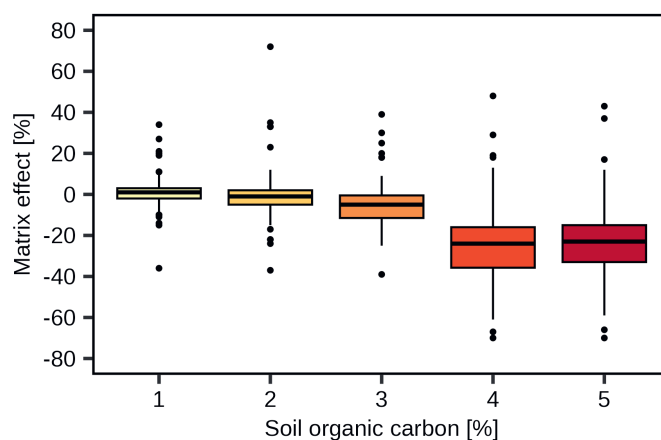


Fig. 4. Soil-specific matrix effects for all pesticides included in the analytical method, observed in soils with organic carbon contents ranging from approximately 1% to 5% (values on the x-axis are rounded to the nearest integer percentage). Signal intensities were referenced against calibration standards prepared in acetonitrile containing 2.5% formic acid.

Following extraction, a clean-up step can be employed to remove interfering matrix constituents. However, it may also cause analyte losses^[45,60] and prolong sample preparation, making it less suitable for routine high-throughput soil monitoring. We achieved sufficient instrumental sensitivities (median value of 0.025 ng/mL, corresponding to 0.125 pg per 5 μL injection) without sample clean-up by directly injecting 5 μL of undiluted final extract in pure organic solvent into a high-flow LC system operating at 750 $\mu\text{L}/\text{min}$. This approach eliminates the need to adjust the solvent composition of the final extract to that of the initial mobile phase, which would otherwise require additional dilution and would thereby compromise sensitivity.

Multi-residue methods, as commonly employed in pesticide analysis in soil, require the simultaneous detection of a large number of analytes and ILIS. Even when operating in the dynamic MRM scan mode on a triple quadrupole MS, the number of ion transitions that can be integrated into a single acquisition method is ultimately limited by the instrument's scan speed. Optimizing the interplay between the LC gradient, detection window, target cycle time, and the resulting dwell times (*i.e.* the time the instrument dedicates to a specific ion transition) is essential. If too many transitions are monitored simultaneously, dwell times may become too short, which compromises peak shapes and peak areas, ultimately impairing both instrumental precision and sensitivity.

3.3 Challenges in the Comparison of Monitoring Results

The comparison of soil pesticide monitoring studies in agricultural land uses is complicated by multiple factors. First, it is impacted by the sampling strategy. The timing of soil sampling – whether it takes place before, during, or after the growing season – has a major impact on the pesticide concentration levels detected, given that most applications occur during the growing period. Moreover, obtaining a soil sample that is representative of the studied parcel depends on both the number of subsamples collected and their spatial distribution within the field. Pesticide monitoring generally targets topsoil, though the exact sampling depth varies across studies, commonly including depths from 0 up to 30 cm.^[61] In tilled land uses such as croplands, homoge-

neous mixing of the topsoil is generally assumed, which allows for direct comparison of studies using different sampling depths within the topsoil. However, for no-till systems such as orchards and vineyards, this assumption does not hold due to limited soil disturbance, leading to vertical stratification of pesticides.^[51]

Second, multi-residue methods for pesticide analysis in soil differ substantially in both the number and the types of pesticides included in the analytical methods, and especially in their MLOQs (see Fig. 1). Since pesticides can be found in concentrations in the sub-ng/g range in various (agricultural) land uses,^[24,51,54,55] the detection frequency of a given pesticide within a study is highly dependent on the applied MLOQs. This, in turn, can strongly affect the comparability of monitoring results. Moreover, meaningful comparisons of overall ecotoxicological risks to soil organisms across studies require harmonized analytical methods – particularly regarding substance selection and MLOQs.

Third, regular interlaboratory comparisons (ring trials) based on field soil samples containing numerous aged pesticide residues would substantially improve the comparability of monitoring results. Such external quality assurance would help to ensure method trueness. However, ring trials focusing specifically on pesticides in soil remain limited, with only a few initiatives available, such as the one organized by the Central Institute for Supervising and Testing in Agriculture (ÚKZÚZ) of the Czech Republic, Department of Proficiency Testing Programmes (OdMPZ).

4. Outlook, Perspective, and Future Needs

The forthcoming European Soil Monitoring Law (COM/2023/416)^[11] underscores the need to establish harmonized criteria for soil health across the EU, including the identification of priority organic contaminants that adversely affect soil health, such as pesticides. The selection of these substances is supported by expert groups, including the NORMAN Working Group on Contaminants of Emerging Concern in Soil and the Terrestrial Environment (WG7).^[62]

Moreover, harmonized analytical methods are essential to improve the comparability across different studies. To date, most studies have focused on determining the total extractable pesticide concentration, typically obtained through exhaustive extraction with organic solvents. However, a key question remains: to what extent is pesticide sorption or binding to organic or mineral matrix components irreversible (*i.e.* forming the so called non-extractable residues),^[63,64] and whether, and to what degree, can these residues be remobilized, *e.g.* due to changing environmental conditions. This uncertainty underscores the need to clearly define which pesticide fraction is ecotoxicologically relevant and should be targeted for quantification: (i) the total extractable concentration, (ii) the bioavailable fraction, believed to be most closely linked to ecotoxicological effects, but for which different concepts and definitions are in use,^[65] or (iii) the non-extractable fraction, which is poorly defined and not readily accessible through standard analytical approaches, but may still contribute to long-term environmental risk.

Overall, legally binding, risk-based threshold values for pesticides are required to protect terrestrial ecosystems – similar to those already established for selected pesticides in surface waters within the European Union^[66] and Switzerland.^[67] Within the AP PPP,^[12] a methodology has been proposed for deriving such values for pesticides in soil.^[68] To date, threshold values have been established for four pesticides (<https://www.ecotoxcentre.ch/projects/soil-ecotoxicology/monitoring-concept-for-plant-protection-products-in-soils>), but they have not yet been adopted as legally binding standards.

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Author Contributions

A. R. searched literature, wrote and edited the manuscript. T. D. B. reviewed and helped streamlining the manuscript.

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