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# Extraction Method for Determining Dinotefuran Insecticide in Soil Samples

*Sandro B. Soares,[a] Lázaro C. Sicupira,[b] Gevany P. de Pinho[a] and Flaviano O. Silvério* *,[a]

[a]*Instituto de Ciências Agrárias, Universidade Federal de Minas Gerais (UFMG), 39404-547 Montes Claros-MG, Brazil*

[b]*Instituto de Engenharia, Ciência e Tecnologia, Universidade Federal dos Vales do Jequitinhonha e Mucuri (UFVJM), 39447-790 Janaúba-MG, Brazil*

Dinotefuran is a third-generation neonicotinoid insecticide that has a broad action spectrum in agriculture pests. Dinotefuran was authorized in Brazil in 2019, being classified as a very dangerous product for the environment. Therefore, this study aimed to optimize and validate the solid-liquid extraction with low temperature purification to determine dinotefuran in soil samples using high-performance liquid chromatography coupled diode array detection. The results showed that the best extracting phase was acetonitrile:water (8:2 v/v), followed by the clean-up with 50 mg of primary-secondary amine. The method under these conditions has a linear range of 15.0 to 140 μg $kg^{-1}$ and reached limits of detection and quantification of 10.0 and 15.0 μg $kg^{-1}$, respectively. The validation revealed that the method was selective, precise, accurate, and presented a matrix effect of 15%. Although dinotefuran was not detected in real soil samples, the proposed method proved to be an efficient alternative for monitoring dinotefuran in soil samples.

**Keywords:** neonicotinoid insecticide, neuronal insecticide, third-generation neonicotinoids, SLE-LTP

## Introduction

Neonicotinoids are broad-spectrum systemic insecticides and have been the fastest developed pesticides in recent years.[1-3] We can highlight dinotefuran within this class, which belongs to the third generation of neonicotinoid insecticides (Figure 1).

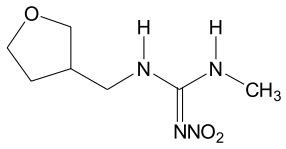


**Figure 1.** Chemical structure of the dinotefuran molecule.

This insecticide presents a high endosmosis penetration capacity with significant insecticidal activity and low toxicity to mammals and birds.[4,5] Furthermore, dinotefuran has been effective in combating pests resistant to conventional insecticides such as organophosphates, carbamates and pyrethroids.[6] These characteristics have contributed to its high use in several countries, which has resulted in episodes of contamination in water,[7-9] soil,[10,11] animals,[12] plants[3] and in humans.[13-15]

Dinotefuran was authorized in Brazil in 2019 to be used in several cultivation plantations such as cotton, rice, cereals, potatoes, coffee, sugar cane, citrus fruit, beans, chickpeas, corn, soybeans, sorghum, tomatoes, and wheat (among others crops), with maximum residue limits (MRL) ranging from 10 to 600 μg $kg^{-1}$.[16]

This molecule presents high uptake by plants, half-life in soil of 80 to 100 days[17,18] and water solubility of 39.8 g $L^{-1}$, which facilitates its drag and leaching to lower soil layers and can lead to groundwater contamination.[7,19] Therefore, Brazilian legislation has classified this insecticide as a very dangerous product for the environment.[16]

To the best of our knowledge, only the QuEChERS (quick, easy, cheap, effective, rugged, and safe) method[10,20-23] and solid phase extraction (SPE)[24,25] have been successfully optimized and validated for monitoring this insecticide for soil matrices so far. However, the development of new extraction methods which are easy to execute, sensitive and efficient has been highly recommended.

In this scenario, we can highlight the solid-liquid

*e-mail: flavianosilverio@ufmg.br
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extraction with low temperature purification (SLE-LTP) method, which consists of extracting an analyte from a solid matrix by adding water and organic solvent and lowering the temperature (–20 ºC).[26] At this stage, the components matrix are entrapped into the ice structure, while the target analyte migrates to the liquid organic solvent, and generally, no additional clean-up step has been necessary.[26-29] Although this method has already been optimized and validated for monitoring several pesticides,[28,30,31] to the best of our knowledge, no studies employing this method have been performed to determine dinotefuran in soil samples.

Therefore, the aim of this study was to optimize and validate SLE-LTP using high-performance liquid chromatography coupled diode array detection (HPLC-DAD) to determine dinotefuran residues in soil samples.

