



Development and greenness evaluation of solid-phase extraction and salting-out liquid–liquid extraction method for determination of herbicides in water, soil and rice

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Abstract

Solid-phase extraction (SPE) and salting-out-assisted liquid–liquid extraction (SALLE) method was optimized and validated for the extraction and quantification of anilofos, bispyribac sodium, butachlor, pendimethalin, pretilachlor and penoxsulam from environmental water, soil and rice samples using HPLC and LC–MS/MS. The limit of detection and limit of quantification ranged from 0.0026 to 0.03 and 0.008 to 0.09 $\mu\text{g mL}^{-1}$ in different matrices using HPLC and LC–MS/MS. Under the optimal conditions, mean percent recoveries ranged from 81.6 ± 4.1 to 98.6 ± 3.5 , 84.1 ± 3.5 to 99.4 ± 3.2 and 81.3 ± 4.2 to 94.6 ± 3.5 in water, soil and rice, respectively, using SPE while 84.9 ± 2.9 to 102.3 ± 2.3 , 90.0 ± 4.1 to 103.2 ± 4.1 and 86.3 ± 2.7 to 94.6 ± 3.5 using SALLE. Acceptable recoveries ($> 80\%$) and precision ($< 10\%$) for studied herbicides in water, soil and rice samples were obtained using SPE and SALLE. Further, the greenness was evaluated using AGREE metrics and Analytical Eco-Scale. SPE and SALLE were found to be greener methods and were efficient for the determination of herbicides from water, soil and rice. However, SALLE is advantageous over SPE in terms of cost-effectiveness, simplicity and easy handling. SALLE was used for extraction and quantification of herbicide from environmental water, soil and rice samples. Herbicide concentrations in soil and water samples at 0 day varied from 0.083 ± 1.65 to $1.381 \pm 1.41 \mu\text{g g}^{-1}$. The concentration of studied herbicides in soil, rice and water at harvest was below the permissible limit ($< 0.01 \mu\text{g g}^{-1}$).

Keywords Herbicides · Penoxsulam · Bispyribac sodium · Butachlor · Anilofos · Pendimethalin · Pretilachlor

Introduction

Herbicides have evolved as the largest consumed crop protection pesticide across the globe with an approximate share of 48.0% in the global pesticide market. Of the total herbicide consumption, rice accounts for a major share of 25.0% in the world market. Anilofos, bispyribac sodium, butachlor, pendimethalin, pretilachlor and penoxsulam are commonly used herbicides for the control of weed in rice crops. These herbicides have moderate to high persistence and can contaminate soil, water and agricultural produce. About 0.09 to 0.312, 0.1 to 0.28, 0.07 to 0.15, 0.21 to 0.81 and 0.05

to 0.11 mg kg^{-1} residues of bispyribac sodium, butachlor, pendimethalin, pretilachlor and penoxsulam, respectively, have been detected in the soil, water and crop produce which were above the accepted maximum residue limit (MRL) value adopted by the FAO/WHO Codex Alimentarius Commission [1–5]. Butachlor and pretilachlor contaminate the aquatic environment and have harmful effects on nontarget organisms [6–8]. Butachlor induce changes in sister chromatide in cultured human lymphocytes [9] and is a retardant of growth and reproduction in earthworms, viz. *Eisenia fetida* and *Perionyx sansibaricus* [10]. Penoxsulam is toxic to aquatic plants with EC_{50} of 0.086 and 0.0033 mg L^{-1} for *Pseudokirchneriella subcapitata* and *Lemna gibba* [1]. Pendimethalin causes physiological, mutagenic and endocrine impacts in animals including damage to the liver and kidney [11]. Considering these environmental impacts, it is of utmost importance to have a straightforward and rapid method of analysis that can provide reliable identification and accurate quantitation of residual amounts of herbicides so that their usage can be monitored and regulated.

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Traditionally, liquid–liquid extraction (LLE) and solid-phase extraction (SPE) have been employed for the extraction of herbicides from various matrices. LLE involves the partitioning of solutes between two phases and requires a large amount of toxic organic solvents which not only pose health risks to the operator but also increase the cost of disposal [12–14]. Additionally, it is also a time-consuming, expensive and tedious process. SPE is a technique for rapid and selective sample preparation that involves multiple steps such as sorbent conditioning, sample application, washing and elution. SPE has tremendous advantages including shorter analysis time, low solvent consumption, high pre-concentration factor, good recoveries, precision and is applicable to a wide range of herbicides having different physicochemical properties [3, 5, 15–23]. Nevertheless, potential variability of SPE packing, irreversible adsorption of some analytes on SPE cartridges and more complex method development are some of the drawbacks of this technique. Currently, different miniaturized sample preparation and concentration techniques such as solid-phase microextraction (SPME) [24, 25] and dispersive liquid–liquid microextraction (DLLME) [26] have been developed for the analysis of herbicides. SPME is a solvent-free technique, but the fiber is expensive, fragile, and has a limited lifetime, and the sample carryover problem cannot be eliminated. There are small number of commercially available stationary phases, thereby limiting the choice for selectivity in SPME. DLLME is performed in manual mode and is limited to a small number of extraction solvents. The use of relatively larger volumes of a disperser solvent is the most significant drawback of DLLME, as it decreases the polarity of aqueous phase which leads to an increase in the solubility of analytes into the aqueous phase and decreases extraction efficiency [27]. Additionally, the stable cloudy solution formed is to be separated by centrifugation which is a time-consuming procedure including problems of low precision. Most of these drawbacks have been overcome in air-assisted dispersive liquid–liquid extraction (AA-DLLME), solidification of floating organic drop-dispersive liquid–liquid extraction (SFO-DLLME) and homogenous LLE-DLLME (HLLD-DLLME) for the extraction of pesticides, phenolic compounds, drugs and parabens from water and vegetable oils [28–33]. Salting-out-assisted liquid–liquid extraction (SALLE) technique is another recently developed extraction technique offering compatibility, quickness, simplicity, easy operation and concentration of analyte extracts [34]. It is based on LLE, in which the addition of salt to a mixture of an aqueous medium containing the analytes and a water-miscible organic solvent causes a separation of the organic phase from the mixture [35]. SALLE has been reported for quantification of sulfonyleurea from water and banana juice [36] and triazines from environmental water, fruits, vegetable and alcoholic beverages [37–40]. However, it is very difficult to reach at a universally accepted analytical

method by extrapolating already reported literature method even when the same analytical technique and instrument is used as sample preparation is a complex procedure that is dependent upon physicochemical properties of analyte (polarity, solubility and volatility), sample type and interactions between them. Till date, there is no available literature on the determination of anilofos, bispyribac sodium, butachlor, pendimethalin, pretilachlor and penoxsulam from water, soil and rice using SALLE.

Additionally, it is very important to evaluate the greenness of the analytical method to determine how well the developed analytical procedure addresses the principles of green analytical chemistry. The greenness of analytical procedures is a multivariant complex parameter that is not easily quantifiable and dedicated metrics are required to measure the degree of greenness of analytical methodologies. Several greenness assessment tools such as National Environmental Methods Index (NEMI), Analytical Eco-Scale, Green Analytical Procedure Index (GAPI) and Analytical GREENness metric (AGREE) have been developed. Analytical Eco-Scale is commonly used greenness assessment tool, and AGREE is one of the latest and most preferred metric system as it evaluates analytical procedure considering all the 12 principles of green analytical chemistry. It is comprehensive, flexible and straightforward assessment approach that provides an easily interpretable result. To the best of our knowledge, this is the first study on the evaluation of the greenness of SALLE method.

The present study aims to develop a simple, facile and cost-effective SALLE method for the quantitative determination of anilofos, bispyribac sodium, butachlor, pendimethalin, pretilachlor and penoxsulam from water, soil and rice so as to ensure consistent, reliable results with the elimination of possible interferences due to complex matrices. Several factors affecting the process of extraction such as type and volume of the organic solvent, ultrasonication time and temperature, type and amount of salt and pH of sample solution were optimized. SALLE method was compared with the traditional SPE method and validated in different water (tube-well, pond, tap and river water), soil (loamy sand, sandy loam, silt loam, loam and clay loam) and rice matrices. The validated SALLE method was used for the determination of the herbicide concentrations in real water, soil and rice samples. The greenness of the proposed methods was evaluated using AGREE metrics and Analytical Eco-Scale.

Materials and methods

Chemicals

Analytical standard of anilofos (99.8%), bispyribac sodium (98.0%), butachlor (97.3%), pendimethalin (94.8%),

pretilachlor (98.2%) and penoxsulam (99.1%) were procured from Sigma Aldrich, Mumbai, India. Analytical- and HPLC-grade solvents used in the study were procured from SRL Chemicals, India. The stock solution of herbicides (1000 $\mu\text{g ml}^{-1}$) were prepared in HPLC-grade acetonitrile. Working standards in the range of 0.006 to 10 $\mu\text{g ml}^{-1}$ were prepared by dilution of stock solution with HPLC-grade acetonitrile.

Sampling sites

Tap, pond, river and tubewell water was collected from Department of Agronomy, Punjab Agricultural, University (30°54'N, 75°48'E), Ludhiana, Village Boparai Kalan, Ludhiana (30°57'N, 75°38'E), Khera Bet (31°0.16'N, 75°52'E), Ludhiana and Chak Chibranwali (30°0.22'N, 74°24'E), Muktsar, Punjab. The water samples from herbicide-free rice fields were collected from Research Farm of Department of Agronomy, Punjab Agricultural University, Ludhiana (30°54'N, 75°48'E), Ludhiana. Water samples were collected in pre-washed polyethylene bottles and filtered using Whatman filter paper. The hardness of water was determined using the standard method [41].

Loamy sand, loam, clay loam, silt loam and sandy loam soils without background of herbicide application were collected from Punjab Agricultural, University, Ludhiana (30°54'N, 75°48'E), Village Bondli, Distt. Ludhiana, Punjab (30°50'19"N, 76°11'00"E), Samrala (30°51'22"N, 76°12'15"E), Pathankot (32°15'28"N, 75°46'66"

E) and Shaheed Bhagat Singh Nagar (31°08'37"N, 75°56'96"E), regions of Punjab, respectively. The physicochemical properties of soil were determined using standard protocols [41–44]. Rice samples without any background of herbicide application were collected from the Research Farm of Department of Agronomy, Punjab Agricultural, University, Ludhiana (30°54'N, 75°48'E). The determined physicochemical characteristics of water and soil are given in Tables 1 and 2.

High-performance liquid chromatography (HPLC)

Residues were quantified using Waters HPLC equipped with 2489 UV visible detector, binary 515 pumps and Rheodyne injector with 20 μL loop. LC separation was performed at 210, 220, 250, 220, 240 and 230 nm for anilofos, bispyribac sodium, butachlor, pendimethalin, pretilachlor and penoxsulam using princeton C18 column (5 μm ODS2, 4 \times 250 mm). Acetonitrile:water (8:2) was used as mobile phase for quantification of anilofos, bispyribac sodium, pendimethalin and penoxsulam while acetonitrile and acetonitrile:0.2% acetic acid (7:3) were used for pretilachlor and butachlor, respectively. The retention time of anilofos, bispyribac sodium, butachlor, pendimethalin, pretilachlor and penoxsulam was 6.29, 7.60, 7.81, 8.32, 4.04 and 3.42 min, respectively.

Liquid chromatography–tandem mass spectrometry (LC–MS/MS)

An Alliance LC–MS/MS–Waters 2695 system equipped with Micromass Quattro triple quadrupole (QQQ) mass spectrometer was used for chromatographic analysis. LC separation was performed on symmetry Xterra C18 (5 μm ODS2 (3.5 \times 150 mm) column. Mass lynx version 4.1 2005 (Micromass, Waters, USA) was used for acquisition. All analysis was performed in positive electrospray ionization (ESI⁺) mode. Acetonitrile:water (80:20) was used as mobile phase at a flow rate of 0.8 mL min^{-1} , and the injection volume was 20 μL . The retention time of anilofos, bispyribac sodium, butachlor, pendimethalin, pretilachlor and penoxsulam was 2.22, 6.36, 2.96, 2.57, 2.55 and 3.97 min, respectively. Optimized MS parameters for herbicides included desolvation gas (L hr^{-1}): 600; desolvation temperature:

Table 1 Physiochemical properties of water samples

Water sample	EC ^a (dS m^{-1})	Calcium and magnesium (meq L^{-1})	pH	TDS ^b (mg mL^{-1})
Distilled water	2.3×10^{-5}	0	7.00	0.011
Tap water	0.92	7.2	7.26	460
Pond water	2.73	8.0	7.40	1365
River water	0.65	5.3	7.53	325
Tubewell water	3.00	17.5	7.39	1500
Field water	0.84	6.3	7.11	420

^aElectrical conductivity, ^btotal dissolved solids

Table 2 Physicochemical properties of soils

Texture class	Clay (%)	Silt (%)	Sand (%)	EC ^a (dS m^{-1})	pH	OC ^b (%)	OM ^c (%)
Loamy sand	2.8	11.0	86.2	0.21	8.8	0.24	0.414
Loam	23.1	35.8	41.1	0.20	8.2	0.40	0.808
Sandy loam	13.8	29.6	56.6	0.24	8.0	0.39	0.672
Silt loam	37.99	59.6	2.41	0.18	8.4	0.46	0.920
Clay loam	39.4	37.1	23.5	0.17	8.6	0.63	1.086

^aElectrical conductivity, ^borganic carbon, ^corganic matter

350°C; source temperature: 150°C; collision gas (L hr⁻¹): 50 and cone voltage: 30 kV. Anilofos showed molecular ion peak (M + H)⁺ at m/z 368.03 (C₁₃H₁₉ClNO₃PS₂) and the fragment ions appeared at m/z 199.16 (M-C₉H₁₁ClN) and 125.98 (M-C₁₁H₁₃ClNO₁S). The mass spectra of bispyribac sodium showed molecular ion peak at m/z 906.88 (2(M + H)⁺), 453.19 (M + H)⁺, 431.20 (M-Na + H)⁺ and fragment ions at m/z ratio 297.98 (M-C₆H₇O₃N₂)⁺ and 275.84 (M-C₆H₇O₃N₂Na + H)⁺. The molecular ion peak (M + H)⁺ of butachlor appeared at m/z 312.3 (C₁₇H₂₆ClNO₂) while fragment ions appeared at m/z 238.33 (M-C₄H₉O) and 227.8 (C₅H₁₁O). Pendimethalin showed molecular ion peak (M + H)⁺ at m/z of 280.8 (C₁₃H₁₉N₃O₄) and fragment ions at 250.8 (M-C₂H₆), 188.8 (M-N₂O₄) and 195.8 (M-C₅H₁₁N). Molecular ion peak (M + H)⁺ of pretilachlor appeared at m/z of 312.1 (C₁₇H₂₆ClNO₂) and fragment ions peak at 252.28 (M-C₄H₁₀) and 177.4 (M-C₇H₁₃ClNO). The mass spectra of penoxsulam showed a molecular ion peak (M + H)⁺ at m/z 484.09 (C₁₆H₁₅F₅N₅O₅S)⁺ and the fragment ions appeared at m/z 258.02 (M-C₁₆H₁₆F₅N₅O₅S)⁺, 195.07 (M-C₉H₆F₃N₅O₃S)⁺, 164.30 (M-C₉H₇F₅O)⁺. MRM transitions m/z 368.03 → 199.16 for anilofos, m/z 453.19 → 297.98 for bispyribac sodium, m/z 312.3 → 238.33 for butachlor, m/z 280.8 → 252.8 for pendimethalin, m/z 312.1 → 252.28 for pretilachlor and m/z 484.09 → 258.02 for penoxsulam were used for the quantification of the herbicides.

Herbicide extraction

Solid-phase extraction (SPE)

SPE cartridges were conditioned by passing 2 × 3 mL of methanol and 5 mL of double distilled water. Five mL of water sample was passed through preconditioned SPE (Octadecyl C18, 5 mg 6 mL⁻¹) cartridges at a flow rate of 0.5 mL min⁻¹ using vacuum manifold (Fig. 1). Columns were then eluted with 2 × 5 mL acetone at a flow rate of 0.5 mL min⁻¹ for the extraction of anilofos, butachlor, penoxsulam and pendimethalin whereas, for extraction of bispyribac sodium and pretilachlor, columns were eluted with methanol (2 × 5 mL) at a flow rate of 0.5 mL min⁻¹. The eluent was collected and concentrated using rotary vacuum evaporator. Residues were reconstituted in 2 mL acetonitrile and analyzed using HPLC/LC-MS/MS. For extraction of herbicides from soil and rice samples, 10 g of sample was transferred into centrifuge tube followed by addition of 40 mL of acetone for extraction of anilofos, penoxsulam, pendimethalin and butachlor and 40 mL of methanol

for bispyribac sodium and pretilachlor. The contents were shaken on orbital shaker for 3 h, vortexed for 1 min and centrifuged at 4500 rpm for 5 min. Then, upper layer of the soil and rice extract was collected and passed through pre-conditioned SPE cartridges at a flow rate of 0.5 mL min⁻¹. The eluent was collected, evaporated using rotary vacuum evaporator, reconstituted using 2 mL acetonitrile and were analyzed using HPLC/LC-MS/MS.

