

Electromembrane Extraction for Multiclass Pesticide Assessment in Soil Matrices: Sustainable Analytical Insights

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The extensive use of pesticides in agriculture has led to their accumulation in environmental compartments, especially soils. Given their potential impact on ecosystems and human health, developing effective analytical methods to assess pesticide persistence and mobility in soil is essential. However, soil is a complex matrix with numerous interfering substances that challenge accurate analysis. This study reports the development of a U-shaped electromembrane extraction method coupled with liquid chromatography-mass spectrometry for detecting multiclass pesticides in soil samples. Key extraction parameters are optimized, achieving efficient performance in 15 min using a sample

pH of 8, stirring at 1000 rpm, and 10% (w/v) NaCl. The method demonstrates linearity between 500 and 1000 mg kg⁻¹ with $R^2 > 0.9800$, limits of detection between 91.6 and 171.4 mg kg⁻¹, and recovery rates from 84.5% to 101.2%. Furthermore, the approach is evaluated using AGREEprep and GAPI tools, highlighting its compliance with green analytical chemistry principles. Overall, this work introduces an effective, environmentally friendly methodology for the determination of pesticide residues in soil, reinforcing the potential of electromembrane extraction for complex environmental matrices.

1. Introduction

Pesticides are widely recognized as both organic and inorganic chemical compounds that play a crucial role in enhancing crop yields and safeguarding agricultural practices by protecting these activities.^[1,2] While the benefits of employing pesticides have contributed significantly to meeting humanity's food requirements in the past century, these chemicals have also been extensively reported in the literature regarding their associated environmental risks.^[2–5] Furthermore, among all environmental compartments, soil is particularly impacted by the application of pesticides in agricultural areas. The significant risk posed by the presence of these compounds in this matrix arises from the physicochemical properties of the soil, such as porosity

and organic matter content.^[6] These properties contribute to the retention of pesticides, which may potentially migrate to other environmental compartments, including water compartments.^[7] Therefore, recognizing the substantial risks associated with pesticides in soil, the scientific community has endeavored to implement analytical methods for monitoring these compounds' persistence in these matrices.^[6]

Analytical systems such as liquid chromatography (LC) combined with mass spectrometry (MS) can deepen the insights into pesticide presence in the soil matrix. However, such a task remains challenging due to the inherent complexity of soil compartments.^[8,9] Hence, to overcome the drawbacks associated with the complexities of these challenging matrices, a sample preparation step is employed to ensure the effective analytical

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performance of the method.^[9] The literature has reported the application of conventional sample preparation methods for soil matrix evaluation.^[6] As recently outlined by Brinco et al.,^[6] the quick, easy, cheap, effective, rugged, and safe (QuEChERS) method stands out as the most widely utilized sample treatment technique for the analysis of pesticide residues in soil samples. Moreover, alternative methods such as solid-phase extraction, microwave-assisted extraction (MAE), ultrasound-assisted extraction (UAE), and Soxhlet solvent extraction (SSE) have also found applications in the assessment of soil samples.^[10–12]

Although these conventional methodologies demonstrate proficiency in assessing pesticides in soil matrices, they are not immune to limitations, particularly concerning the principles of green analytical chemistry (GAC).^[13–15] Furthermore, to address traditional limitations, such as excessive chemical waste generation and extensive use of organic solvents, a contemporary approach involves the adoption of miniaturized sample preparation techniques for assessing challenging matrices.^[16] Furthermore, one of the noteworthy miniaturized approaches that has captured the scientific community's attention is electro-membrane extraction (EME). Despite this technique has demonstrated applications in detecting soil multiresidues, such as ions^[17] and insecticides,^[18] its use in soil matrices remains limited compared to its application in biological matrices, thus indicating an unexplored potential for assessing multiresidues in soil samples.

The EME method was first reported in 2006 by Pedersen-Bjergaard and Rasmussen.^[19] The method was conceived by adapting hollow fiber liquid-phase extraction (HF-LPME), a design pioneered by the same authors.^[20] The extraction is based on the application of a potential difference across a hollow membrane immobilized with supported liquid membrane (SLM) solvent and immersed in the sample solution (donor phase) at controlled pH. Inside the membrane is placed an acceptor solution whose pH is also controlled according to the physical-chemistry characteristics of the involved analytes. A potential difference is applied to the system through two electrodes from an inert material, usually platinum. The position of the electrodes (cathode and anode) varies according to the ionic nature of the extracted analyte. Thus, one is inserted into the sample solution and the other in the acceptor phase, both connected to an external power source for applying the potential difference.^[19,21,22] Therefore, considering the chemical characteristics of the pesticide residues in soil samples, the use of EME as a sample pretreatment holds significant promise to bring new horizons for this analysis. The technique uses a reduced solvent volume and is performed in a short analysis time, with a notable sample clean-up ability, exhibiting good recovery values, agreeing with GAC principles.

Hence, this study aims to employ a new design of U-shaped electromembrane extraction-liquid chromatography-mass spectrometry (U-EME/LC-MS) methodology for assessing multiclass pesticides in soil samples. The main method parameters were scrutinized considering the novelty of the proposed application of EME to pesticide determination in soil samples. Moreover, this study delves into a discussion of the environmental sustainability

aspects of the developed methodology based on existing literature. To the best of our knowledge, this was the first time that the U-EME/LC-MS configuration was applied to assess the selected pesticides in soil samples with the reported greenest assessment discussion.

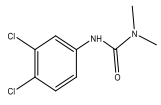
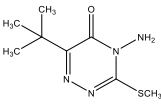
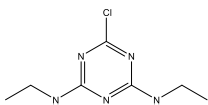
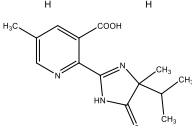
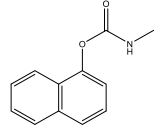
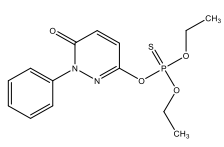
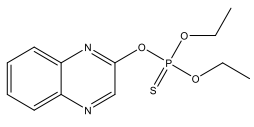
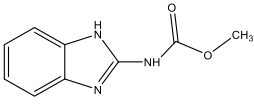
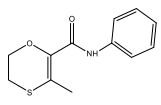
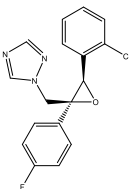
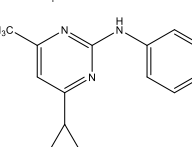
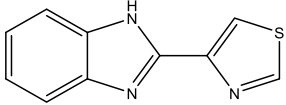
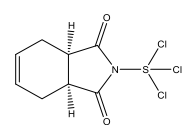
2. Experimental Section

2.1. Materials

Methanol LC grade was purchased from J.T. Baker (Phillipsburg, USA). Octanol, decanol, and dodecanol were obtained from Labsynth (São Paulo, Brazil), and ethanol was purchased from Biograde (Anápolis, Brazil). Ammonium hydroxide (30%) and formic acid were acquired from Sigma-Aldrich (St. Louis, USA), and sodium chloride was purchased from Labsynth (São Paulo, Brazil). Hydrophobic hollow polypropylene fibers (Q3/2 Accurel) with an inner diameter of 600 μm , wall thickness of 200 μm , and pore size of 0.2 μm were obtained from the supplier Membrana (Wuppertal, Germany), platinum wire with a diameter of 0.5 mm was obtained from Platimex (São Paulo, Brazil), and a 100 μL Hamilton syringe was obtained from Allcrom (São Paulo, Brazil). Ultrapure water was obtained from the Gehaka MS2000 WFI equipment (São Paulo, SP, Brazil).

2.2. Soil Extract Obtention

The soil extract was obtained using a red latosol sample collected in Santo Antônio de Goiás, Brazil (latitude: 16° 30' 17" S and longitude: 49° 16' 53" W) and was carefully stored at ambient conditions (25 °C). This type of soil is a highly weathered tropical soil, typically classified as an Oxisol in the USDA Soil Taxonomy. Latosols were characterized by their high degree of mineral weathering, low natural fertility, and predominance of iron and aluminum oxides.^[23] The collected samples were donated by the Escola de Agronomia of the Universidade Federal de Goiás, Goiânia, Brazil, and were characterized according to some determined physicochemical parameters. The soil exhibited specific physicochemical properties, with a measured pH of 4.8 (using 2.0 g of soil in 10 mL of water) and an organic matter content of 3.5%. Additional physicochemical properties of the soil are presented in Table S1, Supporting Information. These physicochemical conditions remained fixed until the execution of this study. Subsequently, 5.0 g of the soil sample underwent enrichment with the assessed multiclass pesticides (Table 1) using stock solutions (10 $\mu\text{g L}^{-1}$) to reach the desired final concentration (mg kg^{-1}). A phosphate buffer solution at pH 6 (0.05 mol L^{-1}) was used as the extraction medium solution (5 mL). The extraction process was carried out for 30 min under controlled stirring conditions (1000 rpm). Lastly, the extract underwent centrifugation for 10 min (Thermo Scientific, Asheville, USA), and the resulting supernatant was meticulously collected and utilized in the following EME assays.