## Experimental

### Reagents and solutions

Dinotefuran standard with 99.9% purity (m/m) was purchased from Sigma-Aldrich (St. Louis, USA). HPLC-grade acetonitrile (ACN) was purchased from J.T. Baker (Phillipsburg, USA). The adsorbents such as primary-secondary amine (PSA) and the C18-reversed phase silica gel were purchased from Sigma-Aldrich (St. Louis, USA), while the silica was obtained from Macherey-Nagel (Düren, Germany). PA-grade solvents such as ethyl acetate (EtOAc) were purchased from Dinâmica (Diadema, Brazil), acetonitrile (ACN) was purchased from Êxodo Científica (Sumaré, Brazil) and formic acid (FA) was purchased from Sigma-Aldrich (St. Louis, USA). Solid reagents such as sodium hydroxide were purchased from Alphatec (São José dos Pinhais, Brazil) and sodium chloride was purchased from Vetec (Rio de Janeiro, Brazil). Stock and working solutions were prepared at concentrations of 20 and 5 mg $L^{-1}$, respectively, both in HPLC-grade acetonitrile. All solutions were stored in an amber bottle at –20 °C.

### Soil samples

Loamy clay soil was used to optimize the extraction method, and the chemical composition can be seen in Table S1 (Supplementary Information (SI) section).

### Equipment

An analytical scale from Shimadzu (São Paulo, Brazil), a digital pHmeter from Quimis (São Paulo, Brazil), a vacuum pump from Prismatec (Itu, Brazil), a vortex from Scilogex (Rocky Hill, USA), an ultraviolet and visible Cary 60 model spectrophotometer from Agilent Technologies (St. Clair, USA), and a Kindly KC5 model centrifuge (Guarulhos, Brazil) were used in this study. The micropipettes used were Labmate Pro 20-200 ± 0.1, 100-1000 ± 1 and 1000-5000 ± 5 µL HTL (Warsaw, Poland), and 0.22 µm polytetrafluoroethylene (PTFE)-membrane from Filtrilo (Colombo-PR, Brazil).

### Chromatographic analyzes

The chromatographic analyzes were performed in a high-performance liquid chromatograph coupled to a diode array detector (HPLC-DAD, model 1290, Agilent Technologies, St. Clair, USA). The extracts were analyzed according to the chromatographic conditions described in a previous study,[32] with injection volume of 10 µL, Kinetex (C18) column (100 Å, 150 mm × 4.6 mm, 5 µm) (St. Clair, USA). The column temperature was 20 ºC, mobile phase flow was 0.3 mL $min^{-1}$, and the wavelength was 270 nm. The mobile phase composition was ACN with formic acid at 0.1% (v/v) (A) and water with formic acid at 0.1% (v/v) (B); in gradient: 50% A (0 min), increased to 100% A (0-7 min), remained at 100% A (7-8.5 min), returned to 50% A (8.5-8.6 min), then maintained until the final time (13 min).

### Clean-up step

The PSA, silica and C18-reversed phase silica gel adsorbents were used in the clean-up step of soil extracts, according to Table 1.

**Table 1.** Study of the clean-up of soil extracts

| Adsorbent | | |
|---|---|---|
| PSA / mg | C18 / mg | Silica / mg |
| 25 | 25 | 25 |
| 50 | 50 | 50 |
| 100 | 100 | 100 |

PSA: primary-secondary amine; C18-reversed phase silica gel.

### SLE-LTP optimization

The SLE-LTP was optimized by evaluating extracting phase compositions, freezing time, extracting phase acidification, ionic strength by adding NaCl, sample mass and water volume added to the sample for extracting dinotefuran from the soil, as can be seen in Table 2. The analysis of variance and the Scott-Knott test ($P < 0.05$) were used to compare the recovery means. First, 4 g of dinotefuran-free soil were added to a 22 mL glass vial and

fortified with 72.65 µL of the working solution containing dinotefuran at 5 mg $L^{-1}$ to obtain a concentration of 90 µg $kg^{-1}$ in the soil, and kept at rest for one hour. Then, 4 mL of ultrapure water and 8 mL of extracting phase were added. This mixture was then vortexed for 30 s and placed in a freezer at –20 °C until complete freezing of the aqueous phase. Next, 3 mL of the liquid organic phase were placed in a centrifuge tube containing one of the evaluated PSA, silica and C18-reversed phase silica gel (Table 1). The mixture was again vortexed for 30 s, centrifuged 4000 rpm for 8 min, and all of the supernatant (3 mL) was transferred to a 5 mL glass vial, completely evaporated and resuspended in 400 µL of the mobile phase. Finally, the extracts were filtered using a nylon filter (0.22 µm) and stored in a 2 mL vial at –20 °C until analysis by HPLC-DAD. This procedure was performed for all experiments described in Table 2.

### Method validation

The method was validated as recommended by the National Institute of Metrology, Standardization and Quality (INMETRO)[33] and SANTE[34] guidance. Selectivity, limit of detection (LOD), limit of quantification (LOQ), precision, accuracy, linearity and matrix effect were evaluated.