Salting-out-assisted liquid-liquid extraction (SALLE) method

Five mL of water sample and 10 mL of acetonitrile were added in 50-mL centrifuge tube, and contents were ultrasonicated (220 KWh) at 30 C for 3 min. Two g of sodium chloride (NaCl) was added, and the mixture was vortexed for 2 min for phase separation (Fig. 1). The mixture was allowed to stand for 5 min, and upper layer was withdrawn and transferred to round-bottomed flask. The collected organic layer was evaporated, residues were reconstituted in 2 mL acetonitrile and analyzed using HPLC/LC-MS/MS. For extraction of herbicides from soil and rice, 5 mL of distilled water was added to 5 g of soil/rice sample in 50 mL centrifuge tube. To this, 10 mL of acetonitrile for the extraction of anilofos, bispyribac sodium, penoxsulam and pretilachlor and 25 mL for the extraction of butachlor and pendimethalin was added. The contents were ultrasonicated (220 KWh) at 30 C for 3 min. NaCl (2 g) was added and the mixture was vortexed for 2 min for phase separation. The mixture was allowed to stand for 5 min, and supernatant was withdrawn, transferred to round-bottomed flask and evaporated using rotary vacuum evaporator. Residues were reconstituted in 2 mL acetonitrile and analyzed using HPLC/LCMS-MS.

Method validation

The analytical performance of the developed SPE and SALLE method was evaluated in different water (tubewell, pond, tap and river water), soil (loamy sand, sandy loam, silt loam, loam and clay loam) and rice matrices using HPLC and LC-MS/MS. Parameters such as linearity, limit of quantification (LOQ), limit of detection (LOD), matrix effect, accuracy and inter- and intra-day precision were evaluated.

To evaluate matrix effect, two different types of calibration curves, viz. matrix-matched and solvent calibration, were prepared in the concentration range of 0.0026 to 5.0 µg g⁻¹. Matrix-matched calibration curves were prepared by spiking blank samples. Solvent calibration curves were prepared in acetonitrile. Matrix effect (ME) was calculated using equation [45]:

$$\text{Matrix effect (\%)} = \left[\frac{\text{Slope of calibration curve for analyte in matrix}}{\text{Slope of calibration curve for analyte in organic solvent}} - 1 \right] \times 100$$

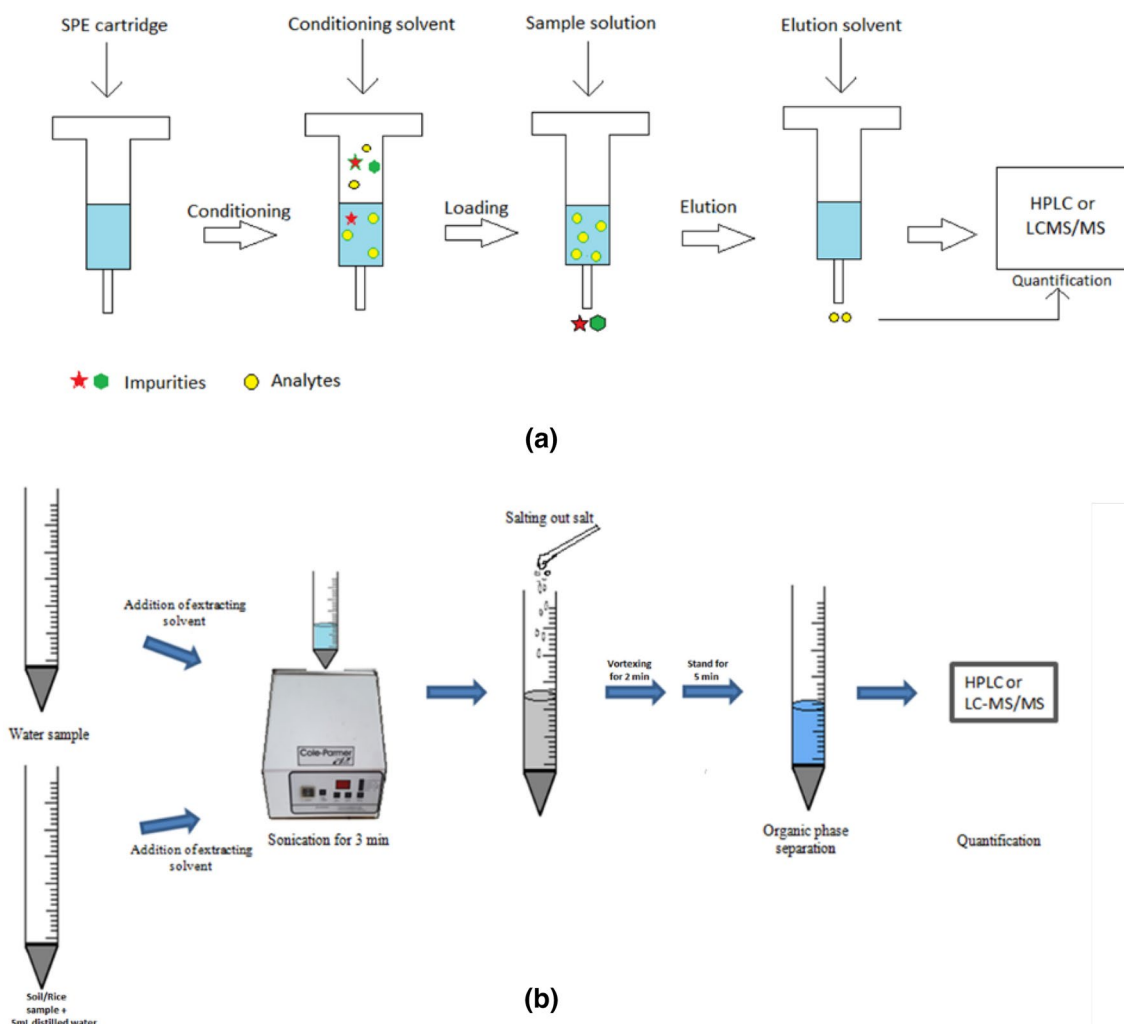


Fig. 1 Schematic representation of **a** solid-phase extraction, **b** salting-out liquid–liquid extraction

LOD and LOQ were established at the signal-to-noise ratio (S/N) of 3:1 and 10:1, respectively. Recovery studies were carried out in triplicate at fortification levels of LOQ, 2LOQ and 3LOQ. The intraday precision expressed as $\%RSD_r$ was evaluated by analyzing samples spiked at 2LOQ three times a day and for interday precision studies ($\%RSD_R$), and samples were analyzed three times for the three consecutive days.

Assessment of greenness of extraction methods

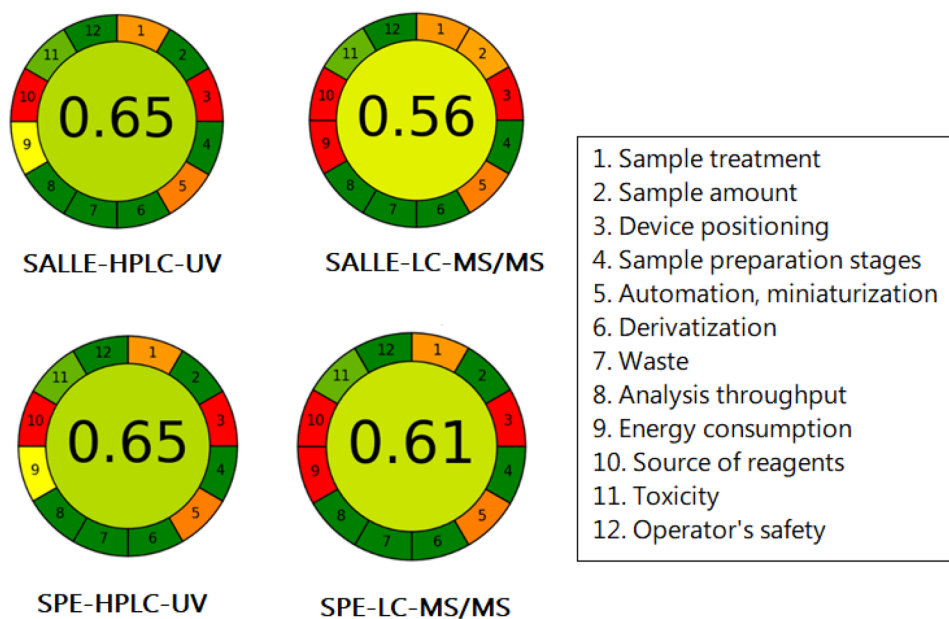
The greenness of the developed methods was assessed with Analytical Eco-Scale and AGREE metrics using software downloaded from <https://mostwiedzy.pl/AGREE>. Analytical Eco-Scale is a semiquantitative procedure, where penalty points are assigned to different parameters such as generation of waste, reagent used and energy consumed in the analytical process [46]. The maximal score of Eco-Scale is 100

from which the total penalty points are deducted. Score > 75 represents excellent green analysis, > 50 represents acceptable green analysis and < 50 represents inadequate green analysis. In AGREE metrics, the input criteria involve twelve principles of green analytical chemistry (Fig. 2). The final result is the product of assessment result of each principle. The output is clock like graph and the overall score is shown in middle of the pictogram. The performance of procedure in each principle is reflected with intuitive red–yellow–green color scale while the weight of each principle is reflected by width of its corresponding segment. The values close to 1 and dark green color indicate that the assessed procedure is greener.

Real sample analysis

For real sample analysis, soil and water samples were collected from rice fields sprayed with anilofos, bispyribac

Fig. 2 Comparison of methods according to the 12 principles of green analytical chemistry performed using the AGREE algorithm



sodium, butachlor, pendimethalin, pretilachlor and penoxsulam at recommended application rates [47]. Soil and water samples were taken at 0 and 10 days after the application of herbicides while rice samples were collected at harvest. The tubewell water samples were collected randomly from farmer's fields in different districts of southwest (Bathinda, Sri Muktsar Sahib, Fazilka), central (Kapurthala, Jalandhar, Ludhiana, Sangrur, Patiala, Barnala) and eastern (Pathankot, Gurdaspur, Hoshiarpur) Punjab and samples from each region were pooled in order to constitute 48 representative samples of different zones of Punjab. Herbicide's residues were extracted using optimized SALLE method and analyzed using HPLC and LC-MS/MS.

Data analysis

All the experiments were performed in triplicate. The data were analyzed using CPCS1 statistical software at 5 percent probability level.

The recoveries of the herbicides were computed using:

$$\text{Percent Recovery} = \frac{\text{Amount recovered}}{\text{Amount added}} \times 100$$

Results and discussion

Distilled water, loamy sand and rice samples were fortified with $1.0 \mu\text{g ml}^{-1}$ of anilofos, bispyribac sodium, butachlor, pendimethalin, penoxsulam and pretilachlor for optimizing

the best extraction conditions for extraction of these herbicides from water, soil and rice.

Optimization of SPE procedure

The efficiency of SPE depends on the type and volume of the elution solvent. In initial experiments, several organic solvents, viz. acetonitrile, acetone, methanol, 1% acetic acid in acetonitrile and 1% acetic acid, in methanol and their volume were evaluated for the extraction of herbicides from water, soil and rice. Anilofos, butachlor, pendimethalin and penoxsulam were efficiently extracted with acetone, whereas methanol was selected as an eluting solvent for bispyribac sodium and pretilachlor (Fig. 3a, b, c).

As different samples require a different volume of eluent, therefore the volume of eluting solvent should be examined to efficiently elute the analyte with less solvent consumption and consequently avoid solvent disposal issues and environmental hazards. Maximum percent recovery was obtained when samples were eluted with 10 mL of the eluting solvent and further increase in the volume of solvent did not cause a significant change in extraction efficiency of the herbicides (Fig. 3d, 3e, 3f).

Optimization of the SALLE procedure

Several factors such as the type of the organic solvent, sample-to-solvent ratio, ultrasonication time and temperature, type and amount of salt and pH of the sample solution that affects the extraction efficiency were studied.

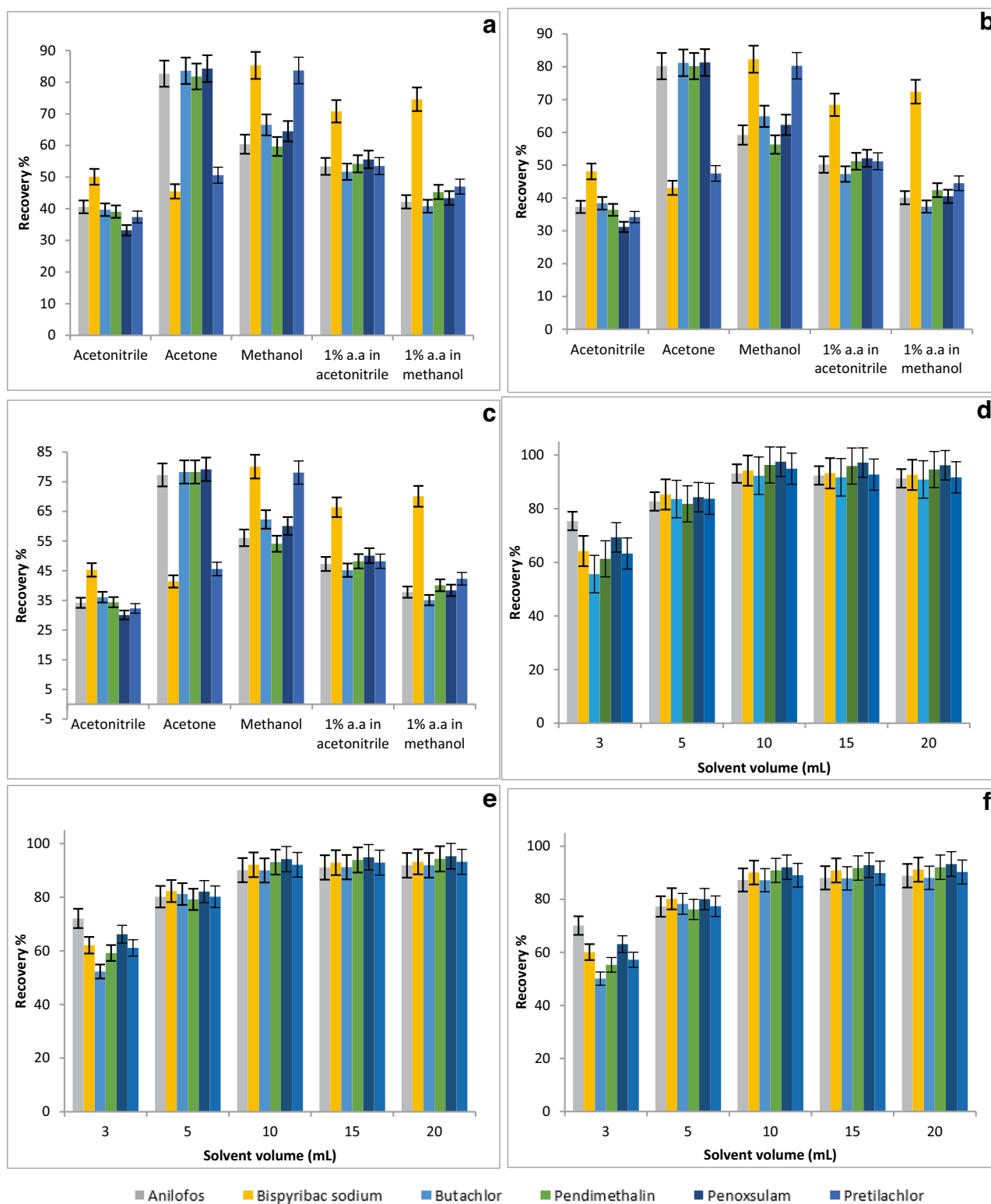


Fig. 3 Effect of eluting solvent on extraction of herbicides from **a** water, **b** soil, **c** rice and volume of eluting solvent from **e** water, **f** soil, **g** rice (* acetone is used as eluting solvent for anilofos, butachlor, penoxsulam and pendimethalin and methanol for bispyribac sodium and pretilachlor)