Table 1. Molecular formula, molecular weight, pKa, and LogP of the multiclass pesticides according to their application.						
Classification according to their use	Pesticide	Molecular formula	pKa	Molecular weight	LogP	Structure
Herbicides	Diuron	C ₉ H ₁₀ Cl ₂ C ₂ O	13.1	233.1	2.5	
	Metribuzin	C ₈ H ₁₄ N ₄ OS	2.1	214.3	1.9	
	Simazine	C ₇ H ₁₂ ClN ₅	4.4 and 14.7	201.6	1.7	
	Imazapic	C ₁₄ H ₁₇ N ₃ O ₃	1.8 and 2.6	275.3	1.5	
Insecticides	Carbaryl	C ₁₂ H ₁₁ NO ₂	14.7	201.2	2.4	
	Pyridaphenthion	C ₁₄ H ₁₇ N ₂ O ₄ PS	–	340.3	3.1	
	Quinalphos	C ₁₂ H ₁₅ N ₂ O ₃ PS	0.6	298.3	3.2	
Fungicides	Carbendazim	C ₉ H ₉ N ₃ O ₂	4.8 and 9.7	191.2	1.8	
	Carboxin	C ₁₂ H ₁₃ NO ₂ S	13.2	235.3	1.5	
	Epoxiconazole	C ₁₇ H ₁₃ ClFN ₃ O	2.0	329.7	3.7	
	Cyprodinil	C ₁₄ H ₁₅ N ₃	4.4	225.3	3.2	
	Thiabendazole	C ₁₀ H ₇ N ₃ S	4.6 and 10.2	201.2	2.3	
	Captan	C ₉ H ₈ Cl ₃ NO ₂ S	– b)	300.6	3.2	

^{a)}Data obtained on the website www.chemicalize.com; ^{b)}“–” indicates data not available in the consulted source.

2.3. EME Procedure

The primary focus of the presented study was the optimization and subsequent application of the EME method for extracting the selected pesticides (Table 1) from soil samples. Therefore, the EME procedure was performed in two main methodology steps: 1) optimization and 2) application of the optimized EME procedure, outlined as follows:

2.4. Optimization of the U-Shaped EME Procedure

The EME optimization procedure was conducted by fixing the parameters described in the soil extraction section and carrying out a separate study for each parameter associated with the EME method. The study involved the evaluation of the donor and acceptor phase pH (2, 4, 6, 8, and 10) adjusted with an acetate (2 and 4)/phosphate (6 and 8)/borate buffer solutions (10) (0.05 mol L^{-1}), extraction time (5, 15, 30, 45, and 60 min), stirring speed (500, 1000, and 1500 rpm), salt addition (0, 5, 10, and 20% NaCl w/v), organic solvent SLM (octanol, decanol, and dodecanol), and voltage (50, 100, 150, 200, 250, and 300 V). The experiments were performed using a high-voltage power supply, 5 kV model U33010, acquired from 3B Scientific (Hamburg, Germany). Additionally, the electrical current was monitored using a potentiostat system from Omnimetra (Rio de Janeiro, Brazil) in order to verify the membrane's stability according to the applied voltage. The present study covered a diverse array of pesticides exhibiting different physicochemical properties, including a LogP range from 1.5 to 3.7 (see Table 1). Therefore, a methanolic solution of the following multiclass pesticides was used for the EME optimization conditions: carbendazim, diuron, metribuzin, imazapic, carboxin, epoxiconazole, thiabendazole, simazine, carbaryl, cyprodinil, pyridaphenthion, quinalphos, and captan, with a final concentration of $1.0 \mu\text{g mL}^{-1}$.

The EME system was assembled using two electrodes in a three-wire platinum system and a conical vial containing 5 mL of the donor phase (sample). Moreover, 20 μL of the acceptor phase was deposited inside a polypropylene hollow fiber (HF) tube (8 cm) containing the impregnated SLM solvent. Two platinum electrodes were inserted at the terminal ends of the fiber to form a U-shaped configuration and finally brought into contact with the donor solution inside the conical vial. Simultaneously, to increase the electrode surface area in contact with the donor solution, a spiral configuration of the electrode was employed. The illustration of the proposed system is presented in **Figure 1**. The EME system was set up and placed in a stirring instrument. Therefore, the connector cables were connected to an external power source for voltage application. The spiral-shaped electrode (immersed in the donor phase) was connected to the negative pole, while the electrodes inside the U-shaped HF (immersed in the acceptor phase) were connected to the positive pole. Lastly, the high-voltage power supply was turned on at the studied voltage, and the system was kept under agitation (IKA, Staufen, Germany) throughout the EME extraction. After the extraction procedure, $\pm 15 \mu\text{L}$ of the acceptor solution was

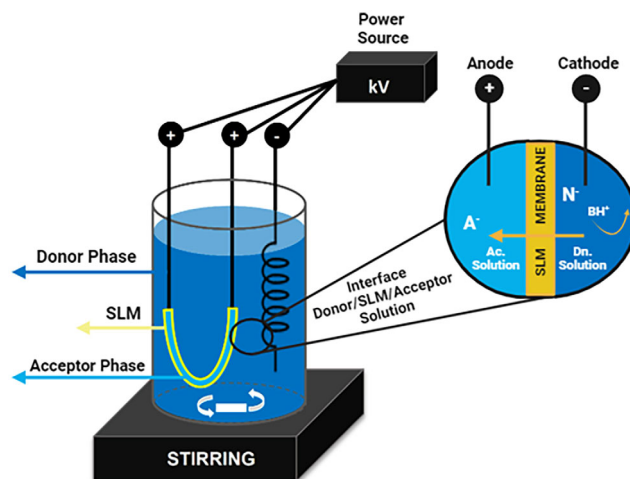


Figure 1. Schematic representation of the conventional EME apparatus featuring the U-shaped configuration and incorporating a spiral electrode.

collected using a 100 μL syringe and inserted into a conical vial, followed by solvent drying under vacuum in a SpeedVac Savant system (Thermo Scientific, Asheville, USA). Subsequently, the residue was reconstituted with 100 μL of the mobile phase (water (80%)/methanol (20%)), and the final solution was analyzed using mass spectrometry.

Furthermore, the EME performance was thoroughly investigated using electrochemical impedance spectroscopy (EIS) to obtain valuable insights into the intricacies of interface phenomena. All EIS measurements were carried out in a three-electrode cell setup connected to an Autolab PGSTAT100N potentiostats/galvanostat (Metrohm, Herisau, Switzerland). The U-shaped membrane, impregnated with the acceptor phase containing two Pt wires inserted at both terminal ends, was used as the working electrode. Meanwhile, the reference electrode was Ag/AgCl, with a counter electrode as spiral-shaped Pt wire. The complex plane spectra were analyzed with EIS Spectrum Analyser Software.^[24] The EIS spectra were recorded under open-circuit conditions, ranging from 100 to 0.0001 kHz with an AC voltage amplitude of 10 mV. The frequency interval was divided into 61 logarithmically equidistant measurement points. The EIS measurements were performed in a non-Faradaic mode in the absence of a redox probe. The investigated systems were composed of 1) a pH 8.0 phosphate buffer solution (0.05 mol L^{-1}), 2) a mixture of pesticides in pH 8.0 phosphate buffer solution (0.05 mol L^{-1}), 3) the soil extract, and 4) soil extract containing a mixture of pesticides. The four systems were evaluated in three different SLM phases (octanol, decanol, and dodecanol). For comparison, the U-shaped membrane was replaced with a Pt wire electrode ($\varnothing = 0.5 \text{ mm}$) in the electrochemical cell to perform EIS measurements under same conditions (1–4).

2.5. U-Shaped EME Procedure for Pesticide Extraction in Soil Samples

The U-shaped EME extraction was carried out using the previously obtained soil extract. Therefore, an 8 cm polypropylene

HF tube was first soaked in acetone and placed in an ultrasonic bath to remove potential impurities. Following this, the HF membrane was immersed in the SLM solvent for 30 s to achieve impregnation, followed by introduction of the acceptor phase inside the membrane. The fiber was then connected to two platinum wires to form a U-shaped configuration and finally brought into contact with the donor solution. As previously described, to enhance the electrode's surface contact area with the donor phase, a spiral configuration was adopted (Figure 1). Finally, the connector cables were connected to a high-voltage power supply for voltage application. The spiral-shaped electrode (donor phase) was connected to the negative pole, while the U-shaped electrodes (acceptor phase) were connected to the positive pole. Lastly, the power source was turned on at the studied voltage, and the system was kept under agitation throughout the extraction. The extraction of pesticides (Table 1) was carried out using the optimized parameters previously described. These parameters included a sample pH of 8.0, an applied voltage of 100 V, octanol as the SLM solvent, an extraction time of 15 min, a stirring speed of 1000 rpm, and 10% (w/v) NaCl. After extraction, the resulting solution was dried under a SpeedVac system. The residue was reconstituted in 100 μ L of the mobile phase (water (80%)/methanol (20%)) and then followed for the analysis by liquid chromatography-mass spectrometry (LC-MS).

2.6. MS Analysis

The optimization of the EME method was assessed by analyzing the recovery of pesticides postextraction and comparing their obtained MS spectral response with standard solutions (1.0 μ g mL⁻¹) using a micrOTOF II mass spectrometer from Bruker Corporation for each assessed parameter. At this study stage, the LC-MS analysis was not performed once only a standard analyte solution was used for EME method parameter optimization. The MS analysis of the final solution was executed by direct infusion into the micrOTOF II equipment with a capillary voltage of 4500 V, a nebulizer pressure of 4 bar, and a drying gas flow of 10 L min⁻¹ at 200 °C. Electrospray ionization in positive mode was applied for the analysis within a mass window ranging from 170 to 600 *m/z*. The findings were graphically represented, showcasing the extraction recovery (%) of pesticides for each evaluated parameter. The MS absolute intensity obtained from standard solutions (1.0 μ g mL⁻¹) was considered as 100% (nominal value) for reference. The obtained spectra were evaluated using the Bruker Compass Data Analysis 5.0 SR1 software.