### Selectivity

Selectivity was evaluated by comparing the chromatograms of the dinotefuran-spiked matrix extract and the dinotefuran-free matrix extract (blank) in six independent replicates.

### LOD and LOQ

LOD and LOQ were determined by the signal/noise ratio. The LOD was determined as the lowest concentration of dinotefuran-spiked matrix extract that provided a signal three times greater than the noise signal at the same retention time of dinotefuran, and the LOQ the lowest concentration of dinotefuran-spiked matrix extract that provided a signal ten times greater than the noise signal in the same retention time of dinotefuran.

### Precision and accuracy

Accuracy was evaluated by spiked and recovery experiments at three concentrations of 15.0, 90.0 and 115.0 µg $kg^{-1}$, with three replicates each. The method was considered accurate if the analyte recovery presents values between 70 and 120%. Precision was evaluated using the concentration level of 90.0 µg $kg^{-1}$ with seven repetitions. The acceptability criterion was the relative standard deviation (RSD) of the replicates less than 20%.

### Linearity

Linearity was evaluated by plotting a calibration curve with six concentration levels of: 15.0, 40.0, 65.0, 90.0, 115.0 and 140.0 µg $kg^{-1}$, with three independent replicates for each level. The linear regression parameters of slope, intercept and determination coefficient ($R^2$) were estimated by the method of ordinary least squares. Outliers were detected according to the Jackknife test, where the maximum exclusion of 22.2% of the original data was allowed, and exclusion of all repetitions of the same concentration level was not allowed.

**Table 2.** Optimized parameters in SLE-LTP

| Exp. | Parameter | | | | | | |
|---|---|---|---|---|---|---|---|
| | Extracting phase / mL | Water / mL | Sample / g | FA | NaOH | NaCl | Freezing time / h |
| 1 | 8 ACN | 4 | 4 | – | – | – | 1 |
| 2 | 8 ACN | 4 | 4 | + | – | – | 1 |
| 3 | 6.5 ACN/1.5 EtOAc | 4 | 4 | – | – | – | 1 |
| 4 | 8 ACN | 4 | 4 | + | – | – | 0.5 |
| 5 | 8 ACN | 4 | 4 | – | – | + | 2 |
| 6 | 8 ACN | 4 | 4 | + | – | + | 2 |
| 7 | 6.5 ACN/1.5EtOAc | 4 | 4 | – | – | – | 2 |
| 8 | 8 ACN | 4 | 4 | + | – | – | 2 |
| 9 | 8 ACN | 4 | 4 | + | – | – | 3 |
| 10 | 6.5 ACN/1.5 EtOAc | 4 | 4 | – | – | – | 3 |
| 11 | 8 ACN | 2 | 4 | – | – | – | 1 |
| 12 | 8 ACN | 4 | 2 | – | – | – | 1 |
| 13 | 8 ACN | 4 | 4 | – | + | – | 1 |

Exp.: experiment; ACN: acetonitrile; EtOAc: ethyl acetate; FA: formic acid solution 0.1% (v/v); NaCl: 0.2 g sodium chloride for extract; NaOH: aqueous solution $10^{-6}$ mol $L^{-1}$. (+) present and (–) absent.

The normality, homoscedasticity and independence of the regression residues were evaluated using the Ryan and Joiner, Brown and Forsythe and Durbin and Watson tests, respectively. Analysis of variance (ANOVA) was applied to data from calibration curves to verify regression significance and linearity deviations.

### Matrix effect

This parameter was evaluated by two calibration curves, with the first in solvent (acetonitrile) and the second in spiked soil matrix extract, both containing the dinotefuran at the concentrations of 15.0, 40.0, 65.0, 90.0, 115.0 and 140.0 μg $kg^{-1}$, in triplicate. Both curves were evaluated according to the linearity procedure, as previously described. The matrix effect was determined by equation 1.

$$\text{Matrix effect}(\%) = 100 \times \left( \frac{a_{matrix}}{a_{solvent}} - 1 \right) \quad (1)$$

where $a_{matrix}$ = slope of the calibration curve in spiked soil extract; $a_{solvent}$ = slope of the calibration curve in solvent (acetonitrile).

### Determination of dinotefuran in real samples

A total of 19 soil samples were collected in the municipality of Poço Fundo, in the south of the Minas Gerais state. This region has intense agricultural activity in coffee cultivation. This crop is among those authorized by Brazilian legislation for the use of dinotefuran insecticide. Thus, 300 g of soil sample were collected, placed in plastic bags and stored at room temperature until analysis. The samples were separated from the organic material, homogenized, sifted through a 0.6 mm sieve and taken for analysis. The geographical coordinates of each sample can be seen in Table S2 (SI section).