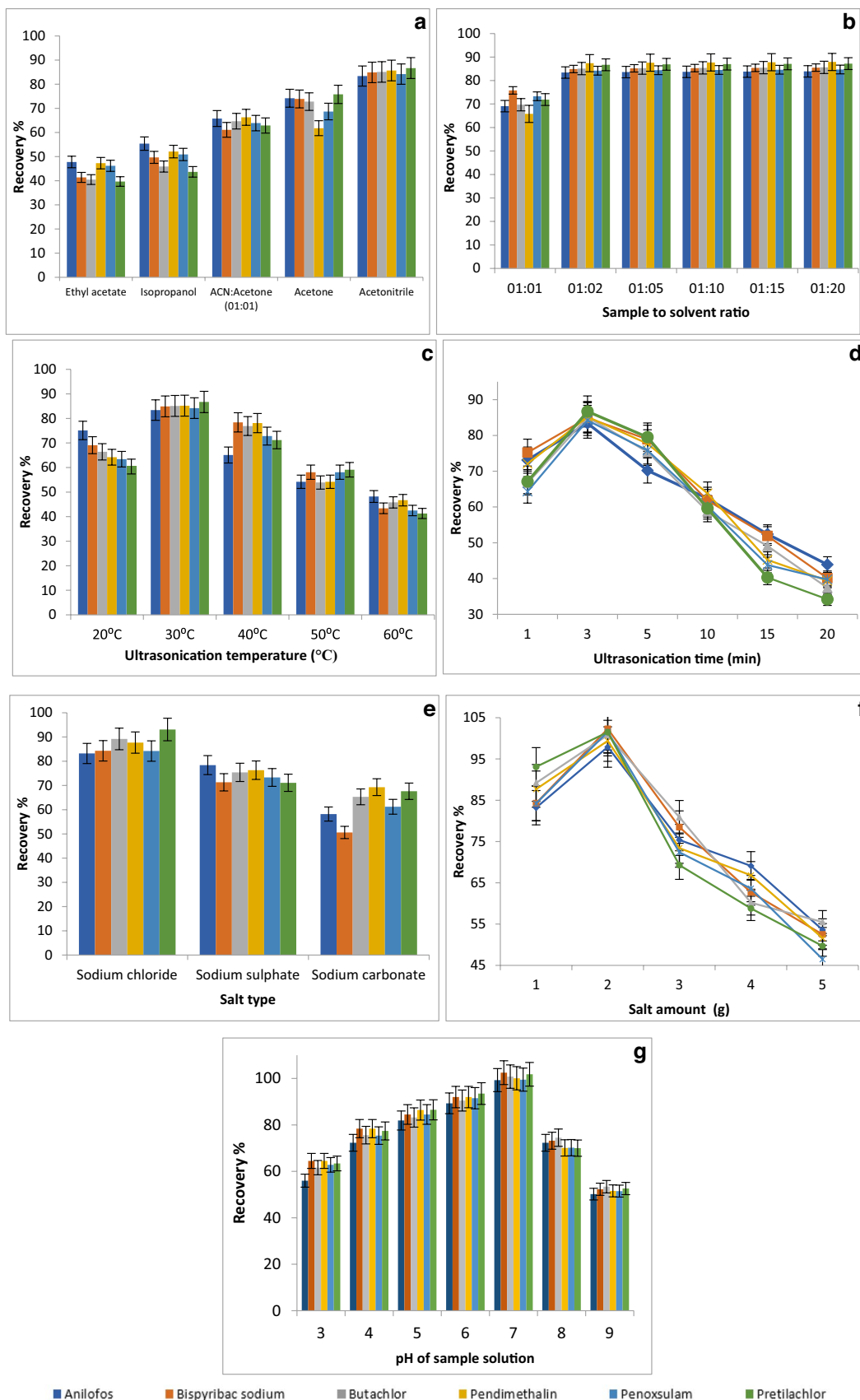


Fig. 4 Effect of **a** extracting solvent, **b** sample-to-solvent ratio, **c** ultrasonication temperature, **d** ultrasonication time, **e** salt type, **f** amount of salt, **g** pH of sample solution on extraction efficiency of herbicides from water

Selection of the organic solvent

Organic solvents such as isopropanol, ethyl acetate, acetonitrile, acetone and acetonitrile:acetone (01:01) were selected for extraction of herbicides from water, soil and rice. Irrespective of physicochemical properties of herbicides, mean percent recoveries varied from 39.7 ± 2.24 to 86.7 ± 3.45 , 37.6 ± 4.23 to 83.4 ± 2.77 and 36.4 ± 3.21 to 81.9 ± 3.67 from water, soil and rice. Maximum recoveries were obtained when acetonitrile was used as an extracting solvent due to the close proximity of its polarity to water as compared to other solvents (Figs. 4a, 5a, 6a).

Effect of sample-to-solvent ratio

The volume of solvent plays a vital role in the extraction of herbicide from the matrix. Increase in volume of solvent results in an increase in extraction efficiency due to effective dissolution of analyte, but this would also induce solvent wastage. On the contrary, the less solvent volume would result in the lower extraction of the analyte. Therefore, different sample-to-solvent ratios, viz. 01:01, 01:02, 01:05, 01:10, 01:15 and 01:20, were evaluated. For the extraction of herbicides from water, sample-to-solvent ratio of 01:01 resulted in low extraction efficiency (49.6 ± 6.1 to $54.8 \pm 6.2\%$) probably due to difficulty in the separation of the organic layer from the aqueous phase and due to less dissolution of herbicides in solvent in contrast to water. Extraction efficiency increased with further increase in sample-to-solvent ratio from 01:01 to 01:02 and mean percent recoveries of studied herbicides ranged from 83.2 ± 3.3 to 86.6 ± 3.4 . Further increase in the sample-to-solvent ratio to 01:20 resulted in no significant increase in percent recoveries (Fig. 4b).

For the extraction of herbicides from soil and rice, the maximum extraction efficiency of anilofos, pretilachlor, bispyribac sodium and penoxsulam was obtained at sample-to-solvent ratio of 01:02 while butachlor and pendimethalin were efficiently extracted with a sample-to-solvent ratio of 01:05 (Figs. 5b, 6b). Greater volume of solvent required in extraction of butachlor and pendimethalin was due to their stronger adsorption to the matrix with adsorption coefficient (K_F) ranging from 26.56 to 39.45 and 190.5 to 220.05 $\mu\text{g}^{1-1/n} \text{g}^{-1} \text{ml}^{1/n}$, respectively [48, 49], as compared to other herbicides ($K_F = 0.37$ to $16.826 \mu\text{g}^{1-1/n} \text{g}^{-1} \text{ml}^{1/n}$) [50–53]

Effect of ultrasonic temperature

Extraction efficiency increased as the temperature was increased from 20 ± 2 to 30 ± 2 C because increase in temperature not only increase the solubility of the analyte but also decrease the viscosity and surface tension of the solvent thus enhancing the penetration of solvent into the matrix (Figs. 4c, 5c, 6c). However, the mean percent recoveries decreased for all herbicides with further increase in ultrasonication temperature to 60 ± 2 C probably due to breaking of bonds of analyte and solvent volatilization.

Effect of ultrasonication time

Ultrasonication time is another factor that influences the extraction rate of the analyte as it affects the mass transfer process. Thus, ultrasonication time was varied from 1 to 20 min to determine its effect on the extraction of herbicides. Maximum mean percent recoveries (78.2 ± 3.4 to 86.7 ± 3.4) were obtained at an ultrasonication time of 3 min (Fig. 4d, 5d, 6d). Beyond the optimum ultrasonication time, average recovery decreased which could be probably due to the degradation of herbicides with an increase in ultrasonication time.

Effects of the salt type and concentration

The addition of salt decreases the solubility of hydrophilic compounds in the aqueous phase through a salting-out effect and consequently increases the partition of analytes into the organic phase [54–57]. Since different salts have different degrees of phase separation, several salts such as sodium chloride, ammonium sulfate and sodium carbonate were evaluated. All salts induced phase separation, but reliable results in terms of reproducibility and extraction efficiency were observed when sodium chloride was used as salting-out reagent (Figs. 4e, 5e, 6e). This could be due to greater salting-out ability and more solubility of sodium chloride in water as compared to other salts. The amount of sodium chloride must be optimized so as to separate the two phases clearly without any precipitation [58]. To investigate the effect of the amount of salt on mean percent recovery of herbicides, varied amount of NaCl (1 to 5 g) was added to the sample solution and 2 g of NaCl gives better extraction of herbicides with mean percent recoveries varying from 98.3 ± 3.1 to 102.4, 96.9 ± 3.2 to 101.0 ± 3.9 and 94.2 ± 3.1 to 98.4 ± 3.1 from water, soil and rice, respectively (Figs. 4f, 5f, 6f).

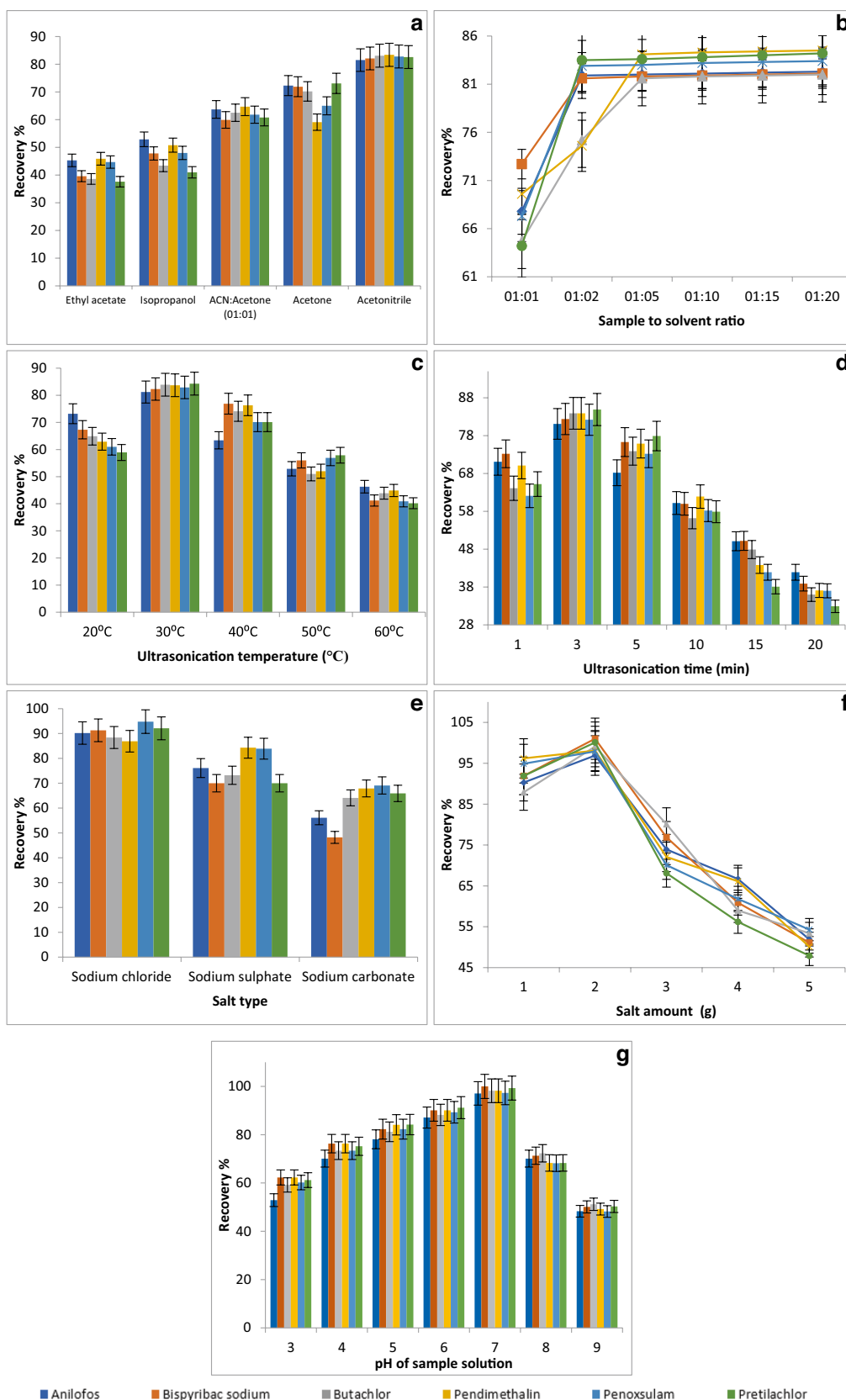


Fig. 5 Effect of **a** extracting solvent, **b** sample-to-solvent ratio, **c** ultrasonication temperature, **d** ultrasonication time, **e** salt type, **f** amount of salt, **g** pH of sample solution on extraction efficiency of herbicides from soil

Effect of pH

For efficient extraction of ionizable and relatively polar compounds, the pH of the sample solution plays a decisive role [59, 60]. Sample solution pH was varied from 3.0 to 9.0 and extraction efficiency increased with an increase in pH from 3.0 to 7.0 with mean percent recoveries varying from 56.0 ± 3.2 to 102.5 ± 2.3 , 52.9 ± 2.6 to 100.0 ± 1.8 and 49.2 ± 2.8 to 97.9 ± 2.8 from water, soil and rice, respectively (Figs. 4g, 5g, 6g). Less extraction efficiency of studied herbicides at lower pH was due to their incomplete conversion to neutral form. With a further rise in sample solution pH from 7.0 to 9.0, extraction efficiency decreased from 102.5 ± 2.3 to 50.2 ± 4.3 , 100.0 ± 1.8 to 48.3 ± 2.5 and 97.9 ± 2.8 to 45.3 ± 3.1 in water, soil and rice, respectively, due to hydrolysis of herbicides. Therefore, a sample solution pH of 7.0 was chosen as optimum pH.

Method validation

The solvent calibration curves and matrix-matched calibration curves were linear in the range of 0.0026 to $5.0 \mu\text{g mL}^{-1}$ with a coefficient of determination (R^2) more than 0.991 (Tables 3–4). Matrix effect was lower than 20% indicating that the proposed sample treatment was able to recover studied herbicides efficiently by decreasing matrix effect without any significant analyte loss. Though the matrix effect was low, quantification of herbicides was done using matrix-matched calibration curve to eliminate error in quantification and improve accuracy.

LOD and LOQ ranged between 0.0026 to 0.03 and 0.008 to $0.09 \mu\text{g mL}^{-1}$ in different matrices using HPLC and LC–MS/MS (Tables 3–4). Mean percent recoveries ranged from 81.6 ± 4.1 to 98.6 ± 3.5 , 84.1 ± 3.5 to 99.4 ± 3.2 and 81.3 ± 4.2 to 94.6 ± 3.5 in water, soil and rice, respectively, using SPE while 84.9 ± 2.9 to 102.3 ± 2.3 , 90.0 ± 4.1 to 103.2 ± 4.1 and 86.3 ± 2.7 to 94.6 ± 3.5 using SALLE (Tables 5, 6, 7, 8). The $\text{RSD}_r\%$ and $\text{RSD}_R\%$ was $< 10\%$ for all the studied herbicides. Extraction efficiencies obtained using SPE and SALLE were $> 80\%$ and $\text{RSD} < 10\%$ which is acceptable for an ideal extraction method [61]. However, recoveries obtained using SALLE were comparatively higher ($p > 0.05$) (Tables 5, 6, 7, 8). SALLE also offers additional advantages over SPE. SALLE is a simple and facile extraction procedure offering less sample loss and is cost-effective. On the contrary, SPE requires additional establishment set up and expensive SPE cartridges which cannot be regenerated and reused for extraction of the analyte. Also, repeated extraction is required for the extraction of strongly adsorbed analytes which sometimes plug the SPE membrane decreasing the flow rate and hence reduced extraction efficiency. Taking into consideration the simplicity, sensitivity, cost-effectiveness and extraction efficiency, SALLE procedure

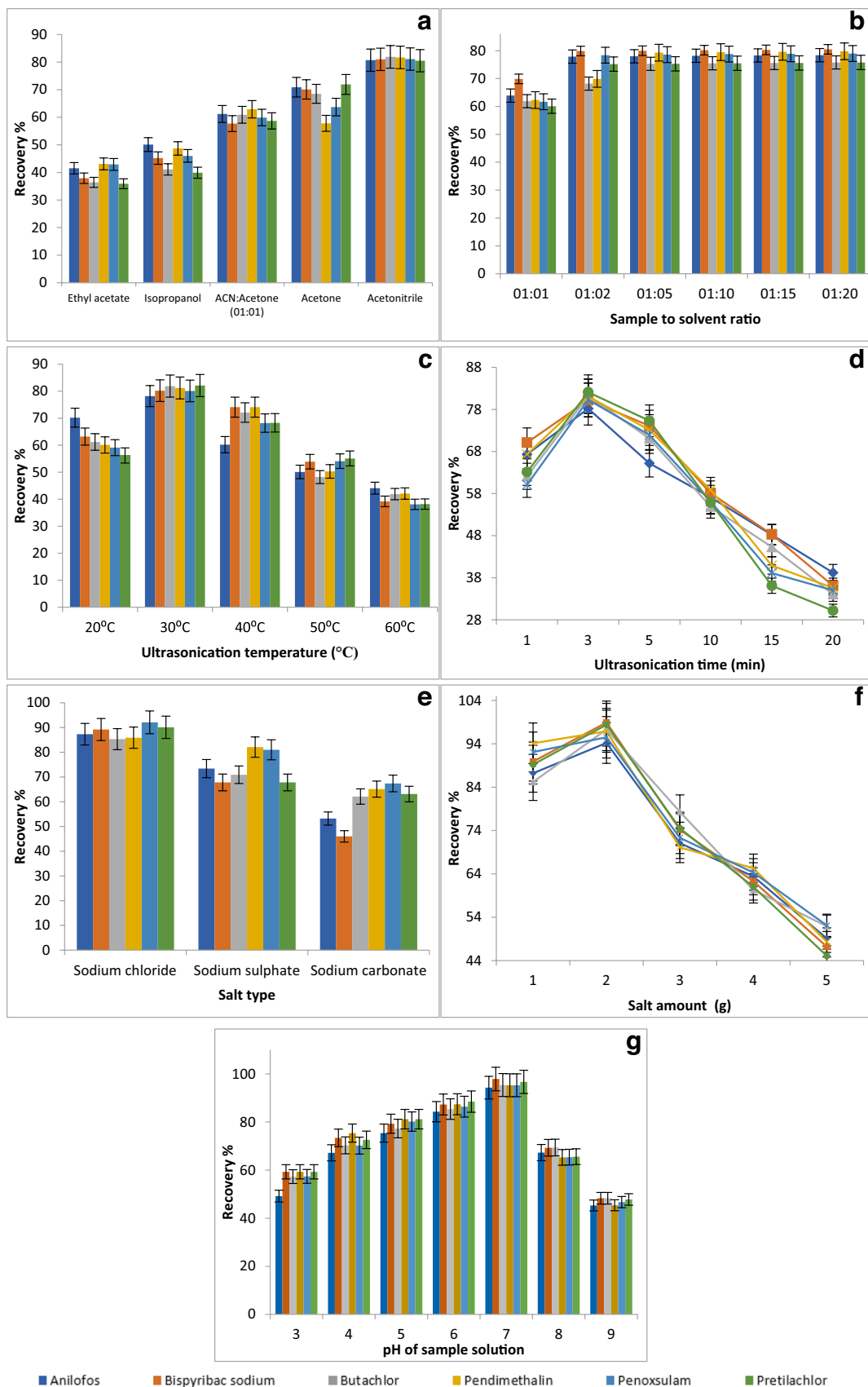
can be considered as an efficient and reliable method for extraction of the herbicides from water.