2.7. LC-MS Analysis

LC-MS analysis was employed to evaluate the presence of the targeted pesticides in soil samples, utilizing a Shimadzu LC-20A (Kyoto, Japan) system coupled with a micrOTOF II mass spectrometer from Bruker Corporation (Billerica, USA). For chromatographic analysis, a C18 column (3.0 $\times$ 100 mm, 2.7 μ m) (Agilent, Santa Clara, USA) was used. Chromatographic conditions

involved an isocratic elution with solvents A: water/methanol (95:5 v/v) and solvent B: methanol/water (95:5 v/v), with a composition of 70/30% for phases A and B, respectively, over 10 min analysis time. The oven temperature was maintained at 35 °C, and the mobile phase flow rate was set at 0.350 mL min⁻¹, utilizing a 5 μ L sample injection volume. The MS conditions were the same as previously described.

2.8. Figures of Merit

The assessment of some figures of merit of the proposed methodology involved the evaluation of key analytical parameters, to demonstrate the potential applicability of the reported method for multiclass pesticides in soil samples. For the U-EME/LC-MS performance study, a blank reference soil sample spiked with pesticide across the concentration range of the study was employed. Therefore, the method's linearity was evaluated by analytical curves through linear regression of pesticide peak areas (*Y*) against pesticide concentrations (*X*, mg kg⁻¹), ranging from 500 to 1000 mg kg⁻¹. Intra- and interassay precision were determined using the pesticide solution covering the entire range of the analytical curve (*n* = 5). Precision was indicated as the percentage of relative standard deviation (RSD%) of the specified concentrations. Furthermore, the determination of the limit of quantification (LOQ) and limit of detection (LOD) adhered to the guidelines outlined by the International Union of Pure and Applied Chemistry (IUPAC).^[25,26] The LOD and LOQ were obtained as three and ten times, respectively, the standard deviation of the intercept(s) of the calibration curve divided by the slope of the calibration curve (3/10 $\frac{S}{a}$). The assessment of matrix effects involved examining the parallelism between the analytical and calibration curves within the range of 500–1000 mg kg⁻¹, followed by a *t*-test confirmation. Recovery values were determined through quintuplicate assays (*n* = 5) at three concentration levels (600, 800, and 1000 mg kg⁻¹). The results were expressed in % according to Equation (1) where FC represents the final analyzed concentration (mg kg⁻¹) and IC represents the initial concentration (mg kg⁻¹), as follows.

$$R_{ec}(\%) = \left(\frac{FC}{IC} \right) \times 100\% \quad (1)$$

3. Results and Discussion

Since its introduction, the EME procedure has seen continual advancements in comprehending the mass transfer procedure, thus demonstrating that the target analytes in the EME system undergo a dual mass-transferring mechanism.^[27] The literature underscores the existence of two primary phenomena, encompassing both partitioning (manifested as diffusive migration) and electrophoresis procedures (involving electrokinetic migration). Both procedures collaboratively propel the analytes from the donor phase to the acceptor solution.^[21,22] Furthermore, for a comprehensive understanding of the kinetic movement of analytes toward the acceptor solution as well as a thorough

exploration of the key analytical parameters influencing the mass transport between phases, the literature extensively documents the application of the Nernst–Planck flux equation, as follows in Equation (2).^[27]

$$J_i = \frac{-D_i}{h} \left(1 + \frac{v}{\ln}\right) \frac{(\chi - 1)}{\chi - \exp(-v)} (C_{ih} - C_{i0} \exp(-v)) \quad (2)$$

In Equation (2) D_i refers to the diffusion coefficient of the molecule, h denotes the thickness of the SLM membrane, v is a dimensionless driven force, and χ accounts for the ion balance between the donor and acceptor phases. Moreover, the C_{ih} corresponds to the analyte concentration at the SLM/sample interface. Finally, C_{i0} represents the concentration of the target analyte at the acceptor–SLM interface. As assumed by Equation (2), we can infer that the mass transfer, governed by the Nernst–Planck flux, is predominantly influenced by 1) the analyte's diffusion coefficient within the SLM, 2) the thickness of the SLM, 3) the ion balance across the SLM, 4) the temperature of the medium, and 5) the applied voltage. While the use of Equation (2) has significantly advanced the comprehension of the physicochemical phenomena within EME procedures, new studies have introduced a time-dependent model to comprehensively unravel the primary influencing parameters in EME extraction processes (Equation (3)).^[27]

$$C_{Ai}(t) = \frac{V_D C_{Di}^0 - C_{Di}^0 \times \exp(-A_f \times P_i^{D \rightarrow A} \times t) (V_D + K_d^* \times V_m)}{V_A} \quad (3)$$

According to Equation (3), V_D represents the total volume of the sample. C_{Di}^0 is the initial concentration of the target analyte in the sample. A_f is the active membrane's surface. $P_i^{D \rightarrow A}$ refers to the permeability of the analyte from the donor to the acceptor phase. V_m is the respective volume presented in the SLM membrane. V_A is the symbol of the acceptor solvent volume. Finally, K_d^* regards the distribution coefficient. The elucidation provided by Equation (3) offers a more comprehensive insight into the key parameters governing mass transfer of target analytes between phases in EME extraction. These parameters encompass 1) the composition of the SLM, 2) the duration of extraction, and 3) the applied extraction voltage. With this settled, the subsequent sections of this study will undertake a thorough examination of the parameters inherent in the EME extraction process, delving into their intricate interplay and assessing their impact on the extraction efficiency of multiclass pesticides.

3.1. Optimization of the EME Procedure

As stated before, the optimization of the EME method proposed in this study was evaluated assuming the extraction recovery of the pesticide postextraction for each study parameter. Furthermore, a univariate examination was provided, focusing on sample pH, extraction time, stirring speed, salt addition, SLM solvent, and voltage by a direct MS infusion of the EME-extracted pesticides. The optimization assessment using the

MS directly infusion approach was proposed in this study to facilitate a straightforward and rapid analysis of the parameters involved in the EME extraction process. The parameters employed for the soil extract obtention (as outlined in the soil extract obtention section), besides a voltage of 50 V, and octanol as SLM solvent were held constant, while the mentioned parameters underwent evaluation in each experimental condition. The criterion for selecting the optimal condition was based on identifying the analytical parameters that yielded the highest extraction recovery across the largest number of pesticides.

3.2. The Donor and Acceptor pH Evaluation

In EME, pH control is typically implemented in both phases of the system. As discussed earlier, the electrophoretic phenomenon driving the analyte from the donor to the acceptor phase predominantly involves charged molecules. Consequently, pH control is commonly applied to facilitate the ionization of target analytes in both the aqueous of the donor and acceptor phases. While controlling the pH of both the donor and acceptor phases can promote the ionization of pesticides, achieving such optimization poses a challenge in the extraction of multiclass pesticides. As indicated in Table 1, the extensive range of pKa values (0.6–14.7) for the pesticides in this study complicates the selection of an ideal pH value. Consequently, as previously indicated, the optimum pH value (2–10) was chosen based on its ability to yield the highest extraction recovery for the largest number of pesticides. The extraction recovery for each pesticide according to the pH and the fixed parameters for this assay is presented in Figure S1 (Supporting Information).

According to the observations, the pesticides carbendazim, thiabendazole, carbaryl, and cyprodinil exhibited the highest extraction recovery at distinct pH levels. To better understand such behavior, it is necessary to consider the pKa values stipulated in Table 1. A trend of increasing extraction recovery can be observed at pH values of 4, 6, and 8, notably for the pesticides carbendazim, thiabendazole, simazine, carbaryl, and cyprodinil. According to the data established in Table 1, these pesticides have acidic and basic pKa values ranging from 4.4 to 10.6, indicating a higher ionized population at pH values of 6 and 8.

Nevertheless, an interesting observation was made regarding the extraction behavior of the pesticide cyprodinil, which showed a significant extraction recovery both at acidic pH (pH 2) and alkaline pH (pH 8) medium conditions. According to Table 1, cyprodinil presents a pKa value reported as 4.44; Rodríguez-Salgado^[18] elucidated that the pesticide undergoes protonation at pH levels below 4.4, thereby facilitating its mass transfer through electrophoretic mechanisms. Conversely, at higher pH levels, it exists predominantly as a free base. It is also imperative to emphasize the significance of diffusion phenomena within the context of the EME technique. Elevated pH levels, surpassing 4.44, are shown to positively impact carbaryl's recovery in the acceptor phase. Such observation can indicate the influence of diffusion aspects in alkaline conditions by enhancing the pesticide's interaction with the SLM solvent and later delivery in the acceptor solution.

Nonetheless, in the context of a multiresidue methodology, comprehensively assessing each analyte's interaction with the system proves challenging. Thus, further individual research is essential to fully grasp the observed behaviors.

A distinct behavior was also noted for captan, which achieved the optimal extraction performance at a pH value of 10, as illustrated in Figure S1, Supporting Information. Since Table 1 lacks a pKa value for captan according to the *chemicalize* database, attributing the pH influence in the EME experiment for this pesticide is challenging. Nonetheless, its distribution coefficient ($\text{LogP} = 3.2$) may contribute to enhanced interaction between the pesticide and the SLM solvent immobilized in the membrane's porous structure, later facilitating its release into the acceptor phase due to differences between the donor and acceptor phase ratios. In the context of the multiresidue method developed in this study, the meticulous selection of parameters for each assessment is of paramount importance. However, optimal parameters for a specific group of pesticides may not necessarily yield the best results for all analytes collectively. This necessitates a trade-off where the performance of certain analytes must be compromised. In the author's view, it is essential to individually evaluate the pH dependence of each analyte to elucidate their interaction with the EME phenomena. Conversely, as previously discussed, in the context of a multiresidue methodology, it is crucial to identify parameters that optimize the performance across the majority of analytes. Despite variations in the observed extraction recovery across pH values, pH 8 was selected as the most favorable condition for subsequent assays.

3.3. Voltage Evaluation

As indicated by Equation (3), voltage significantly influences the mass transport of target analytes between phases. Consequently, it stands out as one of the most important parameters that require optimization during EME extraction.^[22] Although the application of voltage undeniably enhances the overall performance of EME extraction, reducing the required time for the analyte to cross the donor/SLM/acceptor interface through electrophoretic phenomena, the literature underscores specific drawbacks associated with utilizing voltage in EME systems.^[22,28] The primary consequence of applying high voltage is the occurrence of electrolysis, which can be observed by the formation of bubbles along the electrodes.^[29] In an EME system, an intense electrolysis process can decrease the mass transport rate of the analytes between phases. Furthermore, as described by Moazami et al.,^[30] subjecting an EME system to a high voltage may result in joule heating phenomena that can potentially affect the integrity of the membrane and cause alterations to the physicochemical properties of the SLM solvent. Having this in mind, the voltage range of 50–300 V was selected in order to ensure the main stability of the EME system. Above 300 V ($>150 \mu\text{A}$), there was an increase in the electrolysis process, thereby affecting the EME extraction performance of pesticides.

As observed in Figure S2, Supporting Information, the use of voltages of 50 and 100 V provided a better extraction

performance for most of the studied pesticides. While both voltages increased the response of the pesticides, the voltage of 100 V presented as the best option among the evaluated voltage range. Therefore, through the obtained results, it is possible to affirm that at 100 V, the electrophoretic phenomenon is enhanced, thus increasing the electrokinetic movement of the analytes to the acceptor phase. Nevertheless, beyond 100 V, the aforementioned drawbacks exert a negative impact on the migration of analytes, resulting in a reduction of the extraction recovery for all the pesticides under evaluation. Due to this, 100 V has been selected for the following assays. It is worth noting that no experiment was performed at 0 V; under such a condition, mass transport would rely solely on passive diffusion and partitioning, and, within the same extraction time (15 min), significantly lower recoveries would be expected. At sufficiently long extraction times, however, and in the absence of pH trapping effects, the system would tend toward equilibrium with similar concentrations in donor and acceptor phases. This explanation is particularly relevant for cyprodinil ($\text{pKa} 4.4$, $\text{LogP} 3.2$), which under alkaline conditions exists mostly in its neutral form. In this case, extraction without voltage would primarily occur by diffusion into the SLM, aided by its hydrophobic character. Further investigations are required to comprehensively elucidate the behavior of neutral compounds in EME systems, particularly to clarify the actual contribution of voltage application to their extraction efficiency.

3.4. SLM Solvent Evaluation

Since the EME extraction originated from concepts well-established by the HF-LPME method, it is accurate to assert that the solvents employed in HF-LPME can also find application in EME.^[31] According to the literature, an ideal SLM solvent should meet the following criteria: 1) low water solubility, 2) low vapor pressure, 3) high polarity and polarizability, 4) robust hydrogen bonding capability (high hydrogen bond basicity for cations and high hydrogen bond acidity for anions), and 5) reasonable hydrophobicity ($6 > \log p > 2$).^[22,32] Furthermore, the selection of the ideal SLM solvent is typically influenced by the polarity of the target analytes. As indicated in Table 1, this study encompasses the evaluation of pesticides with diverse basic and acidic properties. Consequently, considering the differences in the polarity of the target analytes, determining the optimal SLM solvent poses a significant challenge. Despite the challenge of selecting the best SLM solvent, typical candidates for EME extraction can be identified in the literature. Aliphatic alcohols, such as 1-octanol and 1-nonanol, have been shown to be potential SLM solvents for extracting various target analytes, with a particular emphasis on the extraction of acidic compounds.^[22,33] Therefore, this study evaluated the application of 1-octanol, decanol, and dodecanol as the SLM solvent. The obtained extraction recovery for each SLM, as well as the fixed parameters for this assay, is presented in Figure S3, Supporting Information.

Although the electrophoretic phenomenon stands out as the primary process driving analytes to the acceptor phase, the liquid partition of analytes also plays a crucial role in mass transport

between phases. As illustrated in Figure S3, Supporting Information, superior extraction performances were attained through the use of octanol and decanol as the SLM solvents. Moreover, employing dodecanol proved to be particularly challenging due to its physicochemical properties, as it solidifies at temperatures below 20 °C. Given that this study primarily focuses on providing an EME extraction under laboratory ambient conditions (22 °C), the utilization of dodecanol as the SLM solvent presented challenges that were reflected in observed extraction recoveries by using this solvent. On the other hand, looking back to Figure S3, Supporting Information, it becomes apparent that the pesticide captan exhibited its highest extraction recovery when dodecanol was utilized as the SLM solvent. The rationale behind this observation regarding captan will be further investigated in the forthcoming EIS analysis section. According to the literature, both solvents (octanol and decanol) can effectively interact with target analytes by hydrogen interaction from the presence of the hydroxyl (–OH) group.^[33]

Even though both octanol and decanol contributed to an improved method's performance, it is evident that the use of octanol significantly enhanced the obtained response compared to decanol. The LogP values from Table 1 indicate the following order of affinity to the organic solvent: cyprodinil (3.2) > carbaryl (2.4) > thiabendazole (2.3) > simazine (1.7). Figure S3, Supporting Information, shows a similar recovery trend for the pesticides carbaryl, thiabendazole, and simazine, owing to the proximity of their LogP values. The findings underscored the significant influence of solvent-pesticide affinity on extraction recovery, highlighting the crucial role of diffusion phenomena in determining results. Notably, cyprodinil displayed superior extraction recovery compared to other pesticides, likely due to its interaction with the solvent immobilized within the polymeric porous membrane of the SLM. Therefore, according to the obtained results, octanol was chosen as the optimum SLM solvent.

3.5. Extraction Time Evaluation

Following the introduction of the time-dependent model represented by Equation (2), it was determined that extraction time and voltage are the most crucial parameters influencing the analytical performance of the method.^[32] Extraction time primarily regards the duration required for analytes to cross the donor/SLM interface and reach the acceptor phase. This parameter is closely associated with the physicochemical properties of the analytes, as the interaction between analytes and the SLM solvent predominantly considers the LogP of the analytes.^[27] Moreover, as discussed in this study, for being able to perform two phenomena simultaneously (electrophoresis and diffuse migration), the extraction times of EME procedures are inferior to those in HF-LPME methods.^[29] Whereas in HF-LPME, the equilibration time is in the range of 30–60 min, depending on the characteristics of the analytes and the geometry of the system, in EME, the extraction time is never superior to 20 min.^[22] For the multiclass pesticide extraction using EME, this study evaluated a broad spectrum of extraction times, ranging from 5 to 60 min. The results of

this assessment and the fixed parameters for this evaluation are presented in Figure S4, Supporting Information.

As noted in Figure S4, Supporting Information, a trend in the extraction recovery increase is observed between the times of 15 and 30 min, with the latter representing the highest recovery obtained for a significant portion of the pesticides. An interesting observation was made at time values above $T_{15\text{min}}$ for most of the studied pesticides. Beyond $T_{15\text{min}}$, there is a noticeable decline in the obtained response, indicating a negative effect at this condition.

Similar to HF-LPME methodologies, passive diffusion of analytes can occur after the ideal extraction time in EME, a phenomenon commonly referred to as back extraction.^[34] However, in contrast to HF-LPME, where the analyte may diffuse back into the donor aqueous phase, in EME, the analytes tend to be reincorporated into the SLM organic solvent before returning to the donor aqueous phase. Such phenomena can be better visualized by analytes that have their preference for the organic phase ($\text{LogP} > 1.5$). The decrease in extraction recovery is evident, especially for pesticides with high LogP values, such as cyprodinil, carbaryl, simazine, and thiabendazole (LogP 1.7–3.2). Consequently, after reaching the equilibrium time ($T_{15\text{min}}$), these pesticides tend to return to the SLM solvent in the membrane due to their affinity with the organic phase of these compounds, thereby reducing their presence in the acceptor phase (inside the membrane). However, this statement is not universally true as demonstrated by Figure S4, Supporting Information. The obtained results highlight a distinct behavior for the pesticide captan, which was better extracted at $T_{45\text{min}}$ of extraction. Despite captan having a LogP value similar to cyprodinil (3.2), we can assume that captan took longer to cross the donor/SLM (octanol) interface, thus requiring a longer equilibrium time than the others. The extended duration of interaction between pesticides and the SLM membrane may be correlated with the size of the molecule. For instance, in the case of epoxiconazole (327.7 Da), extraction recovery remained consistent between time intervals T_{15} and 30 min, suggesting no significant enhancement in extraction over this period. Conversely, when making the same comparison, the pesticide cyprodinil (340.3 Da) displayed a significant enhancement in extraction recovery at T_{15} minutes. This observation further emphasizes the complex interplay between electrophoretic and diffusion phenomena, illustrating how each pesticide is distinctly influenced by these mechanisms.