Greenness of method

Penalty points for developed analytical method using Analytical Eco-Scale were calculated in accordance with principles presented in Table 9. Considering penalty points assigned for described procedure for analysis of studied herbicides from soil, water and rice grains, it can be assumed that the developed methodology represents the excellent green analysis and is environmentally friendly. However, Analytical Eco-Scale is a semiquantitative tool and do not provide detailed explanation of non-eco-friendly procedures in studied analytical methods. Hence, the greenness of the developed analytical method was assessed by AGREE metrics as it is more quantitative compared to Analytical Eco-Scale and provide complete information about strong and weak aspects among the twelve principles of green analytical chemistry. The results of the assessment using Analytical Eco-Scale were partially confirmed by AGREE metrics. The output score of the AGREE metrics for studied methods ranged from 0.56 to 0.65 (Fig. 2) which indicated that studied methods are acceptable green analytical methods. The AGREE pictogram shows that the studied methods have some critical points (Fig. 2) and potential for improvement includes area of the off-line analysis, use of nongreen/bio-based solvents, moderate waste generation and use of instruments like ultra-high-performance liquid chromatography (UHPLC) which involves the use of shorter column with finest particle size and at high pressure and will enable shorter analysis time and high throughput.

Comparison with literature reported methods

The analytical performance of the proposed method was compared with other literature reported methods from the viewpoints of the sample weight and extracting solvent volume, detection limits and percent recoveries (Table 10). The reported sample pre-treatment techniques are based on LLE, MSPD, DLLME, SPE, QuEChERS followed by quantification using HPLC, GC-ECD, GC-ECS, LC–QQQ–MS/MS, GC–MS/MS and LC–MS/MS for the extraction of the studied herbicides. The developed method has LOD below the maximum residue limit ($0.05\text{--}0.01 \mu\text{g g}^{-1}$) imposed by EPA and EU [62] and have recovery (88.25 to 103.45%), sample size (5 mL/5 g) and solvent volume (10–25 mL) comparable or even better than most of the other literature reported methods which require sample weight (5–50 g/mL), solvent volume (10–250 mL) and give recovery in the range of 69–108.0%. LLE is laborious, time-consuming, expensive and requires a large amount of toxic solvents up to



◀**Fig. 6** Effect of **a** extracting solvent, **b** sample-to-solvent ratio, **c** ultrasonication temperature, **d** ultrasonication time, **e** salt type, **f** amount of salt, **g** pH of sample solution on extraction efficiency of herbicides from rice

250 mL and raises disposal issues. Moreover, it often results in the formation of emulsion which decreases the extraction efficiency of the analyte [63]. The use of SPE is disadvantageous as it requires expensive cartridges which cannot be regenerated and reused for extraction of the analyte. Repeated extraction is required for the extraction of strongly adsorbed analytes which may plug the SPE membrane decreasing the flow rate and hence resulting in a reduction of extraction efficiency [64]. The fiber used in SPME is expensive and fragile and the sample carryover problem cannot be eliminated. DLLME involves the consumption of relatively large volumes of disperser solvents which usually decreases the partition coefficient of analytes into the extractant solvent [24]. The stable cloudy solution formed in DLLME must be separated by centrifugation, which is a time-consuming procedure with inherent problems of low precision. The sorbents, viz. primary secondary amine (PSA), graphite carbon black (GCB) used in QuEChERS, are highly expensive [65]. MSPD involves disruption of the sample with anhydrous sorbents activated at high temperature and sometimes require large amount of solvent for extraction and clean up [66, 67]. The proposed SALLE method is therefore a good alternative for extraction of studied herbicides from water, soil and rice and offers advantages like inexpensive and do not require extensive sample preparation for effectively eliminating matrix interferences. The whole procedure allows an increased throughput of samples and more than 50 samples can be extracted in one day in a medium-sized laboratory.

Real sample analysis

The initial concentration of anilofos, bispyribac sodium, butachlor, pendimethalin, pretilachlor and penoxsulam in water and soil samples varied from 0.114 ± 2.14 to 0.123 ± 3.07 , $0.141 \pm 0.176 \pm 2.54$, 0.125 ± 2.41 to 0.131 ± 3.21 , 0.132 ± 3.41 to 0.145 ± 1.41 , 0.07 ± 1.65 to 0.1 ± 2.54 and 0.125 ± 4.12 to $0.131 \pm 2.14 \mu\text{g g}^{-1}$, respectively (Figs. 7 and 8). The concentration of studied herbicide decreased over time and after 10 days of application of anilofos, bispyribac sodium, butachlor, pendimethalin, pretilachlor and penoxsulam concentration

varied from 0.009 ± 3.11 to 0.013 ± 1.54 , 0.009 ± 2.55 to 0.016 ± 2.01 , 0.01 ± 1.32 to 0.014 ± 1.44 , 0.007 ± 3.21 to 0.014 ± 1.22 , 0.011 ± 3.02 to 0.019 ± 3.02 and 0.009 ± 2.12 to 0.015 ± 3.11 and 0.007 ± 3.21 to $0.016 \pm 1.65 \mu\text{g g}^{-1}$, respectively. The decrease in the concentration of herbicides with time was because of degradation of herbicide after application due to photochemical, microbial and chemical processes. The slopes of the linear equations obtained by comparison of quantification of water and soil samples with HPLC and LC-MS/MS ranged from 0.993 to 1.108 indicating HPLC quantification was in accordance with MS quantification (Figs. 7 and 8). The representative chromatograms for the herbicide's residues are presented in Fig. 9. The residues of the studied herbicides determined in tubewell water collected from farmer's fields and rice samples at harvest were below the permissible limit ($< 0.01 \mu\text{g g}^{-1}$) [62].

Conclusion

In the present study, SPE and SALLE methods were developed, validated and compared for quantification of anilofos, bispyribac sodium, butachlor, pendimethalin, penoxsulam and pretilachlor from water, soil and rice samples. Several factors, viz. extracting solvent, sample-to-solvent ratio, ultrasonication temperature, ultrasonication time, salt type and concentration and pH of sample solution, have been investigated and optimized to achieve improved sensitivity. Mean percent recoveries obtained using SPE and SALLE ranged from 81.6 ± 4.1 to 99.4 ± 3.2 and 84.9 ± 2.9 to 103.2 ± 4.1 , respectively, with RSD $< 10\%$. Matrix effect was $< 20\%$ indicating that the method is efficient and reliable for quantifying residues with minimal matrix interferences. The experimental results indicated that the developed methods are simple, rapid, sensitive and precise. However, SALLE offers some advantages over SPE such as being inexpensive and do not require extensive sample preparation for effectively eliminating matrix interferences. The results obtained by the green assessment tools also proved that the methods were green and eco-friendly. The developed SALLE method was used for the extraction of herbicides from real samples. Herbicide concentrations in soil and water samples collected at 0 day varied from 0.083 ± 1.65 to $1.381 \pm 1.41 \mu\text{g g}^{-1}$. Concentration of studied herbicides in soil, rice and water at harvest were below the permissible limit ($< 0.01 \mu\text{g g}^{-1}$).

Table 3 Linearity, limit of detection and limit of quantification of the proposed methods for extraction of herbicides using HPLC

Herbicides	Matrices	SPE ^a						SALLE ^b					
		Linearity	LOQ ^c	LOD ^d	R ²	RSD _r ^e	RSD _R ^f	Linearity	LOQ	LOD	R ²	RSD _r	RSD _R
Anilofos	Distilled water	0.01–5.0	0.01	0.003	0.99	2.3	2.6	0.01–5.0	0.01	0.003	0.99	3.1	3.2
	Tap water	0.03–5.0	0.03	0.001	0.98	4.5	3.2	0.03–5.0	0.03	0.001	0.98	2.4	3.7
	Pond water	0.06–5.0	0.06	0.02	0.98	3.2	3.1	0.06–5.0	0.06	0.02	0.98	3.7	3.6
	River water	0.02–5.0	0.02	0.006	0.98	2.1	2.7	0.02–5.0	0.02	0.006	0.97	3.4	2.4
	Loamy sand	0.01–5.0	0.02	0.006	0.97	4.3	2.1	0.01–5.0	0.01	0.003	0.94	3.2	3.2
	Sandy loam	0.01–5.0	0.02	0.006	0.98	2.4	2.6	0.01–5.0	0.01	0.003	0.97	2.6	2.9
	Silt loam	0.01–5.0	0.02	0.006	0.98	4.1	3.6	0.01–5.0	0.01	0.003	0.98	3.7	2.1
	Loam	0.01–5.0	0.02	0.006	0.98	2.6	3.2	0.01–5.0	0.01	0.003	0.95	3.4	3.6
	Clay loam	0.01–5.0	0.02	0.006	0.98	3.1	3.1	0.01–5.0	0.01	0.003	0.96	2.5	3.1
Rice	0.03–5.0	0.02	0.006	0.97	2.3	2.6	0.03–5.0	0.03	0.001	0.98	2.1	2.4	
Bispyribac sodium	Distilled water	0.01–5.0	0.01	0.003	0.98	3.5	2.4	0.01–5.0	0.01	0.003	0.98	3.5	3.7
	Tap water	0.03–5.0	0.04	0.013	0.97	2.1	2.9	0.03–5.0	0.03	0.01	0.97	2.1	2.1
	Pond water	0.06–5.0	0.06	0.02	0.98	1.6	2.2	0.06–5.0	0.06	0.02	0.98	3.6	3.6
	River water	0.02–5.0	0.02	0.006	0.97	2.9	2.1	0.02–5.0	0.02	0.006	0.98	3.1	3.1
	Loamy sand	0.01–5.0	0.01	0.003	0.98	2.3	3.1	0.01–5.0	0.01	0.003	0.97	3.7	3.7
	Sandy loam	0.01–5.0	0.01	0.003	0.98	1.9	2.4	0.01–5.0	0.01	0.003	0.96	3.4	3.4
	Silt loam	0.01–5.0	0.01	0.003	0.98	2.3	3.7	0.01–5.0	0.01	0.003	0.96	2.1	2.5
	Loam	0.01–5.0	0.01	0.003	0.99	2.1	3.4	0.01–5.0	0.01	0.003	0.95	3.2	1.8
	Clay loam	0.01–5.0	0.01	0.003	0.99	1.8	2.5	0.01–5.0	0.01	0.003	0.97	3.2	3.4
Rice	0.03–5.0	0.04	0.013	0.98	3.4	2.1	0.03–5.0	0.03	0.01	0.97	3.7	2.6	
Butachlor	Distilled water	0.05–5.0	0.05	0.016	0.98	2.6	3.5	0.05–5.0	0.05	0.016	0.97	3.6	3.9
	Tap water	0.07–5.0	0.07	0.023	0.98	3.2	3.9	0.07–5.0	0.07	0.023	0.97	2.4	2.5
	Pond water	0.08–5.0	0.08	0.026	0.97	3.7	2.5	0.08–5.0	0.08	0.026	0.97	2.1	3.6
	River water	0.09–5.0	0.09	0.03	0.98	3.6	3.6	0.09–5.0	0.09	0.03	0.98	3.2	3.1
	Loamy sand	0.01–5.0	0.01	0.003	0.97	2.1	3.9	0.01–5.0	0.01	0.003	0.96	2.1	3.6
	Sandy loam	0.01–5.0	0.01	0.003	0.98	3.2	3.6	0.01–5.0	0.01	0.003	0.97	2.6	2.5
	Silt loam	0.01–5.0	0.01	0.003	0.98	2.9	2.5	0.01–5.0	0.01	0.003	0.98	2.5	3.2
	Loam	0.01–5.0	0.01	0.003	0.98	2.3	3.5	0.01–5.0	0.01	0.003	0.97	2.4	1.2
	Clay loam	0.01–5.0	0.01	0.003	0.97	2.6	3.9	0.01–5.0	0.01	0.003	0.98	3.2	3.2
Rice	0.07–5.0	0.08	0.026	0.98	3.2	2.3	0.07–5.0	0.07	0.023	0.97	3.3	2.5	
Penoxsulam	Distilled water	0.01–5.0	0.01	0.003	0.97	2.5	4.6	0.01–5.0	0.01	0.003		3.2	3.1
	Tap water	0.03–5.0	0.03	0.01	0.98	3.2	2.5	0.03–5.0	0.03	0.01	0.98	2.5	2.2
	Pond water	0.06–5.0	0.07	0.023	0.98	2.1	3.1	0.06–5.0	0.06	0.02	0.98	2.4	1.9
	River water	0.02–5.0	0.02	0.006	0.98	2.3	3.9	0.02–5.0	0.02	0.006	0.97	3.2	3.2
	Loamy sand	0.01–5.0	0.01	0.003	0.97	3.2	2.9	0.01–5.0	0.01	0.003	0.98	3.2	2.2
	Sandy loam	0.01–5.0	0.01	0.003	0.98	2.6	3.1	0.01–5.0	0.01	0.003	0.98	2.3	3.6
	Silt loam	0.01–5.0	0.01	0.003	0.98	2.3	2.5	0.01–5.0	0.01	0.003	0.97	3.2	2.3
	Loam	0.01–5.0	0.01	0.003	0.97	2.8	2.4	0.01–5.0	0.01	0.003	0.98	1.9	3.6
	Clay loam	0.01–5.0	0.01	0.003	0.98	3.9	2.7	0.01–5.0	0.01	0.003	0.97	3.2	3.8
Rice	0.03–5.0	0.04	0.013	0.97	3.4	4.8	0.03–5.0	0.03	0.01	0.98			
Pendimethalin	Distilled water	0.01–5.0	0.01	0.003	0.98	2.5	1.9	0.01–5.0	0.01	0.003	0.98	1.2	3.2
	Tap water	0.03–5.0	0.04	0.013	0.99	3.2	3.2	0.03–5.0	0.03	0.01	0.97	3.2	3.9
	Pond water	0.06–5.0	0.06	0.02	0.98	1.2	2.4	0.06–5.0	0.06	0.02	0.98	3.7	2.5
	River water	0.02–5.0	0.03	0.01	0.98	3.2	2.2	0.02–5.0	0.02	0.006	0.98	3.6	3.6

Table 3 (continued)