Offering a comprehensive explanation for all the observations in a multiclass extraction method is inherently challenging. The potential interactions among pesticides and the system may complicate individual interpretations of each pesticide. Nevertheless, based on the primary findings, an extraction time of $T_{15\text{min}}$ was settled to ensure equilibrium for the majority of pesticides and selected for subsequent assays.

3.6. Stirring Speed Evaluation

The agitation of the donor sample can enhance the convection, facilitating the diffusion of analytes in the SLM organic solvent

and consequently reducing the necessary equilibrium time. According to Rouhollahi et al.,^[35] the stirring process is responsible for reducing the thickness of the double layer presented around the SLM membrane, therefore resulting in an improvement of the mass transport between phases. Nevertheless, this parameter has been carefully evaluated as it is also associated with the stability of the system. Employing a high stirring speed can lead to the formation of bubbles, thereby diminishing the mass transport effect. Additionally, the vigorous vortex formation in the sample solution may induce instability in the electrodes and the HF membrane in the U-shaped configuration. To extract the multiclass pesticides, a stirring speed range of 500, 1000, and 1500 rpm (low, medium, and high speed) was assessed. The effects of the stirring speed on the extraction recovery of each pesticide and the fixed parameters for this assay are presented in Figure S5, Supporting Information.

According to the observations, using speeds of 500 and 1000 rpm resulted in higher obtained responses for the studied pesticides. Conversely, when employing 1500 rpm as the agitation speed, a decline in the extraction recovery for a significant portion of the pesticides was noted. In addition to the positive effects generated by the convection phenomenon in the system induced by agitation, negative aspects can also be associated with this parameter, as described before. Although both stirring speeds provided better results in comparison with the 1500 rpm, the best instrument control was particularly achieved by using 1000 rpm as the stirring rate. Based on the main findings, and to ensure the stability of the U-shape EME system, an extraction speed of 1000 rpm was chosen for the upcoming experiments.

3.7. Salt Addition Evaluation

The addition of a certain amount of salt influences the solubility of the target analytes in the sample solution, making them more available for electromigration between phases. The effect of salt addition in EME extractions is described in the literature and is commonly known as the salting-out effect. Since pH control in EME is typically achieved using buffer solutions, some salt is already present in both the donor and acceptor phases. Thus, the evaluation of salt addition mainly focuses on the potential positive or negative effects that the additional amount of salt can have on the extraction of multiclass pesticides in the U-shaped EME system. Therefore, this study mainly focused on the evaluation of adding percentages of NaCl (w/v%) from 0 (no salt) to 20%.

As evidenced in Figure S6, Supporting Information, the addition of NaCl did not have such a great impact on the extraction recovery for most of the evaluated pesticides. The literature underscores certain drawbacks associated with the addition of salts in electromembrane procedures. As noted by Seip et al.,^[36] the presence of salt in the donor solution can lead to the phenomenon known as "ion pairing," involving the formation of ion pairs between the target analytes and chloride ions introduced by the use of NaCl. The ion pairs formed with the salt become consequently trapped in the SLM membrane, making

it impossible for them to overcome this barrier and reach the acceptor phase. Moreover, looking back to Equation (2), the addition of salt increases the presence of ionic species in the solution. This increase of ionic species has an impact on the total ion balance value (χ), therefore impacting the analytical performance of the method. As previously stated, the addition of NaCl (w/v%) in the donor solution did not show a great impact on the extraction efficiency. However, for imazapic, carboxin, epoxiconazole, and captan, the addition of salt showed a slight increase in their extraction recovery. Therefore, the optimal condition for pesticide extraction by EME was chosen to be the addition of 10% (w/v) NaCl to enhance pesticides mentioned before recovery values, once they exhibited the lowest extraction recovery among the others when submitted to multiclass pesticide analysis. The optimal analytical conditions according to the main findings obtained by direct infusion of the U-EME/LC-MS method for multiclass pesticides determination are summarized in Table 2, outlined as follows:

The interfacial properties of the electromembrane were investigated using EIS technique using a three-electrode cell under non-Faradaic mode (absence of redox probes). The electromembrane behavior was evaluated in three different SLM solvents (octanol, decanol, and dodecanol) and the donor phase (a mixture of soil extract and pesticides). The equivalent circuit model used to fit the experimental data was based on the model proposed by Bannwarth et al.^[37] for homogeneous hollow membranes, which comprises the electrolyte resistance ($R_{\text{electrolyte}}$) in parallel with the electrolyte capacitance ($C_{\text{electrolyte}}$), the membrane resistance (R_{membrane}) in parallel with the membrane capacitance (C_{membrane}), and the capacitance of the Helmholtz double layer (C_{dl}) in parallel with charge transfer resistance (R_{ct}).

Moreover, in series with this charge transfer resistance, an additional resistance due to diffusion is present. For ideal linear semi-infinite diffusion, this impedance is usually represented by a Warburg element. In the case of nonlinear diffusion, e.g., spherical or radial diffusion, an additional ohmic resistance must be placed in parallel with this Warburg element, labeled as $R_{\text{si-sd}}$. For non-ideal diffusive behavior, the Warburg element can be replaced by a CPE labeled as CPE_{si-sd}. Table S2 (Supporting Information) shows the fitting parameter values obtained. The acceptor phase containing octanol exhibited higher $R_{\text{electrolyte}}$, R_{ct} , and $R_{\text{si-sd}}$ in comparison to decanol and dodecanol ones. Other systems containing the optimal acceptor phase octanol were evaluated, considering the donor phase as 1) a pH 8.0 phosphate buffer solution (0.05 mol L⁻¹), 2) crude soil extract, 3) a mixture of buffer and pesticides, and 4) a mixture of soil extract and pesticides. The results presented in Table S2, Supporting Information, showed that $R_{\text{electrolyte}}$ and R_{ct} increased in the presence of pesticides.

Table 2. Optimized EME conditions for multiclass pesticide extraction.

Donor/ acceptor pH	Voltage [V]	SLM solvent	Extraction time [min]	Stirring speed [rpm]	Salt addition [w/v%]
8	100	Octanol	15	1000	10%

All the Nyquist plots obtained for the electromembrane systems are shown in Figure S7, Supporting Information. The non-Faradaic condition was also applied to the electrochemical cell containing only the Pt wire electrode (without the membrane), and EIS measurements were performed in the same four systems previously described. The Nyquist plots obtained for the Pt electrode system (Figure S8, Supporting Information) exhibited a dramatically different behavior from those obtained for the electromembranes. Considering that in the absence of a reversible redox probe in the electrolyte solution, only the non-Faradaic impedance is operative, the electron transfer characterizing charge-transfer resistance (R_{ct}) and Warburg impedance becomes infinite.^[37] Randle's equivalent circuit becomes simplified, and the electrochemical transformations occurring at the electrode/electrolyte interface can be modeled by the electrolyte resistance ($R_{electrolyte}$) and by a constant phase element (CPE). The fitting parameters for the Pt electrode systems are shown in Table S3, Supporting Information.

It's noteworthy that the results from EIS for octanol, decanol, and dodecanol exhibited an unexpected outcome compared to the optimization discussed in earlier sections. As octanol was identified as the best SLM solvent for the EME experiments, it was first expected that this solvent could present a lower $R_{electrolyte}$, R_{ct} , and R_{si-sd} in comparison to decanol and dodecanol; however, the opposite behavior was found. This finding provides valuable insights into elucidating the extraction recovery of captan pesticide, as discussed in the previous section (*SLM Solvent Evaluation*). As demonstrated previously by Equation (2), the mass transfer between phases is governed by both electrophoresis and distribution phenomena (K_d^*). While electrophoresis primarily dictates the electrokinetic movement of analytes, the diffusion of these substances also enhances their extraction kinetics.

According to the findings from EIS experiments, it can be inferred that for certain analytes, such as captan pesticides, the diffusion between phases serves as the primary mechanism

driving transfer of analytes from the donor to the acceptor phase within the HF membrane. Therefore, for pesticides exhibiting hydrophobic characteristics, exemplified by captan (with a LogP of 3.2, as per Table 1), their affinity with hydrophobic solvents, such as decanol and dodecanol (in the hydrophobicity order of octanol < decanol < dodecanol) renders the diffusion process more effective than electrophoretic phenomena. While this observation specifically elucidates the extraction behavior of captan, it is noteworthy that octanol emerged as the optimal choice for the entire spectrum of analytes. Despite the apparent resistance encountered with octanol, the application of external voltage mitigated the inherent resistance effect of the solvent. This implies that without the involvement of electrophoretic phenomena, the extraction of pesticides using octanol as the SLM solvent could potentially be delayed, requiring a longer equilibrium time than the 15 min achieved in this study.

3.8. Figures of Merit

After the EME extraction parameter optimization, the developed method U-EME/LC-MS was submitted to the analytical performance evaluation. To this aim, the linearity of the EME method using the U-shaped configuration was assessed by analytical curves for each pesticide under investigation in soil sample extract. Such a task involved applying linear regression to the peak areas of the pesticide (Y) concerning their concentrations (X, mg kg⁻¹) using six concentration levels (500, 600, 700, 800, 900, and 1000 mg kg⁻¹) in quintuplicate ($n = 5$) assay. **Table 3** presents the obtained regression equation and parameters for the evaluated pesticides, which exhibited R^2 values greater than 0.9800, indicating the method's ability to provide linear results concerning pesticide concentration. The obtained LOD and LOQ values are also presented in Table 3.