Herbicides	Matrices	SPE ^a						SALLE ^b					
		Linearity	LOQ ^c	LOD ^d	R ²	RSD _f ^e	RSD _R ^f	Linearity	LOQ	LOD	R ²	RSD _f	RSD _R
Pretilachlor	Loamy sand	0.08–5.0	0.08	0.026	0.97	3.2	2.5	0.08–5.0	0.08	0.026	0.98	2.1	3.9
	Sandy loam	0.01–5.0	0.01	0.003	0.97	1.9	2.5	0.01–5.0	0.01	0.003	0.97	3.2	3.6
	Silt loam	0.01–5.0	0.01	0.003	0.97	2.1	3.2	0.01–5.0	0.01	0.003	0.98	2.9	3.2
	Loam	0.01–5.0	0.01	0.003	0.98	2.6	1.2	0.01–5.0	0.01	0.003	0.98	2.3	2.6
	Clay loam	0.01–5.0	0.01	0.003	0.98	2.5	3.2	0.01–5.0	0.01	0.003	0.98	4.5	2.5
	Rice	0.03–5.0	0.04	0.013	0.98	3.4	2.8	0.03–5.0	0.03	0.01	0.97		
	Distilled water	0.01–5.0	0.01	0.003	0.98	2.4	2.5	0.01–5.0	0.01	0.003	0.98	3.2	3.2
	Tap water	0.03–5.0	0.03	0.01	0.97	3.2	3.1	0.03–5.0	0.03	0.01	0.97	2.1	2.7
	Pond water	0.06–5.0	0.06	0.02	0.98	3.3	2.2	0.06–5.0	0.06	0.02	0.98	2.7	3.2
	River water	0.02–5.0	0.02	0.006	0.98	3.6	3.6	0.02–5.0	0.02	0.006	0.98	4.3	1.2
	Loamy sand	0.01–5.0	0.01	0.003	0.98	2.6	3.6	0.01–5.0	0.01	0.003	0.98	3.1	2.5
	Sandy loam	0.01–5.0	0.01	0.003	0.98	2.5	3.8	0.01–5.0	0.01	0.003	0.98	3.9	3.1
	Silt loam	0.01–5.0	0.01	0.003	0.97	3.2	3.2	0.01–5.0	0.01	0.003	0.97	2.4	2.2
	Loam	0.01–5.0	0.01	0.003	0.98	2.7	3.1	0.01–5.0	0.01	0.003	0.98	2.9	3.6
Clay loam	0.01–5.0	0.01	0.003	0.97	3.2	3.8	0.01–5.0	0.01	0.003	0.97	3.1	2.3	
Rice	0.03–5.0	0.04	0.013	0.98	2.1	3.6	0.03–5.0	0.03	0.01	0.98	2.5	3.6	

^aSolid-phase extraction, ^bsalting-out liquid–liquid extraction, ^climit of quantification, ^dlimit of detection, ^einterday precision, ^fintraday precision

Table 4 Linearity, limit of detection and limit of quantification of the proposed methods for extraction of herbicides using LC–MS/MS

Herbicides	Matrices	SPE ^a						SALLE ^b					
		Linearity	LOQ ^c	LOD ^d	R ²	RSD _f ^e	RSD _R ^f	Linearity	LOQ	LOD	R ²	RSD _f	RSD _R
Anilofos	Distilled water	0.009–5.0	0.009	0.003	0.98	3.2	2.6	0.008–5.0	0.008	0.0026	0.99	3.4	2.3
	Tap water	0.01–5.0	0.01	0.003	0.95	2.3	3.5	0.009–5.0	0.009	0.003	0.98	4.2	3.2
	Pond water	0.01–5.0	0.01	0.003	0.97	3.6	3.6	0.01–5.0	0.01	0.003	0.93	2.3	2.6
	River water	0.008–5.0	0.008	0.0026	0.98	3.5	3.8	0.008–5.0	0.008	0.0026	0.95	2.6	3.2
	Loamy sand	0.008–5.0	0.008	0.0026	0.93	2.6	3.5	0.008–5.0	0.008	0.0026	0.98	3.3	3.2
	Sandy loam	0.008–5.0	0.008	0.0026	0.95	2.7	3.5	0.008–5.0	0.008	0.0026	0.99	2.5	3.5
	Silt loam	0.008–5.0	0.008	0.0026	0.92	3.2	2.2	0.008–5.0	0.008	0.0026	0.92	2.9	2.6
	Loam	0.008–5.0	0.008	0.0026	0.97	2.3	3.1	0.008–5.0	0.008	0.0026	0.92	3.6	3.7
	Clay loam	0.008–5.0	0.008	0.0026	0.93	3.2	2.5	0.008–5.0	0.008	0.0026	0.93	3.9	2.6
Rice	0.01–5.0	0.01	0.003	0.93	1.9	2.5	0.009–5.0	0.009	0.003	0.99	2.1	2.5	
Bispyribac sodium	Distilled water	0.009–5.0	0.009	0.003	0.93	2.1	3.2	0.008–5.0	0.008	0.0026	0.97	2.8	3.9
	Tap water	0.01–5.0	0.01	0.003	0.95	2.6	1.2	0.009–5.0	0.009	0.003	0.97	2.6	3.7
	Pond water	0.01–5.0	0.01	0.003	0.95	2.1	3.2	0.01–5.0	0.01	0.003	0.94	2.5	3.5
	River water	0.008–5.0	0.008	0.0026	0.95	3.2	2.5	0.008–5.0	0.008	0.0026	0.95	2.9	2.6
	Loamy sand	0.008–5.0	0.008	0.0026	0.97	2.3	3.2	0.008–5.0	0.008	0.0026	0.98	2.3	2.5
	Sandy loam	0.008–5.0	0.008	0.0026	0.98	4.5	2.4	0.008–5.0	0.008	0.0026	0.98	1.5	3.5
	Silt loam	0.008–5.0	0.008	0.0026	0.98	3.2	2.2	0.008–5.0	0.008	0.0026	0.96	3.2	3.5

Table 4 (continued)

Herbicides	Matrices	SPE ^a						SALLE ^b					
		Linearity	LOQ ^c	LOD ^d	R ²	RSD _r ^e	RSD _R ^f	Linearity	LOQ	LOD	R ²	RSD _r	RSD _R
Butachlor	Loam	0.008–5.0	0.008	0.0026	0.98	2.1	3.1	0.008–5.0	0.008	0.0026	0.96	2.5	2.6
	Clay loam	0.008–5.0	0.008	0.0026	0.98	2.7	2.5	0.008–5.0	0.008	0.0026	0.96	1.4	3.5
	Rice	0.01–5.0	0.01	0.003	0.95	4.3	2.5	0.009–5.0	0.009	0.003	0.97	2.6	3.1
	Distilled water	0.009–5.0	0.009	0.003	0.95	4.5	3.2	0.01–5.0	0.01	0.003	0.94	2.6	2.9
	Tap water	0.03–5.0	0.03	0.001	0.95	3.2	1.2	0.03–5.0	0.03	0.001	0.95	3.7	2.4
	Pond water	0.04–5.0	0.04	0.013	0.95	1.6	3.2	0.04–5.0	0.04	0.013	0.96	1.9	3.4
	River water	0.01–5.0	0.01	0.003	0.96	3.2	2.5	0.01–5.0	0.01	0.003	0.96	2.5	2.5
	Loamy sand	0.01–5.0	0.01	0.003	0.96	2.4	3.4	0.01–5.0	0.01	0.003	0.95	2.6	3.5
	Sandy loam	0.01–5.0	0.01	0.003	0.97	2.5	3.2	0.01–5.0	0.01	0.003	0.93	3.5	2.9
	Silt loam	0.01–5.0	0.01	0.003	0.93	3.7	2.5	0.01–5.0	0.01	0.003	0.95	3.9	4.1
Penoxsulam	Loam	0.01–5.0	0.01	0.003	0.95	2.6	2.7	0.01–5.0	0.01	0.003	0.96	3.2	3.9
	Clay loam	0.01–5.0	0.01	0.003	0.95	3.8	4.3	0.01–5.0	0.01	0.003	0.97	1.9	3.2
	Rice	0.009–5.0	0.009	0.003	0.92	2.5	4.3	0.03–5.0	0.03	0.001	0.97	3.2	1.6
	Distilled water	0.008–5.0	0.008	0.0026	0.95	2.6	2.5	0.008–5.0	0.008	0.0026	0.97	2.6	2.5
	Tap water	0.01–5.0	0.01	0.003	0.93	2.5	3.6	0.009–5.0	0.009	0.003	0.96	2.9	2.9
	Pond water	0.01–5.0	0.01	0.003	0.92	3.9	2.5	0.01–5.0	0.01	0.003	0.95	3.5	3.2
	River water	0.008–5.0	0.008	0.0026	0.91	3.5	3.4	0.008–5.0	0.008	0.0026	0.94	2.7	3.4
	Loamy sand	0.008–5.0	0.008	0.0026	0.94	2.6	3.2	0.008–5.0	0.008	0.0026	0.95	3.4	1.5
	Sandy loam	0.008–5.0	0.008	0.0026	0.92	3.5	2.5	0.008–5.0	0.008	0.0026	0.96	3.0	3.5
	Silt loam	0.008–5.0	0.008	0.0026	0.93	3.4	3.6	0.008–5.0	0.008	0.0026	0.97	1.9	3.9
Pendimethalin	Loam	0.008–5.0	0.008	0.0026	0.94	2.5	3.9	0.008–5.0	0.008	0.0026	0.97	2.6	2.6
	Clay loam	0.008–5.0	0.008	0.0026	0.93	2.4	2.5	0.008–5.0	0.008	0.0026	0.97	3.4	2.6
	Rice	0.01–5.0	0.01	0.003	0.97	4.5	3.5	0.009–5.0	0.009	0.003	0.98	4.3	3.5
	Distilled water	0.008–5.0	0.008	0.0026	0.91	2.2	2.5	0.008–5.0	0.008	0.0026	0.95	2.5	2.6
	Tap water	0.01–5.0	0.01	0.003	0.93	3.7	3.6	0.009–5.0	0.009	0.003	0.95	3.4	2.9
	Pond water	0.01–5.0	0.01	0.003	0.94	2.4	2.3	0.01–5.0	0.01	0.003	0.96	2.4	3.2
	River water	0.008–5.0	0.008	0.0026	0.94	3.6	3.5	0.008–5.0	0.008	0.0026	0.96	3.4	2.4
	Loamy sand	0.008–5.0	0.008	0.0026	0.96	3.2	3.5	0.008–5.0	0.008	0.0026	0.94	3.1	2.9
	Sandy loam	0.008–5.0	0.008	0.0026	0.97	2.7	1.6	0.008–5.0	0.008	0.0026	0.93	3.2	3.6
	Silt loam	0.008–5.0	0.008	0.0026	0.92	2.5	2.5	0.008–5.0	0.008	0.0026	0.94	3.9	3.5
Pretilachlor	Loam	0.008–5.0	0.008	0.0026	0.95	2.9	2.3	0.008–5.0	0.008	0.0026	0.95	3.8	2.5
	Clay loam	0.008–5.0	0.008	0.0026	0.96	3.6	2.8	0.008–5.0	0.008	0.0026	0.96	2.6	3.7
	Rice	0.01–5.0	0.01	0.003	0.99	3.4	2.4	0.009–5.0	0.009	0.003	0.94	3.1	2.6
	Distilled water	0.008–5.0	0.008	0.0026	0.92	3.5	3.1	0.008–5.0	0.008	0.0026	0.97	2.4	3.6
	Tap water	0.01–5.0	0.01	0.003	0.91	2.7	2.8	0.009–5.0	0.009	0.003	0.97	2.9	2.4
	Pond water	0.01–5.0	0.01	0.003	0.94	3.1	2.4	0.01–5.0	0.01	0.003	0.98	2.8	3.1
	River water	0.008–5.0	0.008	0.0026	0.93	2.8	3.6	0.008–5.0	0.008	0.0026	0.94	2.4	3.4
	Loamy sand	0.008–5.0	0.008	0.0026	0.94	3.4	3.4	0.008–5.0	0.008	0.0026	0.94	3.7	3.6
	Sandy loam	0.008–5.0	0.008	0.0026	0.95	2.5	2.6	0.008–5.0	0.008	0.0026	0.94	3.6	3.4
	Silt loam	0.008–5.0	0.008	0.0026	0.95	2.6	3.2	0.008–5.0	0.008	0.0026	0.93	3.4	2.6
	Loam	0.008–5.0	0.008	0.0026	0.92	3.6	3.6	0.008–5.0	0.008	0.0026	0.96	3.3	3.7
	Clay loam	0.008–5.0	0.008	0.0026	0.94	2.6	3.3	0.008–5.0	0.008	0.0026	0.96	3.1	2.5
	Rice	0.01–5.0	0.01	0.003	0.92	3.1	2.7	0.009–5.0	0.009	0.003	0.96	2.8	2.2

^aSolid-phase extraction, ^baltling-out liquid–liquid extraction, ^climit of quantification, ^dlimit of detection, ^einterday precision, ^fintraday precision

Table 5 Percent recovery of herbicides quantified using HPLC from water

Herbicide	Fortification level ($\mu\text{g mL}^{-1}$)	Tap water		Pond water		River water		Distilled water	
		SPE ^a	SALLE ^b	SPE	SALLE	SPE	SALLE	SPE	SALLE
Anilofos	3LOQ ^c	88.2±2.7 ^d	91.9±3.5	92.9±2.5	95.3±2.7	87.1±3.4	90.1±3.5	94.9±3.4	98.2±4.3
	2LOQ	86.3±4.1	89.3±3.7	90.9±3.5	93.1±2.5	84.2±2.8	87.9±2.7	93.7±6.5	97.1±5.6
	LOQ	84.3±3.8	88.4±3.7	87.5±3.7	91.2±4.7	82.1±2.1	86.1±3.7	93.2±4.2	96.7±7.8
	CD ^e	2.15–2.31		1.87–2.05		2.26–2.75		1.16–1.51	
Bispyribac sodium	3LOQ	91.3±4.7	96.4±3.4	93.7±2.5	100.8±3.5	89.1±3.6	93.2±3.6	94.8±2.9	102.4±2.5
	2LOQ	89.2±3.8	92.4±2.9	91.8±4.8	97.9±4.5	87.2±2.8	90.9±3.7	95.7±4.6	100.8±6.9
	LOQ	86.2±3.9	90.2±3.8	88.7±2.9	96.8±4.1	84.8±4.5	88.1±2.9	93.8±7.3	99.2±5.2
	CD	2.05–2.27		2.05–2.26		2.53–3.30		1.57–2.04	
Butachlor	3LOQ	89.7±4.5	93.2±3.6	91.8±5.6	95.8±2.5	87.9±2.7	91.3±3.2	94.1±2.8	97.4±5.2
	2LOQ	86.8±3.6	90.7±4.7	89.7±2.7	93.7±3.6	84.7±3.2	88.0±4.1	93.4±3.9	96.1±6.4
	LOQ	83.7±3.5	87.9±3.5	85.7±3.8	89.7±3.8	81.6±4.1	84.9±2.9	92.9±6.7	95.8±7.3
	CD	2.27–2.50		1.81–2.28		1.79–2.89		1.73–2.22	
Pendimethalin	3LOQ	90.8±4.3	93.2±2.7	92.8±4.7	95.7±4.2	88.7±3.5	90.8±3.7	94.7±3.9	96.4±3.6
	2LOQ	87.2±3.6	90.7±3.9	89.9±3.7	92.9±3.9	85.9±2.8	88.9±3.3	93.1±6.1	94.7±4.9
	LOQ	85.7±2.8	88.5±3.1	86.8±4.6	90.8±3.7	83.1±2.3	86.9±3.9	92.9±8.5	92.4±7.7
	CD	2.27–2.38		2.26–2.50		2.47–2.53		1.77–3.23	
Penoxsulam	3LOQ	93.7±2.7	96.8±2.9	95.3±3.6	98.1±3.2	91.2±3.6	94.9±3.1	97.2±4.9	98.4±2.7
	2LOQ	91.8±4.7	94.0±3.7	92.7±3.8	95.4±2.8	89.7±3.7	92.8±4.9	96.7±3.8	99.3±6.1
	LOQ	87.2±2.8	92.9±3.0	89.3±4.7	91.9±3.8	85.7±3.1	89.1±2.7	95.1±7.1	98.3±3.9
	CD	1.86–2.15		1.65–2.78		1.86–2.92		1.72–2.18	
Pretilachlor	3LOQ	90.3±3.8	93.6±2.5	91.6±3.7	93.9±3.9	88.7±2.8	92.9±3.1	94.7±6.8	97.7±3.3
	2LOQ	87.6±4.7	91.8±3.6	89.7±4.1	92.7±4.1	85.7±3.5	89.8±3.8	93.4±7.7	96.9±4.1
	LOQ	85.3±3.7	88.9±1.9	87.2±2.7	90.3±3.5	83.1±2.9	86.9±2.9	92.1±6.3	95.5±6.7
	CD	1.82–2.38		1.99–2.88		2.18–3.22		1.95–2.05	

^aSolid-phase extraction, ^bsalting-out liquid–liquid extraction, ^climit of quantification, ^dCD corresponds to difference in recoveries of SPE and SALLE method, ^emean percent recoveries ± standard deviation