Table 3. Linearity, LOD, and LOQ obtained values in the matrix for the U-EME/LC-MS method for multiclass pesticide in soil sample determination.				
Pesticide	R^2 (matrix) ^{a)}	Linear regression (matrix)	LOD [mg kg ⁻¹] ^{b)}	LOQ [mg kg ⁻¹] ^{b)}
Diuron	0.96	$Y = 2134.8 x - 724\ 830$	94.4	286.3
Metribuzin	0.97	$Y = 2687.9 x - 948\ 891$	171.4	491.0
Simazine	0.97	$Y = 1366.8 x - 392\ 220$	157.1	476.6
Imazapic	0.99	$Y = 420.14 x - 101\ 912$	165.9	495.1
Carbaryl	0.98	$Y = 1990.8 x - 367\ 438$	142.3	431.3
Pyridaphenthion	0.98	$Y = 205.59 x - 3\ 095.4$	76.1	230.5
Quinalphos	0.99	$Y = 100.9 x - 18\ 252$	160.7	487.3
Carbendazim	0.98	$Y = 231.62 x + 20\ 887$	136.1	412.3
Carboxin	0.99	$Y = 72\ 364 x + 562\ 394$	131.9	399.8
Epoxiconazole	0.98	$Y = 142.12 x - 42\ 008$	124.5	377.3
Cyprodinil	0.99	$Y = 231.02 x + 25\ 172$	137.2	415.2
Thiabendazole	0.98	$Y = 1382.7 x - 357\ 407$	146.9	445.5
Captan	0.98	$Y = 161.39 x - 41\ 463$	91.6	270.7

^{a)} R^2 values obtained by linear regression of peak area versus concentration ($n = 3$); ^{b)}LOD and LOQ calculated using three and ten times, respectively, the standard deviation of the intercept (s) of the calibration curve divided by the slope of the calibration curve.

Establishing acceptable LOD and LOQ levels for pesticides in soil poses a formidable challenge. This difficulty arises primarily from the different interactions between soil and pesticides, therefore hampering the assessment of trace-level concentrations. Furthermore, the interactions between soil and pesticides yield various forms of these substances, especially in terms of their solubility and retention capacity within the environment.^[38] These characteristics significantly influence the pesticides' ability to be extracted by soil matrices. Moreover, the continual introduction of new pesticide formulations in agricultural practices adds a complication factor to these compounds' regulation in soil matrices. Consequently, the absence of established maximum residue values by regulatory organs for pesticides in soil samples presents a difficult task in defining the optimal criteria for the detection and quantification of these chemical compounds in soil. Despite the challenges in establishing reference values for pesticides in soil matrices, an exploration of the literature, especially concerning classical methods for pesticide extraction from environmental samples, can provide valuable insights.

In 2021, Valverde et al.^[39] employed two widely used methods for extracting 13 pesticides in agricultural soil. The researchers utilized UAE and QuEChERS methods with both analyses performed by liquid chromatography-tandem mass spectrometry (LC-MS/MS). The key findings revealed that both techniques yielded LOQ values in the nanogram per gram (ng g^{-1}) range for the evaluation of the 13 pesticides. Acosta-Dacal et al.^[40] conducted a comprehensive assessment of the QuEChERS method's applicability for analyzing a diverse range of multiclass pesticides (218 compounds) in clay loam soil, utilizing LC-MS/MS and gas chromatography-tandem mass spectrometry (GC-MS/MS). As delineated by the authors, the proposed methodology could achieve LOD values within the range of $0.024\text{--}6.25 \text{ ng g}^{-1}$ in the examined samples. Various extraction methods, encompassing both traditional approaches and miniaturized procedures, have been explored for the assessment of pesticides in soil samples. Previously, our research group introduced an analytical approach employing a hollow fiber liquid-phase microextraction-liquid chromatography/mass spectrometry (HF-LPME-LC/MS) approach to determine multiclass pesticides in soil matrices. The developed methodology showed LOD and LOQ values within the mg kg^{-1} range.^[34] Moreover, higher concentration levels were found for the pesticides thiamethoxam ($103.4\text{--}770.8 \text{ mg kg}^{-1}$), imazethapyr ($2.4\text{--}293.5 \text{ mg kg}^{-1}$), and fipronil ($2.1\text{--}170.0 \text{ mg kg}^{-1}$) in soil samples by Martins et al.^[41] using QuEChERS extraction following LC-MS analysis. The wide range of concentration levels, for the same pesticides, in soil samples, in the existing literature, suggests a lack of procedures and standard methods for assessing pesticides in soil around the world. Furthermore, the study presented here could offer both qualitative and quantitative assessments of pesticides in soil samples at concentration levels that could be a concern to society as well as to the producers, once these pesticides could compromise the soil production quality.

As elucidated in this section, the absence of established reference values for maximum pesticide residue limits in soil poses a challenge in defining ideal benchmarks for analytical methods.

Nevertheless, the literature emphasizes the scrutiny of trace-level concentrations (nano/microgram per gram/kilo). While the LOD and the LOQ derived in this study may appear higher than certain reported values, it is crucial to underscore that these figures can be lower when evaluating a reduced set of analytes. Additionally, the method presented herein serves as a valuable analytical tool for screening pesticides in soil matrices, contributing to cost efficiency. This approach, characterized by miniaturization and environmentally conscious analytical features, aligns with green analytical principles. Moreover, the effectiveness of the developed U-EME/LC-MS method is guaranteed by the figures of merit that will be discussed in this section.

The assessment of precision for inter- and intraday analyses was conducted in quintuplicate ($n = 5$) at three concentration levels (600, 800, and 1000 mg kg^{-1}). The evaluation of the multiclass pesticide's method utilizing U-EME/LC-MS revealed precision values within the range of $0.1\%\text{--}8.5\%$ for intraday assays and $0.6\%\text{--}8.8\%$ for interday assays. Subsequent to evaluating the pesticides' response to the U-EME/LC-MS method at these specified concentrations, recovery values ranging from 84.5% to 101.2% were obtained for the studied multiclass pesticides (detailed data are presented in Table S4, Supporting Information). Due to the coexistence of electromigration and diffusion phenomena in EME, recovery values are predominantly situated near 100% . This underscores the miniaturized procedure's remarkable capability to mass transport nearly 100% of the analytes to the acceptor phase inside the HF membrane, thereby emphasizing the substantial potential of EME over conventional miniaturized techniques, such as HF-LPME.^[22,42]

The impact of the soil matrix on the EME extraction of pesticides was evaluated by examining the parallelism between the curves of the pesticides obtained in solvent and soil matrices in the concentration range of $500\text{--}1000 \text{ mg kg}^{-1}$ with subsequent assessment by a t-test evaluation. For the matrix effect evaluation, it was deemed significant that values $p < 0.05$ indicated a noteworthy influence of the matrix on both the extraction and detection of the analytes. The results, including linear regression, R^2 , and p values (t-test), are detailed in Table S5 in the Supporting Information. According to Table S5, Supporting Information, the pesticides imazapic, pyridaphenthion, quinalphos, carboxin, epoxiconazole, cyprodinil, and thiabendazole, displayed p -values < 0.05 , suggesting a significant impact of the matrix on the extraction of these particular pesticides for the U-EME/LC-MS method.

As previously explained, the fundamental concept of the EME technique involves the electromigration of charged analytes at controlled pH. Given that the soil matrix is a highly complex sample, it carries numerous endogenous compounds which, under certain pH conditions, may become charged, thereby participating in the mass transfer process of the technique and influencing the extraction of certain pesticides.^[43] Despite the EME method exhibiting matrix effects for some analytes in the study, it still demonstrated recovery values ranging from 82.5% to 101.1% , showcasing its versatility in the extraction of multiresidues in soil. As a proof of concept, the U-EME/LC-MS method was applied for the extraction of the 13 multiclass pesticides at a concentration of

500 mg kg⁻¹ in a soil sample. The extracted MS Chromatogram depicted in **Figure 2** showcases the potential of the developed method to evaluate analytes with diverse physicochemical properties in a complex sample. The reported method in this study ensured chromatogram peak definition, thereby enhancing both the quantitative and qualitative capabilities of the proposed method. Furthermore, the U-EME/LC-MS method developed demonstrated an extraction time of just 15 min, using a reducing solvent volume (± 20 μ L), coupled with a chromatographic analysis lasting 10 min for the comprehensive assessment of multiresidues. The challenge of developing swift methodologies capable of detecting multiresidues in complex samples underscores its potential for practical application in the daily evaluation of residues in environmental samples. The advancement of the proposed method opens new horizons for applying EME procedures in an environmental context, addressing a current gap in the applicability of this technique to such matrices.

3.9. Literature Comparison of the U-EME/LC-MS Method

The extraction and evaluation of pesticides in soil matrices pose significant challenges for both traditional and miniaturized strategies. The introduction of advanced analytical methods seeks to address these challenges and improve the efficiency of multiresidue assessments in soil, which is crucial for controlling contaminants. Therefore, this section aims to provide a concise literature comparison between traditional and miniaturized methods for pesticide extraction in soil, contrasting them with the key advantages that the reported U-EME/LC-MS method achieved compared to these studies.