Table 6 Percent recovery of herbicides quantified using HPLC from soil and rice

Herbicide	Fortification level ($\mu\text{g mL}^{-1}$)	Loamy sand		Sandy loam		Silt loam		Loam		Clay loam		Rice	
		SPE ^a	SALLE ^b	SPE	SALLE	SPE	SALLE	SPE	SALLE	SPE	SALLE	SPE	SALLE
Amifos	3LOQ ^c	96.7 ± 3.2 ^e	99.9 ± 2.7	94.5 ± 2.9	98.1 ± 4.3	92.6 ± 2.8	96.1 ± 3.5	90.6 ± 2.7	94.3 ± 3.5	89.3 ± 3.5	93.1 ± 2.4	85.6 ± 3.5	90.3 ± 3.2
	2LOQ	93.1 ± 2.8	97.4 ± 3.6	91.4 ± 4.3	95.2 ± 3.7	90.6 ± 3.4	94.9 ± 4.2	89.4 ± 3.5	93.4 ± 4.1	87.3 ± 3.9	92.3 ± 3.5	83.4 ± 4.3	88.6 ± 4.3
	LOQ	91.7 ± 3.9	94.9 ± 4.2	90.3 ± 4.6	93.8 ± 4.1	88.3 ± 3.1	92.9 ± 2.6	87.1 ± 4.1	91.2 ± 4.6	86.5 ± 4.5	90.7 ± 4.5	81.9 ± 4.4	86.3 ± 2.7
	CD ^d	2.17–3.34	1.54–2.87	2.62–3.12	2.34–4.51	2.34–4.51	2.98–3.12	2.98–3.12	4.12–5.89	4.12–5.89	4.12–5.89	4.09–5.33	4.09–5.33
Bispyribac sodium	3LOQ	97.8 ± 3.6	100.7 ± 2.6	96.1 ± 3.7	99.4 ± 4.2	95.2 ± 4.2	98.9 ± 2.7	94.3 ± 2.6	97.1 ± 4.2	92.7 ± 4.5	95.4 ± 4.6	90.3 ± 3.6	93.4 ± 4.2
	2LOQ	94.1 ± 2.8	97.8 ± 3.9	92.9 ± 3.8	96.1 ± 4.8	90.1 ± 4.8	94.8 ± 3.6	88.3 ± 3.6	93.2 ± 2.7	86.4 ± 4.8	92.7 ± 2.8	84.5 ± 4.1	90.4 ± 3.5
	LOQ	91.7 ± 4.2	95.6 ± 4.1	90.1 ± 4.6	93.8 ± 2.7	88.8 ± 2.8	92.5 ± 4.2	87.4 ± 4.1	91.4 ± 3.8	85.8 ± 2.7	90.4 ± 3.5	82.3 ± 3.5	88.7 ± 4.1
	CD	2.55–3.45	2.62–3.12	2.62–3.12	3.87–4.23	3.87–4.23	3.29–4.32	3.29–4.32	3.09–5.98	3.09–5.98	3.09–5.98	3.45–5.32	3.45–5.32
Butachlor	3LOQ	96.9 ± 3.6	99.9 ± 4.1	95.1 ± 3.1	99.1 ± 3.6	94.4 ± 3.7	98.1 ± 4.1	93.5 ± 4.1	97.0 ± 4.1	92.6 ± 3.6	95.9 ± 4.2	90.6 ± 2.6	94.5 ± 3.6
	2LOQ	95.8 ± 2.9	98.7 ± 3.7	93.1 ± 4.5	97.4 ± 4.8	92.1 ± 3.6	96.2 ± 4.7	91.1 ± 2.6	95.3 ± 3.6	89.4 ± 4.8	94.1 ± 3.6	86.5 ± 3.5	90.1 ± 2.6
	LOQ	91.2 ± 4.2	95.2 ± 3.9	89.3 ± 4.1	93.4 ± 2.7	87.0 ± 2.8	92.1 ± 3.6	86.0 ± 3.5	91.1 ± 4.6	85.7 ± 2.5	90.0 ± 4.5	82.3 ± 3.7	87.5 ± 3.7
	CD	2.21–3.21	1.67–2.54	1.67–2.54	3.21–4.24	3.21–4.24	2.98–5.13	2.98–5.13	4.32–6.90	4.32–6.90	4.32–6.90	3.12–4.09	3.12–4.09
Pendimethalin	3LOQ	98.3 ± 3.9	100.8 ± 4.8	96.4 ± 3.8	99.7 ± 3.7	94.5 ± 3.5	98.2 ± 2.7	93.1 ± 3.5	96.2 ± 2.7	91.2 ± 2.7	95.0 ± 4.1	88.5 ± 3.7	93.0 ± 3.1
	2LOQ	96.1 ± 4.7	99.5 ± 3.8	94.2 ± 4.7	98.3 ± 2.6	93.6 ± 4.7	96.4 ± 3.8	91.4 ± 4.1	95.3 ± 4.7	89.3 ± 3.8	93.4 ± 2.6	87.6 ± 2.7	92.4 ± 2.8
	LOQ	93.2 ± 4.6	96.8 ± 2.5	91.5 ± 4.9	95.2 ± 3.7	90.2 ± 3.7	94.7 ± 3.4	88.3 ± 2.6	93.4 ± 3.5	87.4 ± 3.5	92.3 ± 3.4	85.3 ± 3.4	90.1 ± 4.2
	CD	1.82–2.45	2.63–3.34	2.63–3.34	2.44–3.87	2.44–3.87	4.39–5.09	4.39–5.09	4.12–5.05	4.12–5.05	4.12–5.05	3.10–6.01	3.10–6.01
Penoxsulam	3LOQ	96.4 ± 4.5	99.4 ± 4.1	93.8 ± 3.8	97.6 ± 4.5	92.9 ± 4.2	96.1 ± 2.6	91.3 ± 4.2	95.2 ± 2.6	90.3 ± 4.7	93.9 ± 3.5	88.4 ± 2.8	92.1 ± 2.9
	2LOQ	94.5 ± 3.7	98.1 ± 3.6	92.6 ± 4.1	97.3 ± 2.8	90.1 ± 2.7	94.6 ± 4.6	88.4 ± 3.5	92.3 ± 3.6	87.3 ± 3.5	90.9 ± 4.1	85.3 ± 4.1	88.4 ± 3.6
	LOQ	92.9 ± 3.1	96.2 ± 2.5	90.9 ± 4.9	95.1 ± 4.5	88.4 ± 3.5	93.8 ± 4.0	86.2 ± 3.6	92.3 ± 2.7	85.4 ± 2.7	90.4 ± 4.4	83.2 ± 4.2	88.5 ± 3.7
	CD	1.77–2.55	1.54–2.87	1.54–2.87	2.18–3.98	2.18–3.98	5.02–6.11	5.02–6.11	4.19–6.03	4.19–6.03	4.19–6.03	3.56–6.54	3.56–6.54
Pretilachlor	3LOQ	95.2 ± 2.6	99.4 ± 3.6	94.1 ± 4.5	98.5 ± 2.8	92.8 ± 3.4	96.2 ± 2.6	91.4 ± 2.6	95.1 ± 4.2	88.5 ± 4.2	93.4 ± 3.6	83.4 ± 3.6	90.3 ± 3.2
	2LOQ	92.7 ± 2.7	97.1 ± 3.8	90.9 ± 2.8	95.3 ± 4.6	89.4 ± 3.7	94.6 ± 3.5	87.3 ± 3.6	93.6 ± 3.6	86.4 ± 4.6	92.3 ± 4.5	82.3 ± 3.8	88.7 ± 2.8
	LOQ	90.4 ± 1.9	95.3 ± 3.5	88.3 ± 3.6	94.2 ± 3.7	87.4 ± 2.7	93.4 ± 4.1	86.4 ± 4.1	92.9 ± 3.7	84.1 ± 3.5	90.0 ± 4.1	81.3 ± 4.2	86.6 ± 2.9
	CD	1.67–2.56	2.54–3.86	2.54–3.86	3.09–4.44	3.09–4.44	4.65–6.02	4.65–6.02	2.98–4.98	2.98–4.98	2.98–4.98	4.11–6.24	4.11–6.24

^aSolid-phase extraction, ^bsalting-out liquid–liquid extraction, ^climit of quantification, ^dCD corresponds to difference in recoveries of SPE and SALLE method, ^emean percent recoveries ± standard deviation

Table 7 Percent recovery of herbicides quantified using LC–MS/MS from water

Herbicide	Fortification level ($\mu\text{g mL}^{-1}$)	Tap water		Pond water		River water		Distilled water	
		SPE ^a	SALLE ^b	SPE	SALLE	SPE	SALLE	SPE	SALLE
Anilofos	3LOQ ^c	89.8 ± 2.4 ^e	93.5 ± 2.7	93.4 ± 3.4	96.4 ± 3.6	88.8 ± 4.4	91.6 ± 4.1	95.2 ± 8.6	99.4 ± 4.8
	2LOQ	86.6 ± 2.9	90.4 ± 2.4	91.9 ± 4.1	94.2 ± 3.2	86.7 ± 3.9	88.1 ± 3.1	95.4 ± 6.3	98.3 ± 6.1
	LOQ	85.4 ± 4.1	89.7 ± 4.1	88.9 ± 3.7	92.9 ± 3.2	83.9 ± 4.2	87.9 ± 4.1	94.6 ± 4.8	97.8 ± 7.5
	CD ^d	2.34–4.56		2.12–4.56		3.56–6.34		4.32–6.12	
Bispyribac sodium	3LOQ	92.9 ± 3.2	97.5 ± 3.4	94.9 ± 3.4	100.8 ± 3.5	90.3 ± 2.8	93.2 ± 3.6	99.8 ± 6.1	102.3 ± 2.3
	2LOQ	90.8 ± 2.7	94.5 ± 3.1	93.4 ± 2.7	98.1 ± 3.2	90.4 ± 3.2	90.9 ± 3.7	97.7 ± 5.4	102.9 ± 8.8
	LOQ	87.8 ± 4.1	91.4 ± 4.4	88.7 ± 2.9	97.9 ± 3.8	85.9 ± 3.5	89.3 ± 3.8	95.7 ± 9.0	101.4 ± 7.3
	CD	2.78–3.98		2.65–4.76		3.09–5.23		2.09–4.98	
Butachlor	3LOQ	90.1 ± 3.5	94.4 ± 2.8	92.9 ± 3.6	96.9 ± 3.7	88.0 ± 3.6	92.8 ± 2.7	93.9 ± 6.3	98.1 ± 3.9
	2LOQ	88.4 ± 2.8	91.8 ± 4.1	90.6 ± 4.2	94.8 ± 4.1	85.2 ± 4.1	89.5 ± 3.2	94.4 ± 2.9	97.3 ± 4.8
	LOQ	85.1 ± 2.9	88.6 ± 4.2	86.9 ± 4.9	90.2 ± 4.2	82.9 ± 2.6	85.7 ± 3.5	94.8 ± 1.7	96.3 ± 6.5
	CD	2.87–4.76		2.39–6.07		2.67–4.98		2.12–4.98	
Pendimethalin	3LOQ	91.7 ± 3.1	95.2 ± 3.2	93.9 ± 5.1	96.2 ± 2.8	88.7 ± 3.5	90.8 ± 3.7	97.8 ± 3.4	99.1 ± 4.1
	2LOQ	88.9 ± 4.5	92.7 ± 2.1	90.3 ± 4.1	93.9 ± 4.1	85.9 ± 2.8	88.9 ± 3.3	95.7 ± 5.4	97.2 ± 2.8
	LOQ	86.2 ± 3.7	90.1 ± 2.9	87.8 ± 3.2	92.1 ± 3.9	83.1 ± 2.3	86.9 ± 3.9	94.9 ± 6.8	98.3 ± 3.1
	CD	2.98–6.56		3.98–6.38		2.12–4.23		3.29–6.31	
Penoxsulam	3LOQ	94.5 ± 3.8	98.8 ± 3.8	96.9 ± 4.7	98.9 ± 4.6	91.2 ± 3.6	94.9 ± 3.1	98.6 ± 3.5	101.9 ± 8.1
	2LOQ	92.8 ± 3.1	95.0 ± 2.8	93.9 ± 3.1	96.7 ± 4.4	89.7 ± 3.7	92.8 ± 4.9	97.5 ± 5.9	100.7 ± 1.9
	LOQ	88.5 ± 3.7	93.9 ± 3.6	90.3 ± 4.8	92.7 ± 4.1	85.7 ± 3.1	89.1 ± 2.7	96.8 ± 7.7	99.1 ± 2.6
	CD	3.29–6.78		2.78–4.23		2.09–4.67		2.76–6.22	
Pretilachlor	3LOQ	91.7 ± 4.5	95.1 ± 3.4	91.6 ± 3.7	94.8 ± 3.9	88.7 ± 2.8	92.9 ± 3.1	97.5 ± 3.4	99.8 ± 5.8
	2LOQ	88.5 ± 3.4	92.8 ± 4.1	89.7 ± 4.1	93.9 ± 4.4	85.7 ± 3.5	89.8 ± 3.8	95.2 ± 2.1	97.1 ± 6.1
	LOQ	86.3 ± 2.8	89.5 ± 3.2	87.2 ± 2.7	91.9 ± 3.9	83.1 ± 2.9	86.9 ± 2.9	93.8 ± 6.2	96.8 ± 7.2
	CD	2.87–4.56		2.98–4.11		2.98–5.12		3.21–6.30	

^aSolid-phase extraction, ^bsalting-out liquid–liquid extraction, ^climit of quantification, ^dCD corresponds to difference in recoveries of SPE and SALLE method, ^emean percent recoveries ± standard deviation

Table 8 Percent recovery of herbicides quantified using LC–MS/MS from soil and rice