A stir-bar sorptive extraction modified with molecularly imprinted polymer was proposed by Días-Alves et al.^[44] for the extraction of triazines in environmental soil samples. The reported miniaturized approach demonstrated a similar extraction process to our study, involving a 15 min extraction with a sample volume of 10 mL, comparable to the 5 mL used in the U-EME/LC-MS method described here. Despite these similarities, the method reported by the authors showed recovery values ranging from 2.4% to 15.4% for six triazine analytes, which are

significantly lower than the recovery values obtained for the 13 analytes in our U-EME/LC-MS method, which ranged from 84.5% to 101.2%. In a recent miniaturized extraction application, Moret et al.^[45] described using an online HF-LPME configuration to extract herbicides and their metabolites from soil samples. Despite the application of an online approach, a significant drawback was the required extraction time, which necessitated 2 h to ensure efficient mass transfer of the analytes from the donor to the acceptor phase. One major advantage of EME protocols over HF-LPME is their enhanced and rapid mass transfer of analytes. This study reported the use of just 15 min to achieve nearly 100% recovery of the analytes, which is a significantly shorter time compared to the 2 h required by Moret et al. using an online HF-LPME protocol for herbicides in soil.

Despite advancements in miniaturized strategies for pesticide extraction in soil samples, traditional methods such as ultrasonic solvent extraction (USE) and SSE remain widely used for this assessment.^[46] In 2021, Aiyesanmi et al.^[47] described the application of the USE method for the extraction of organochlorine pesticides in floodplain soils, followed by gas chromatography-mass spectrometry (GC-MS) analysis. The extraction process consumed ≈ 100 mL of organic solvents, leading to substantial waste production. For instance, performing 10 extractions would generate 1000 mL of chemical waste, which contradicts the key principles of GAC. In contrast, our study reported the use of 20 μ L of organic solvent (octanol) and 5 mL of donor phase, resulting in a total of 5.2 mL per extraction. Over 10 extractions, this amounts to just 52 mL, which is practically half of what Aiyesanmi et al. generated in a single extraction. Additionally, while Aiyesanmi et al. achieved recovery values of over 88% with 8 analytes, our study using the U-EME/LC-MS method demonstrated superior performance, with recovery values ranging from 84.5% to 101.2% across 13 analytes. In another study, Kunene and Mahlambi^[10] reported using both USE and SSE for the extraction of triazines in soil samples. The authors utilized 135 mL of organic solvents in both methods, achieving LOD values of 9.2×10^{-5} – 2.2×10^{-4} mg kg⁻¹ and recovery rates between 70% and 100%. Although the LOD values reported by Kunene and Mahlambi are superior to those in our study, the environmental impact of their methods

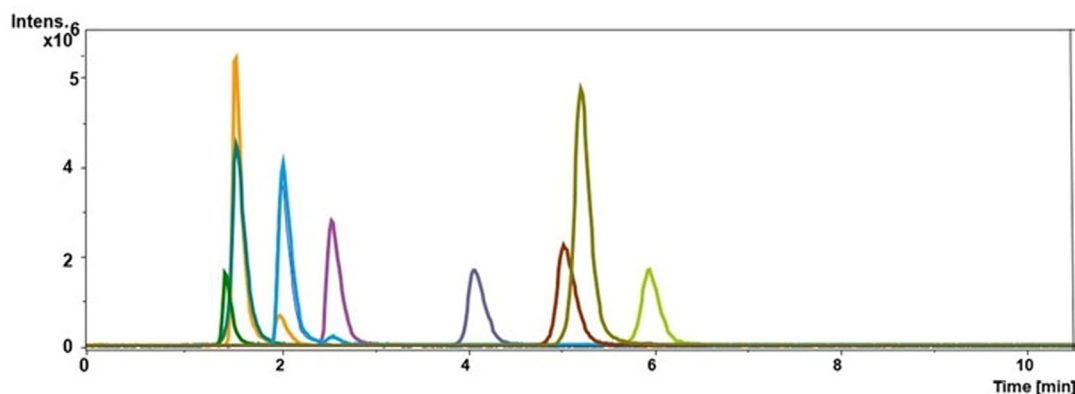


Figure 2. Extracted MS chromatogram obtained by the U-EME/LC-MS method applied for the extraction and detection of the multiclass pesticides (500 mg kg⁻¹) in a soil sample.

Table 4. Traditional and miniaturized extraction methods reported in the literature for pesticide assessment in soil matrices.

Pesticide (s)	Sample	Extraction technique	Solvent volume [mL]	Sample amount	LOD	Recovery [%]	Ref.
Triazines	Environmental soil	SBSE-MIP ^{a)}	16	10 mL	$7.5 \times 10^{-3} \text{ mg kg}^{-1}$	2.4–15.4	[44]
Herbicides	Soil	HF-LPME ^{b)}	± 1	$\pm 20 \text{ mL}$	$1.0 \times 10^{-4} - 3.0 \times 10^{-4} \text{ mg kg}^{-1}$	–	[45]
Organochlorine pesticides	Floodplain soils	USE ^{c)}	100	10 g	$1.6 \times 10^{-3} - 3.4 \times 10^{-3} \text{ mg kg}^{-1}$	88	[47]
Triazines	Soil	USE and SSE ^{d)}	135	100 mL	$9.2 \times 10^{-5} - 2.2 \times 10^{-4} \text{ mg kg}^{-1}$	70–100	[10]
Organochlorine pesticides	Soil	QuEChERS ^{e)}	15	1 g	$1.0 \times 10^{-6} - 1.48 \times 10^{-3} \text{ mg kg}^{-1}$	65.8–172.6	[52]
Herbicides	Soil	d-SPE ^{f)}	10	5 g	$2.0 \times 10^{-4} - 1.0 \times 10^{-3} \text{ mg kg}^{-1}$	87.7–108	[53]
13 multiclass pesticides	Soil	U-EME ^{g)}	0.02	5 mL	76.1 to 171.4 mg kg^{-1}	85.2–101.2	This study

^{a)}SBSE-MIP: stir-bar sorptive extraction modified with a molecularly imprinted polymer; ^{b)}HF-LPME: hollow fiber liquid-phase microextraction; ^{c)}USE: ultrasonic solvent extraction; ^{d)}SSE: Soxhlet solvent extraction; ^{e)}QuEChERS: quick, easy, cheap, effective, rugged, and safe; ^{f)}d-SPE: dispersive solid-phase extraction; ^{g)}U-EME: electromembrane extraction in “U” shaped.

due to high solvent usage must be considered. In contrast, our developed U-EME/LC-MS method provides a qualitative overview of multiresidue pesticides in soil. Moreover, its application is supported by the literature by being aligned with the potential concentrations of pesticides found in environmental soil matrices, as reported by Martins et al.^[41] who found concentrations of pesticides in soil at the same range as our LOQ and LOQ values for our method. Furthermore, despite the higher LOD and LOQ values obtained in our study, the method demonstrates potential applicability in real-world scenarios, especially in countries with extensive agricultural activities, such as Brazil. This highlights the need to balance analytical performance with environmental sustainability when choosing extraction methods. Table 4 presents detailed literature reports on commonly used traditional and miniaturized methods for pesticide assessment in soil matrices.

4. Sustainable Analytical Insights: A Green Analytical Overview of the U-EME/LC-MS for Pesticide Assessment in Soil Matrices

The miniaturization of traditional analytical sample preparation procedures has not only led to increased efficiency but also incorporated some important GAC principles initially introduced by Paul Anastas et al.^[48] These principles, encapsulating 12 key guidelines, have played a pivotal role in laying the foundation for sustainable and eco-friendly practices in the analytical chemistry field. Although these key points have evolved over the years to enhance the definition of the environmental friendliness of analytical methods, establishing a metric for this evaluation remains a challenging endeavor. Consequently, various studies have been introduced in the literature, aiming to furnish metric parameters either through software tools or established principles. These endeavors seek to offer a comprehensive assessment of the ecological footprint associated with the introduction of green sample preparation methods. Two prominent approaches involve the utilization of the AGREEprep analytical tool and the Green Analytical Procedure Index (GAPI).^[49,50] These methods have gained widespread acceptance for assessing the

sustainability and eco-friendly attributes of numerous sample preparation techniques.^[48]

Hence, this study proposed the application of both the AGREEprep analytical tool and the GAPI approaches for a comprehensive insight into the key environmentally sustainable aspects of the developed U-EME/LC-MS method. The score of AGREEprep and the evaluation by the GAPI strategy are presented in Figure 3A,B, while the detailed individual applied weight for each principle can be found in Table S6 within the Supporting Information.

The AGREE methodology, initially introduced in 2020, presented 12 principles outlining key points within the GAC framework for assessing the environmental sustainability of analytical methodologies.^[48] Subsequently, significant enhancements were made to the model, culminating in the launch of the AGREEprep analytical tool in 2022. This advanced tool features a recalibrated set of 10 key categories based on the GAC principles, providing a more refined and effective evaluation of the ecological impact of analytical methods.^[50] Within the AGREEprep analytical tool, a questionnaire comprising 10 questions seeks crucial information about the developed methodology. According to Figure 3A, the green aspects of the method are primarily associated with items 2 and 10. The reported method uses a total volume of $\approx \pm 20 \mu\text{L}$ of solvent, which is significantly less than the volume required by traditional sample preparation methods. Traditional methods often necessitate a considerable amount of solvent, especially with multiple extractions, making this reduction a notable environmental advantage. In a study conducted by Martins et al.^[41] the authors documented the utilization of $\approx \pm 38$ units of mass and volume (g mL^{-1}) of solvents and reagents for a QuEChERS extraction of pesticides in soil samples. The employment of such substantial amounts of reagents and solvents resulted in a final AGREEprep score of 0.17 (refer to Table S7 in the Supporting Information), highlighting adverse environmental implications associated with this conventional procedure.

Yellow and orange items primarily pertain to waste management, sample volume, sample throughput, and postsample preparation analysis, respectively. Although these items are not classified as red, indicating the highest environmental impact,

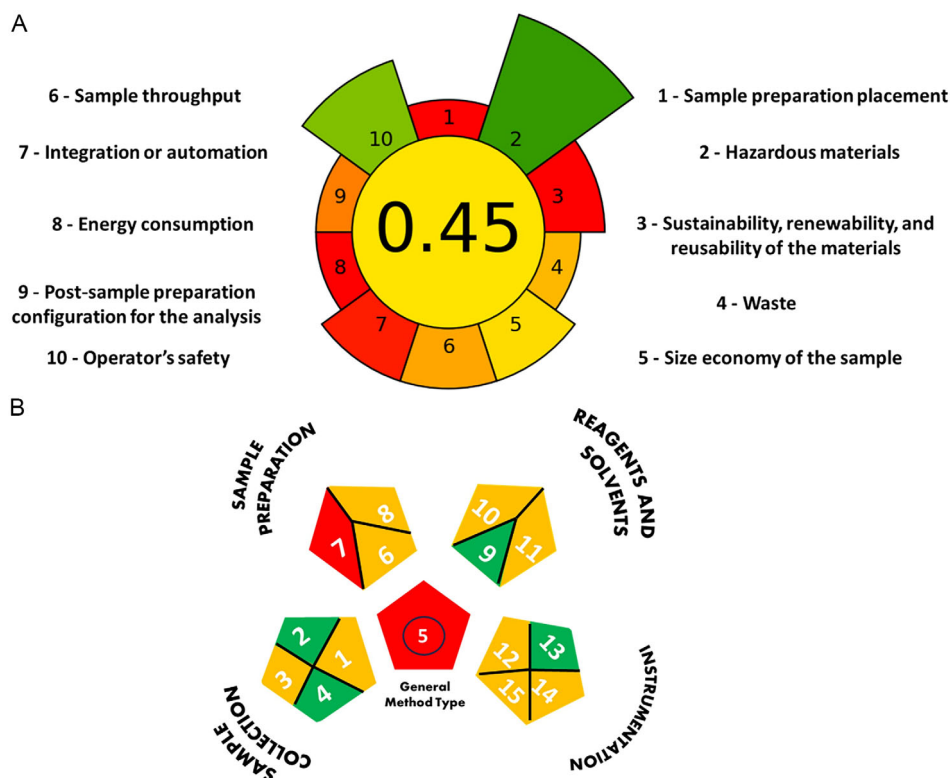


Figure 3. Greenness assessment of the U-EME/LC-MS of multiclass pesticides in soil matrices according to A) AGREEprep tool and B) GAPI guidelines. Circle in the middle of GAPI: procedure for qualification and quantification.

they still require careful attention. For the presented method, ≈ 5.2 mL of chemical waste is generated, which is considerably less than the waste produced by conventional methods. Despite such volume being considered a high amount of solvent by Wojnowski et al.,^[51] the waste volume produced here is less than conventional extraction procedures reported in the literature, such as QuEChERS and MAE for soil matrices. Martins et al.^[41] utilized QuEChERS, resulting in the production of more than ± 30 mL of chemical waste, a consequence of the extensive six-step extraction process detailed in Table S7, Supporting Information. In a parallel study, He et al.^[12] reported the use of ± 8.2 mL for the MAE extraction of pesticides in soil matrices (final AGREEprep score of 0.24 as demonstrated in Table S7, Supporting Information). Moreover, although the sample throughput of the reported method was not considered high (4 samples/per hour), we have described the achievement of recovery values near 100%.

Critical points of the U-EME/LC-MS method were identified in items 1, 3, 7, and 8, indicating challenges in the green analytical assessment of pesticides in environmental matrices. These points highlight the limitations of the offline application of EME extraction. While literature reports suggest the potential for integrating EME procedures, our study specifically focused on evaluating conventional EME as a standalone step for analyzing pesticides in soil samples.^[22] Moreover, there is a necessity to provide reusable materials for EME protocols, as the HF used for this application is typically discarded after use. Energy consumption is also a

drawback of EME, particularly compared with HF-LPME methods. Despite this, the use of external energy in EME approaches shortens the extraction time and increases the potential to achieve recovery values close to 100%. Proposing novel strategies to address these issues could introduce an eco-friendlier perspective for EME applications.

Although the AGREEprep analytical tool offers a thorough assessment of the environmentally friendly aspects of the developed methodology, employing an alternative evaluation strategy can provide diverse perspectives, allowing us to encompass additional eco-friendly dimensions of the proposed analytical strategy. Introduced in 2018 by Plotka-Wasyłka,^[49] the GAPI technique offers a qualitative assessment of the green aspects of an analytical method. It is visualized as a pictogram featuring red, yellow, and green colors. The developed pictogram comprises five sections: 1) sample collection, 2) method type, 3) sample preparation, 4) reagents and chemicals used, and 5) instrumentation. The resulting pictogram for the U-EME/LC-MS method is presented in Figure 3B, while the corresponding questionnaire and responses, aligned with the parameters applied in this study, are detailed in Table S8 in the Supporting Information.

As detailed in Table S8 in the Supporting Information, critical aspects of the method primarily pertain to the offline extractions performed in this study. Additionally, the use of organic solvents remains a drawback according to the evaluation. From the authors' critical perspective, automated or semiautomated

applications for EME extractions need to be introduced. Furthermore, the use of green solvents should be more thoroughly explored in these protocols, as they could significantly improve the evaluation of these green assessment strategies. Employing analytical tools and protocols, such as AGREEp and GAPI, to assess the green aspects of an analytical method represents a viable approach for obtaining a comprehensive overview aligned with GAC principles. This evaluation demonstrates that despite EME extraction being deemed a miniaturized strategy, certain aspects counteract eco-friendly and sustainable practices, particularly regarding the energy consumption of the method. Nevertheless, when compared to conventional methods typically employed for assessing pesticides in soil samples, EME extraction presents distinct advantages, particularly in terms of minimal organic solvent utilization. Consequently, the U-EME/LC-MS method proposed in this study for evaluating multiclass pesticides in soil samples emerges as a promising approach. It not only offers new perspectives for the widespread application of EME procedures but also explores the significant potential of this method across various matrices, extending beyond the commonly utilized biological matrices.

5. Conclusions

In the present study, we introduced a novel approach, an EME with a U-shaped configuration followed by liquid chromatography/mass spectrometry analysis (U-EME/LC-MS), for the comprehensive assessment of multiclass pesticides in soil samples. The optimization of the reported method based on the postextraction recovery revealed superior analytical performance under the following specific conditions: a donor and acceptor phase pH of 8, an extraction voltage of 100 V, a 15 min extraction time, a stirring speed of 1000 rpm, octanol as the solvent for the SLM membrane, and 10% (w/v) NaCl. The evaluation of the analytical performance of the method revealed the attainment of a linear range (500–1000 mg kg⁻¹) with $R^2 > 0.9800$ and LOD/LOQ values ranging from 76.1 to 171.4 mg kg⁻¹ and 270.7 to 495.1 mg kg⁻¹, respectively. Furthermore, a matrix effect was observed for the pesticides pyridaphenthion, quinalphos, carboxin, and imazapic ($p < 0.05$). Despite the matrix effect observed in some of the studied pesticides, recovery values in the range of 84.5%–101.2% were achieved through the EME methodology, demonstrating the efficiency of the proposed method. Finally, the utilization of AGREEp and GAPI as evaluation approaches for assessing the green aspects of the presented method provided a comprehensive insight into the primary advantages and limitations of the developed technique. This analysis, aligned with GAC principles, sheds light on the ecological impact of the method, especially as it provides a comparison with traditional approaches used for assessing pesticides in soil samples. To the best of the author's knowledge, this marks the inaugural application of both methods to evaluate the eco-friendly and sustainable aspects of an EME procedure applied in an environmental context. The U-EME/LC-MS method proposed in this study holds significant

potential for both quantitative and qualitative assessments of residues in soil samples. The presented results highlight the substantial capabilities of the reported EME procedure in assessing complex environmental samples, thereby enhancing the impact of this study in the scientific realm of environmental monitoring. This, in turn, lays the groundwork for a future where miniaturized approaches can find widespread application in residue evaluation.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Livia F. Sgobbi: investigation (equal); methodology (equal); writing—original draft (equal); writing—review and editing (equal). **Rafael O. Martins:** conceptualization (equal); formal analysis (equal); investigation (lead); methodology (lead); validation (lead); visualization (equal); writing—original draft (lead); writing—review and editing (lead). **Gabriela G. Souza:** investigation (equal); methodology (equal); validation (equal). **Anne Varenne:** conceptualization (equal); investigation (equal); supervision (equal); visualization (equal). **Fanny d'Orlyé:** conceptualization (equal); investigation (equal); supervision (equal); visualization (equal). **Pedro V. V. Romanholo:** investigation (equal); methodology (equal). **Maria E. C. Queiroz:** conceptualization (equal); methodology (equal). **Bruno J. G. Silva:** conceptualization (equal); supervision (equal); visualization (equal). **Virginia Damin:** conceptualization (equal); visualization (equal). **Andréa R. Chaves:** conceptualization (lead); investigation (lead); project administration (lead); resources (lead); supervision (lead); writing—original draft (lead); writing—review and editing (lead).

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: electromembrane extraction · green analytical chemistry · miniaturized sample preparation · pesticides · soil samples

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