Herbicide	Fortification level ($\mu\text{g mL}^{-1}$)	Loamy sand		Sandy loam		Silt loam		Loam		Clay loam		Rice	
		SPE ^a	SALLE ^b	SPE	SALLE	SPE	SALLE	SPE	SALLE	SPE	SALLE	SPE	SALLE
Amifos	3LOQ ^c	97.4 ± 2.3	100.1 ± 3.8	96.4 ± 3.2	99.3 ± 2.5	95.3 ± 3.1	98.3 ± 3.1	93.4 ± 3.2	97.4 ± 3.5	92.1 ± 3.1	95.2 ± 3.6	90.1 ± 3.4	94.6 ± 3.5
	2LOQ	94.5 ± 3.1	98.3 ± 3.2	92.3 ± 4.1	96.3 ± 3.7	90.3 ± 2.5	95.1 ± 2.7	89.5 ± 2.5	94.1 ± 4.1	87.4 ± 4.2	93.2 ± 2.7	85.2 ± 4.2	91.6 ± 2.8
	LOQ	92.9 ± 2.9	95.1 ± 3.1	90.5 ± 4.5	94.3 ± 2.3	89.3 ± 4.2	93.1 ± 3.9	88.1 ± 4.1	92.9 ± 3.8	86.3 ± 3.7	91.5 ± 3.8	84.3 ± 2.6	90.1 ± 3.8
	CD ^d	2.11–3.23		1.99–3.43		2.45–3.87		1.24–3.29		2.89–4.78		1.22–3.98	
Bispyribac sodium	3LOQ	99.4 ± 3.2	103.2 ± 4.1	96.3 ± 3.5	99.9 ± 2.8	94.3 ± 3.5	98.4 ± 4.1	93.1 ± 3.1	96.1 ± 2.5	91.4 ± 2.6	95.4 ± 2.7	90.1 ± 3.4	94.3 ± 4.1
	2LOQ	98.3 ± 2.7	101.3 ± 3.1	96.2 ± 3.1	99.1 ± 3.1	95.5 ± 3.4	97.1 ± 3.7	94.3 ± 2.6	96.3 ± 3.6	93.8 ± 3.4	94.3 ± 4.1	89.4 ± 4.1	93.9 ± 4.7
	LOQ	95.2 ± 2.4	98.3 ± 4.2	94.1 ± 3.2	97.1 ± 3.1	93.6 ± 4.7	96.2 ± 3.6	91.4 ± 3.6	95.2 ± 4.1	90.4 ± 4.7	94.2 ± 3.9	85.7 ± 3.6	92.5 ± 2.7
	CD	1.43–2.55		2.34–3.88		2.32–4.34		2.98–3.98		2.09–3.22		2.38–4.98	
Butachlor	3LOQ	96.2 ± 2.9	99.0 ± 2.8	95.1 ± 2.5	98.1 ± 4.2	93.4 ± 3.4	96.9 ± 3.1	92.4 ± 4.5	95.1 ± 3.5	90.1 ± 3.8	93.8 ± 4.3	88.4 ± 2.6	91.8 ± 3.6
	2LOQ	92.9 ± 3.1	96.1 ± 3.1	91.3 ± 3.6	94.5 ± 3.7	90.3 ± 3.7	93.5 ± 3.9	89.4 ± 4.7	92.9 ± 3.9	87.2 ± 2.7	91.4 ± 4.4	85.2 ± 3.7	89.4 ± 4.2
	LOQ	91.2 ± 4.2	95.3 ± 4.1	90.4 ± 4.5	94.3 ± 3.1	88.3 ± 4.1	92.9 ± 4.1	86.2 ± 3.7	91.7 ± 4.1	85.1 ± 4.1	90.2 ± 3.6	82.7 ± 3.5	88.3 ± 2.6
	CD	2.32–4.44		3.87–4.99		2.11–3.23		1.23–3.44		1.98–3.23		1.99–3.23	
Pendimethalin	3LOQ	96.9 ± 4.1	99.3 ± 2.1	95.2 ± 4.7	98.4 ± 3.5	93.1 ± 2.5	96.3 ± 2.6	91.8 ± 2.6	95.2 ± 3.6	90.1 ± 3.7	94.2 ± 2.7	86.5 ± 2.6	92.6 ± 3.6
	2LOQ	92.9 ± 2.9	96.9 ± 4.1	90.4 ± 3.4	95.3 ± 2.5	89.4 ± 3.1	93.4 ± 3.7	87.1 ± 2.8	92.1 ± 4.7	86.3 ± 2.5	90.3 ± 3.9	84.1 ± 2.8	88.3 ± 4.3
	LOQ	91.1 ± 2.5	95.3 ± 3.2	89.4 ± 3.2	94.1 ± 4.1	87.4 ± 2.7	92.3 ± 4.1	85.7 ± 3.5	91.9 ± 2.5	84.2 ± 2.1	90.1 ± 4.2	82.6 ± 2.3	87.4 ± 3.7
	CD	2.39–3.99		1.23–3.54		2.30–3.98		2.12–3.98		1.87–3.98		2.33–3.90	
Penoxsulam	3LOQ	98.3 ± 3.1	101.4 ± 2.1	96.3 ± 4.1	99.4 ± 4.1	94.5 ± 2.6	98.3 ± 3.2	92.7 ± 4.1	96.1 ± 3.6	90.1 ± 4.1	94.7 ± 2.7	87.5 ± 2.6	92.7 ± 3.3
	2LOQ	97.4 ± 2.5	100.4 ± 3.2	95.3 ± 3.5	98.4 ± 3.6	92.6 ± 3.6	96.1 ± 3.7	90.1 ± 4.7	95.4 ± 4.2	88.3 ± 2.7	94.1 ± 3.6	85.3 ± 3.7	90.3 ± 3.8
	LOQ	94.9 ± 3.5	97.4 ± 4.2	92.5 ± 3.6	96.3 ± 4.1	90.3 ± 3.9	95.3 ± 4.2	88.5 ± 2.6	94.8 ± 3.5	86.2 ± 4.1	92.8 ± 4.1	82.3 ± 4.1	89.5 ± 2.9
	CD	2.02–4.03		2.32–3.90		1.98–3.87		1.28–3.67		2.34–4.76		1.45–4.98	
Pretilachlor	3LOQ	97.3 ± 2.7	100.5 ± 2.4	96.3 ± 3.5	98.4 ± 3.4	94.2 ± 3.8	97.1 ± 2.6	92.8 ± 3.6	95.1 ± 3.5	90.1 ± 3.8	93.6 ± 3.6	87.4 ± 3.7	91.0 ± 3.6
	2LOQ	96.3 ± 3.6	99.3 ± 3.2	94.4 ± 3.6	97.5 ± 4.1	92.3 ± 2.6	96.4 ± 2.5	90.1 ± 3.8	94.5 ± 4.3	88.3 ± 2.6	92.6 ± 3.1	85.1 ± 4.6	90.4 ± 2.5
	LOQ	93.2 ± 3.8	97.4 ± 2.6	92.5 ± 2.7	96.3 ± 3.6	90.1 ± 2.9	94.5 ± 2.9	88.5 ± 4.1	93.9 ± 2.6	86.2 ± 2.8	91.8 ± 2.7	83.3 ± 2.7	89.3 ± 3.8
	CD	2.09–3.22		2.39–4.98		2.34–3.77		2.34–4.78		1.23–3.90		2.87–4.98	

^aSolid-phase extraction, ^bsalting-out liquid–liquid extraction, ^climit of quantification, ^dCD corresponds to difference in recoveries of SPE and SALLE method, ^emean percent recoveries ± standard deviation

Table 9 Results of Analytical Eco-Scale tool

Extraction method	Parameter	Reagents	Penalty points
SALLE-HPLC	Amount hazard	Acetonitrile (10 mL)	2
		Herbicide standard in acetonitrile (< 10 mL)	1
		NaCl	1
		Mobile phase: Acetonitrile: water	2
	Energy	Instruments	0
		Sonicator HPLC–UV	1
	Occupational hazard	–	0
	Waste	30 mL	5
Total penalty points			12
Analytical Eco-Scale total score			88
SALLE-LC–MS/MS	Amount hazard	Acetonitrile (10 mL)	2
		Herbicide standard in acetonitrile (< 10 mL)	1
		NaCl	1
		Mobile phase: Acetonitrile: water	2
	Energy	Instruments	0
		Sonicator LC–MS/MS	2
	Occupational hazard	–	0
	Waste	30 mL	5
Total penalty points			13
Analytical Eco-Scale total score			87
SPE HPLC	Amount hazard	Acetonitrile (10 mL)	2
		Acetone (10 to 40 mL)	2
		Methanol (6 to 40 mL)	2
		Herbicide standard in acetonitrile (< 10 mL)	1
		NaCl	2
		Mobile phase: Acetonitrile: water	
	Energy	Instruments	0
		Sonicator HPLC–UV	1
Occupational hazard	–	0	
Waste	34 mL	5	
Total penalty points			16
Analytical Eco-Scale total score			84
SPE LC–MS/MS	Amount hazard	Acetonitrile (10 mL)	2
		Acetone (10 to 40 mL)	2
		Methanol (6 to 40 mL)	2
		Herbicide standard in acetonitrile (< 10 mL)	1
		NaCl	2
		Mobile phase: Acetonitrile: water	
	Energy	Instruments	0
		Sonicator LC–MS/MS	2
Waste	34 mL	5	
Total penalty points			15
Analytical Eco-Scale total score			85

Table 10 Comparison of SALLE method with other similar methods for detection of studied herbicides from water, soil and rice

Herbicide	Matrix	Method	Technique	LOD ($\mu\text{g mL}^{-1}/\mu\text{g g}^{-1}$)	Linearity ($\mu\text{g mL}^{-1}$)	Recovery%	Sample volume (mL/g)	Extracting solvent (mL)	Reference
Bispyribac sodium	Water	SPE	LC-DAD	$0.04\text{--}1.7 \times 10^{-3}$	0.05–10	80–88.5	250	4	[15]
		DLLME	LC-MS/MS	0.04×10^{-3}	0.05–20	82.8–91.5	10	0.25	[26]
		SPE	HPLC-DAD	0.02	0.05–10	72.5–92.0	50	100	[16]
		SPE	LC-MS/MS	0.005–0.002	0.05–10	71.0–92.0	250	1	[17]
	Soil	LLE	HPLC	0.01	0.01–2.5	72.9–82.1	50	100	[13]
Butachlor	Water	QuEChERS	LC-MS/MS	0.0003	10–100	69–83	10	50	[68]
		SPME	GC-MS/MS	7×10^{-6}	0.01–10	85.6–98.0	25	–	[24]
		LLE	GC-ECD-MS	0.05×10^{-3}	0.5–20	81.0–93.0	500	120	[14]
	Soil	SPE	GC	0.02×10^{-3}	0.0025–2.5	75.6–97.0	9	7	[5]
		QuEChERS	GC-MS	0.01	0.001–1	81.5–102.7	10	20	[69]
		SPE	HPLC	0.006	–	84–93.2	50	250	[18]
	Rice	SPE	GC-MS/MS	0.0002	5×10^{-5} – 0.02	87.7–108	5	20	[3]
		MSPD	HPLC	0.0159	0.0000125–0.0005	89.4–108.7	2	3	[70]
Pendimethalin	Water	SPE	GC-MS	0.03×10^{-4}	0.1–20	82.6–91.0	1000	3	[19]
		SPME	GC-MS	0.03×10^{-4}	0.1–10	83.6–93.6	3	–	[25]
		LLE	GC-ECD/MS	0.05×10^{-3}	0.5–20	76.0–86.9	500	120	[14]
		QuEChERS	HPLC-MS/MS	1.0×10^{-7}	0.02–0.2	81.6–106.3	200	8	[3]
	Soil	SPE	GC-MS/MS	0.01×10^{-4}	0.1–10	82.6–97.6	250	9	[20]
		MSPD	HPLC	0.001	0.003–5.0	80.3–101.3	10	50	[71]
		GC-MS/MS	10	0.00001	78.8–119.8	10	40	[72]	
Rice	UAE	HPLC	0.001	0.003–5.0	81.7–103.1	10	40	[71]	
Penoxsulam	Water	SPE	HPLC	0.02– 0.03×10^{-2}	0.2–10	78.6–89.0	200	2	[21]
		SPE	LC-MS-MS	0.01–0.04	0.1–10	71.0–98.6	250	1	[17]
		SPE	LC-UV	0.07×10^{-3}	0.1–1	80.6–99.6	1000	12	[22]
	Soil	SPE	LC-QQQ-MS/MS	0.001	0.1–20	70–106	10	50	[23]
Pretilachlor	•Water	LLE	GC-ECD-MS	0.05×10^{-2}	0.5–100	81.6–97.6	500	120	[14]
		QuEChERS	UHPLC-MS/MS	0.0001–0.01	0.5	77–117	–	–	[73]
	Soil	SPE	GC-MS/MS	0.0002	0.05–5.0	87.7–108	5	10	[3]
		MSPD	CE-ECL	0.008	0.03–2.0	88.7–95.5	0.5	12	[74]
		QuEChERS	UHPLC-MS/MS	3×10^{-5} – 4×10^{-5}	0.5	74–111	2	20	[73]
	Rice	dSPE	GC-MS/MS	0.002–0.01	0.005–0.5	87.7–108.0	2	10	[3]
Anilofos	Water	SPE	HPLC	0.0254	0.0025–0.5	89.4–108.7	2	3	[75]
	Soil	SPE	LC-HRMS	> 0.015	0.0001–0.1	70.5–80.3 ng/l	10	10	[76]
	Soil	SPE	HPLC	1×10^{-4}	0.0002–0.01	90.2–98.3	10	–	[77]

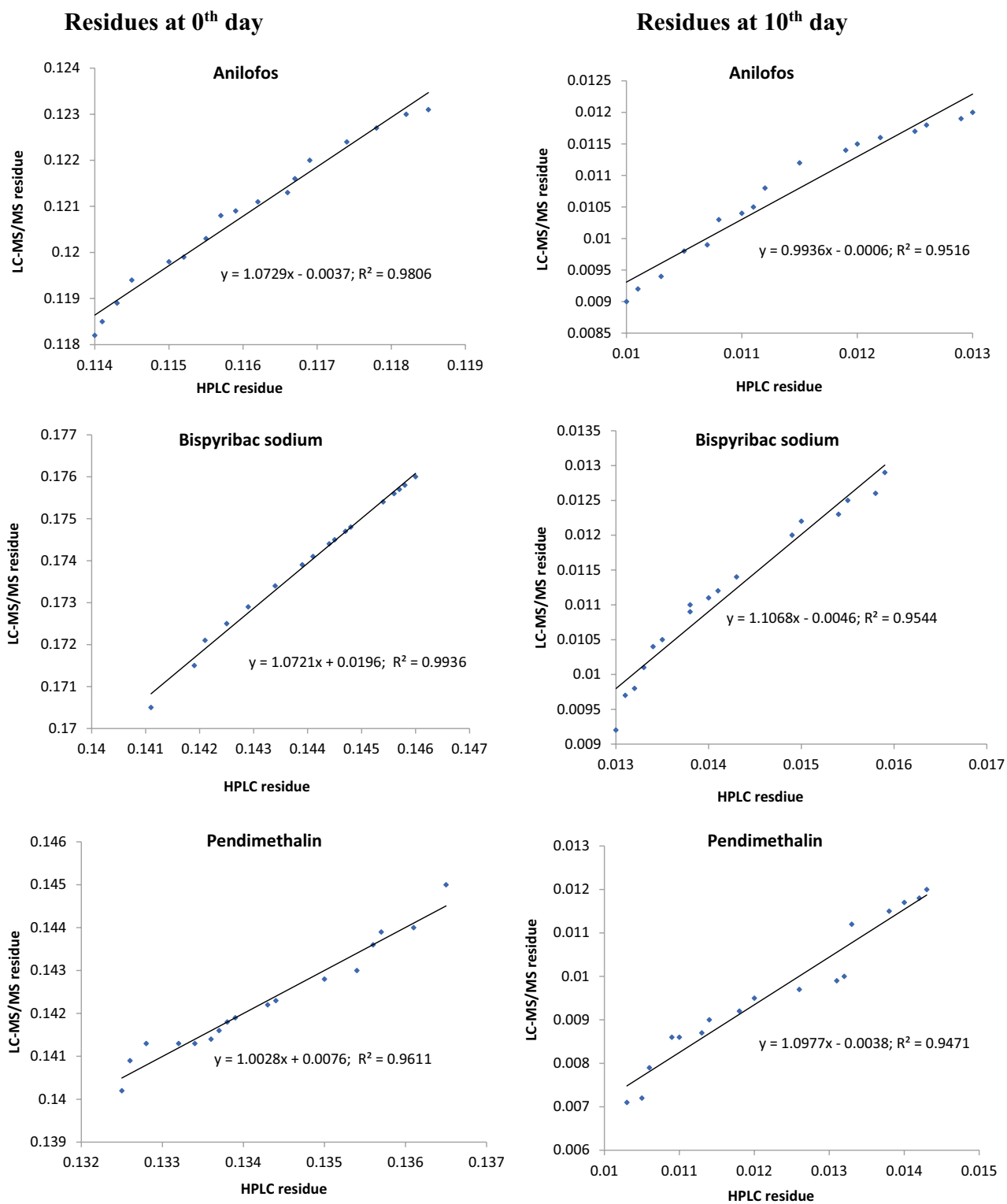


Fig. 7 Comparison of the quantification of six herbicides from water with the UV detector (x-axis) and mass detector (y-axis)

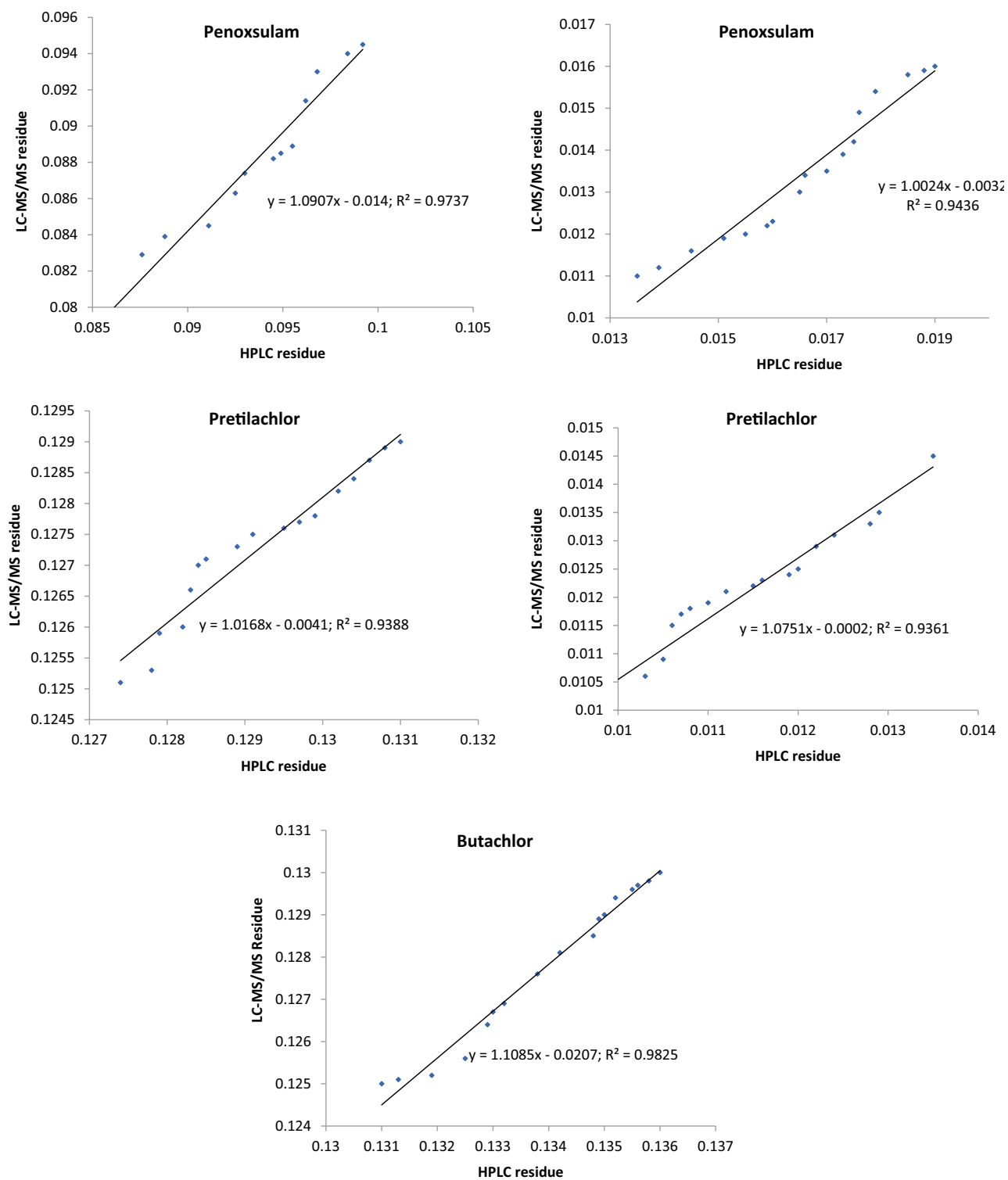


Fig. 7 (continued)

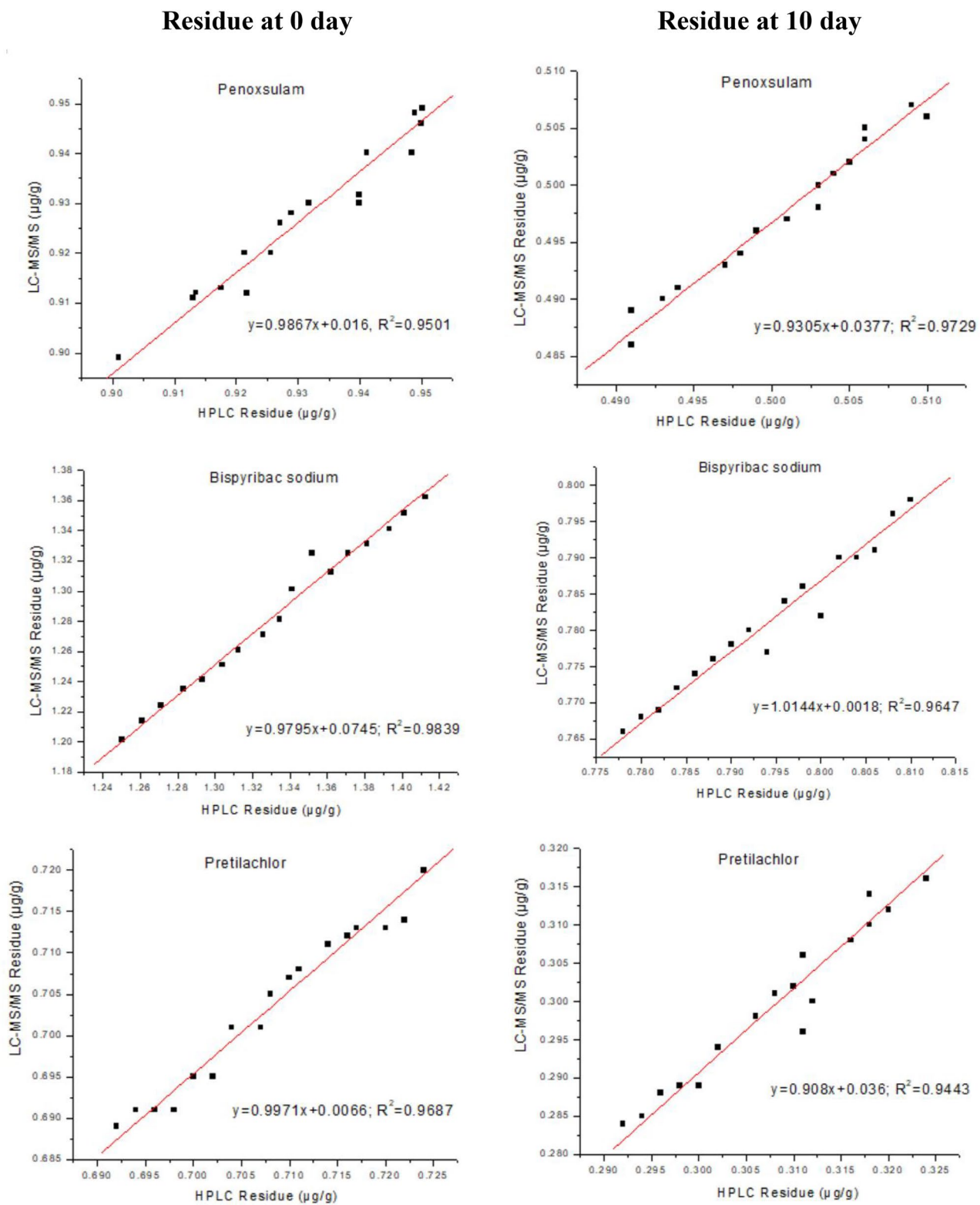


Fig. 8 Comparison of the quantification of six herbicides from soil with the UV detector (y-axis) and mass detector (x-axis)

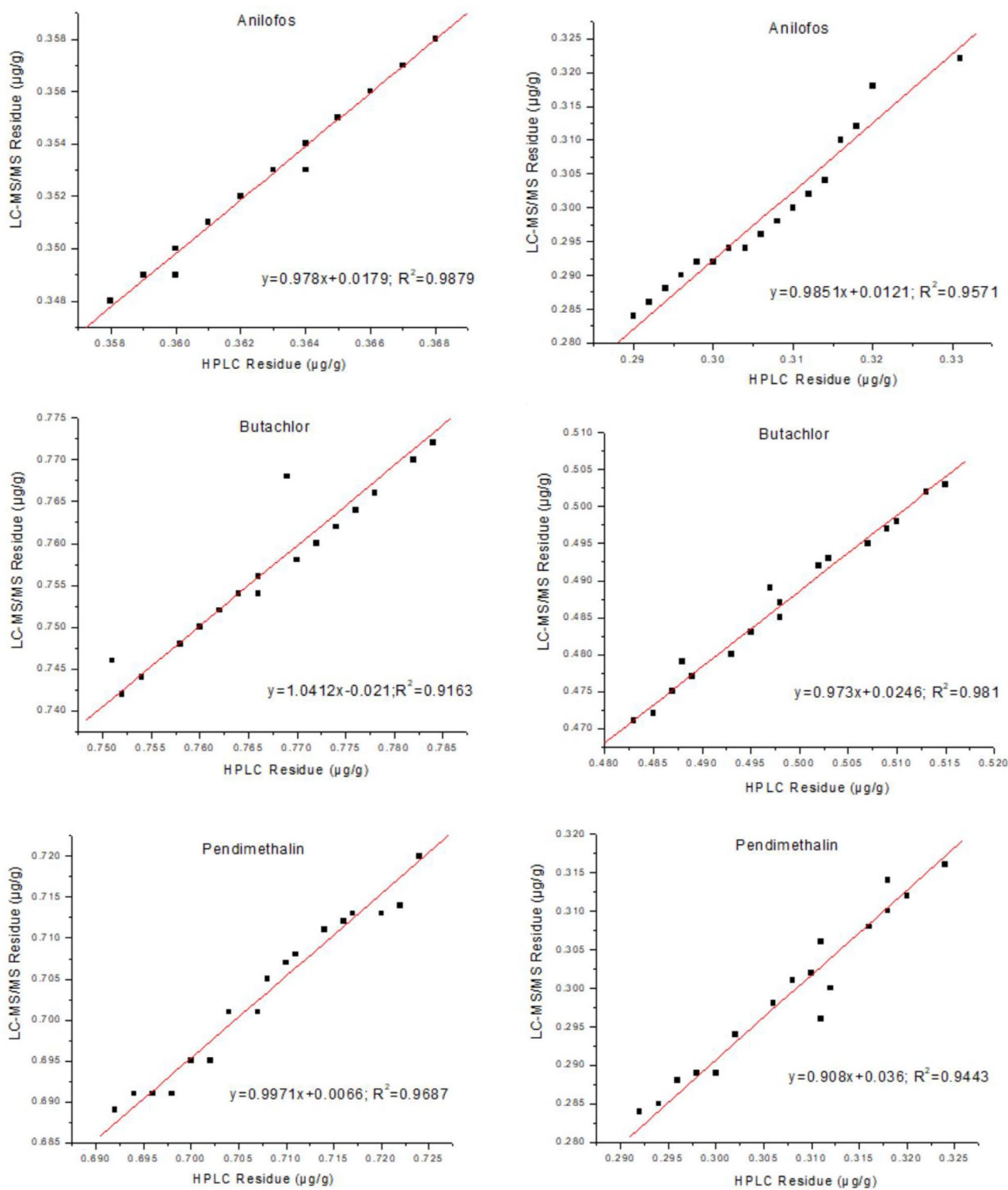


Fig. 8 (continued)

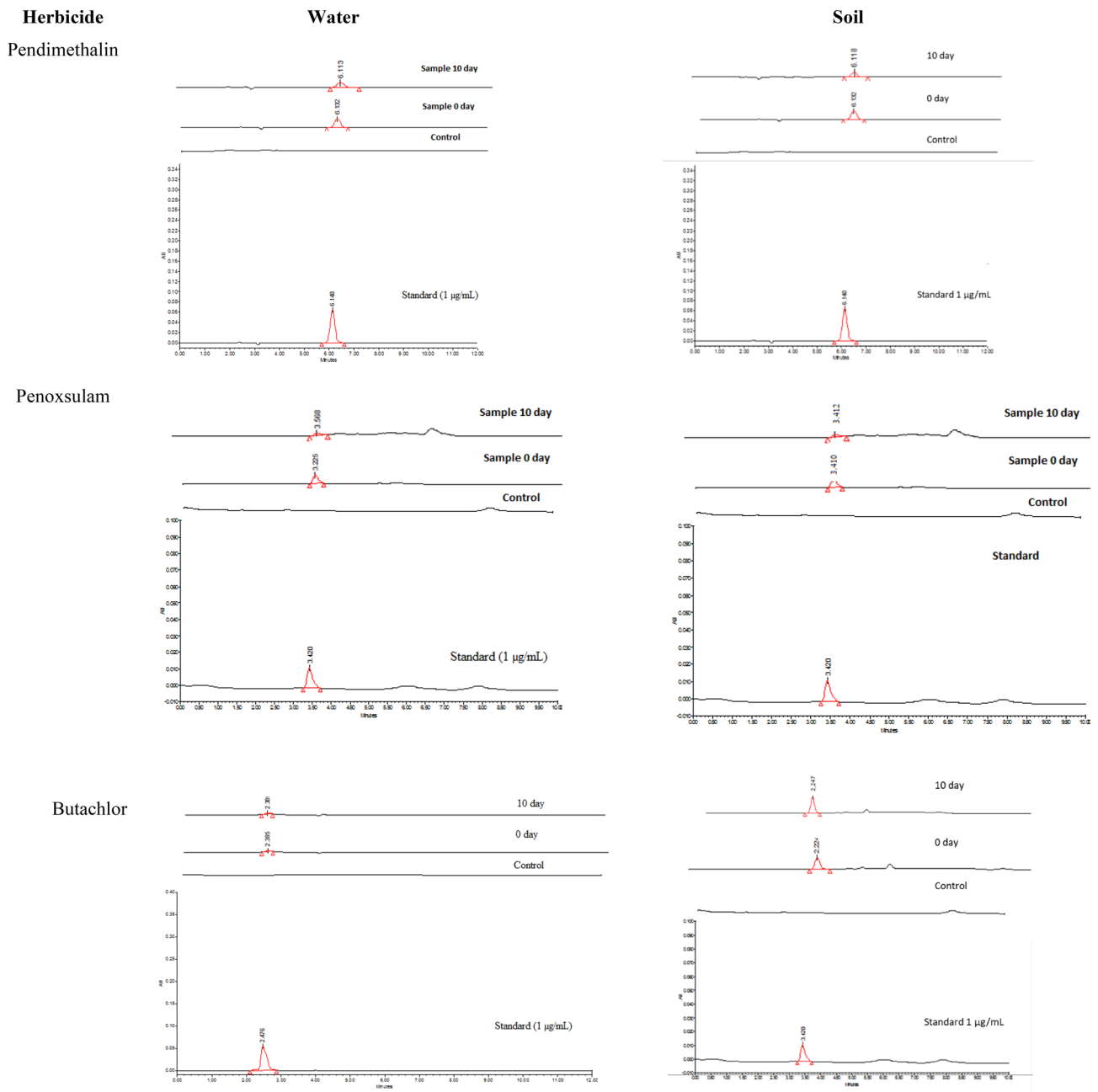


Fig. 9 Chromatograms of environmental water and soil samples

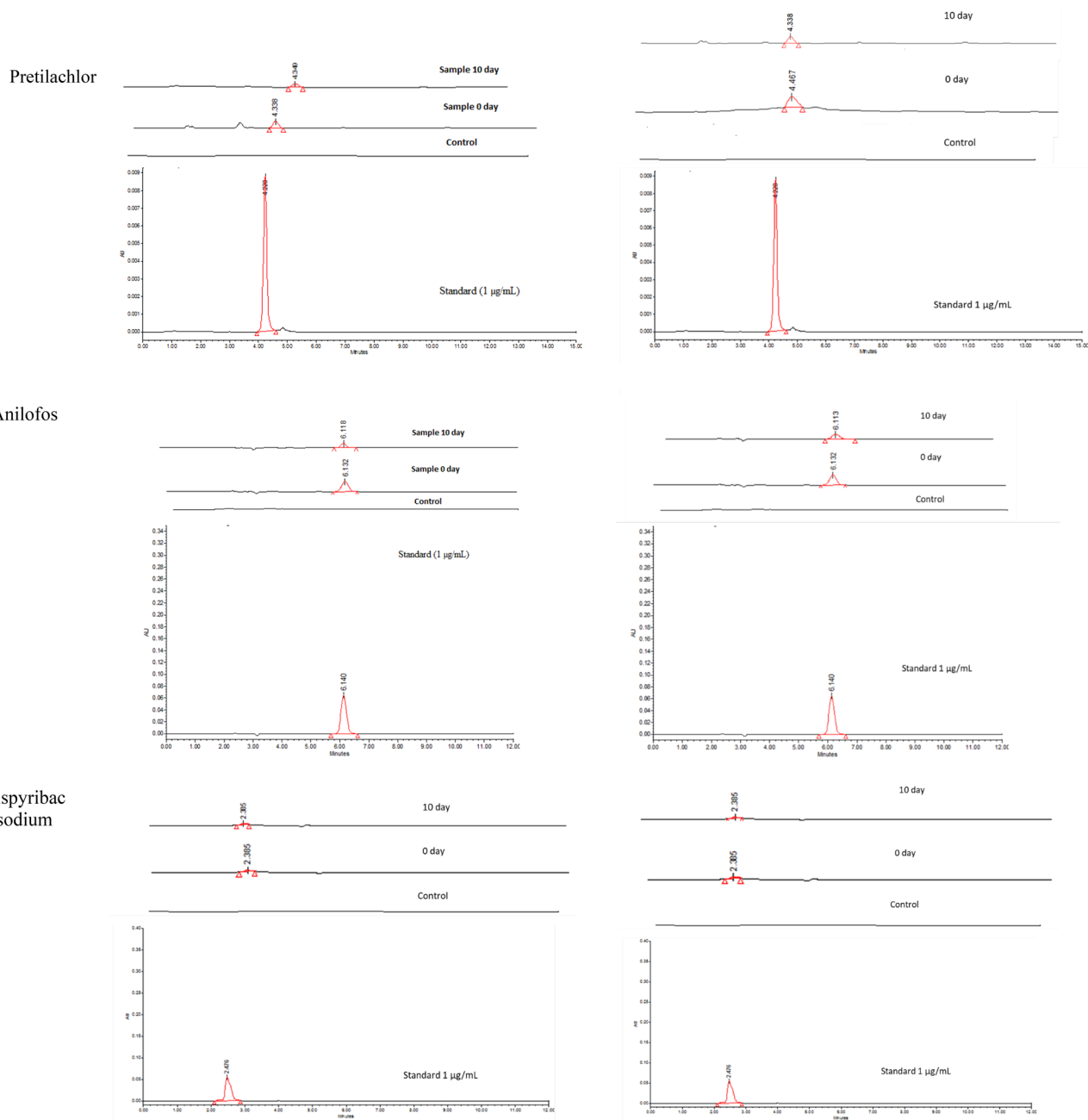


Fig. 9 (continued)

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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