## Results and Discussion

### Optimization of chromatographic conditions

A recent study[32] revealed the chromatographic conditions to determine dinotefuran in water samples. These chromatographic conditions were used to determine this insecticide in soil samples and the chromatogram obtained is shown in Figure S1 (SI section).

Although most interferents freeze with the aqueous phase, soil is a very complex matrix and the results revealed a chromatogram with many interfering signals and with baseline elevation, so it was necessary to add a cleanup step of the extracts before the chromatographic analyses.

### Clean-up of the extracts

In general, organic extracts obtained through the SLE-LTP method do not need cleaning up. However, in this study, an additional clean-up step was necessary to remove an interferent with a retention time close to the dinotefuran peak. Therefore, three adsorbents in three levels were evaluated, as can be seen in Table 1. The obtained results are shown in Figure 2.

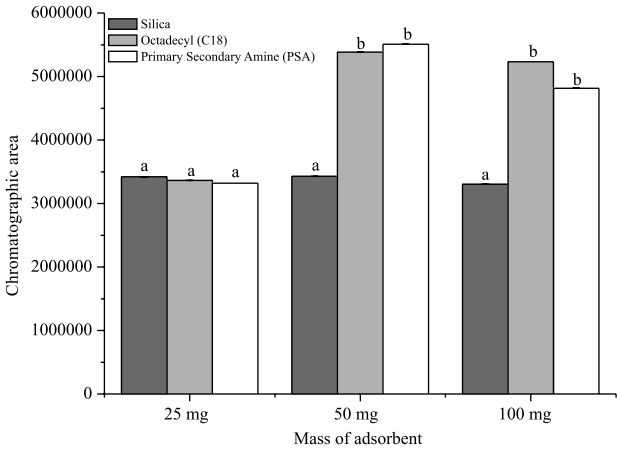


**Figure 2.** Chromatographic areas of dinotefuran in the spiked matrix extract at 90 μg $L^{-1}$ using silica, C18-reversed phase silica gel and primary-secondary amine (PSA) as adsorbents. Different letters mean different recovery means by the *t*-test at 5% significance.

The results revealed that the largest chromatographic areas for the dinotefuran signal were obtained using 50 mg of PSA or 50 mg of C18-reversed phase silica gel as adsorbents. The chromatograms obtained in each of these experiments are shown in Figure S2 (SI section).

The addition of silica in the three amounts promoted a smaller chromatographic area for the dinotefuran peak, as may be seen in Figure 2. The clean-up using PSA and C18 showed similar results using 50 or 100 mg and lower results using 25 mg. Therefore, 50 mg of PSA was chosen for the next stages of this study, because this chromatogram showed a smaller amount of interferents and did not reduce the dinotefuran signal.

A previous study[10] revealed that PSA was the best adsorbent used to clean up soil extracts containing neonicotinoids. However, C18 was chosen as the best adsorbent for clean-up in another study[20] that aimed to determine dinotefuran in soil and cucumber.

### SLE-LTP optimization

The optimized parameters in this study were extracting phase compositions, freezing time, extracting phase acidification, ionic strength by adding NaCl, sample mass

and water volume added to the sample for extracting dinotefuran from the soil (Table 2). The dinotefuran recovery percentages obtained in each experiment are shown in Figure 3.

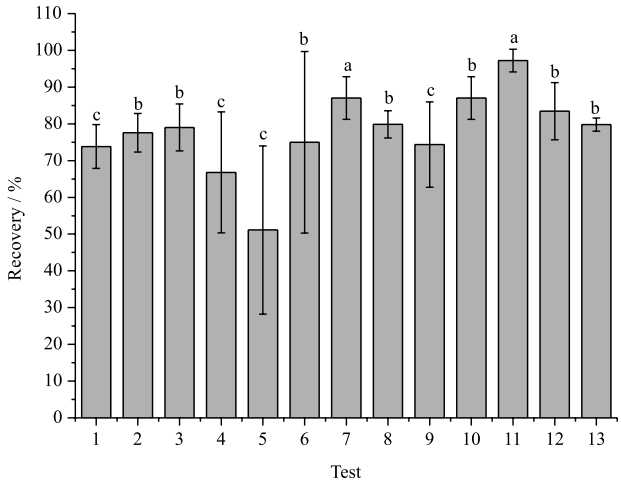


**Figure 3.** Dinotefuran recovery percentages using different extraction phases in SLE-LTP, according to Table 2. Different letters mean different recovery means by the Scott-Knott test at 5% significance.

The RSD of experiments 4, 5 and 6 were higher due to the partial freezing of the extractor phase. This happened due to the shorter freezing time in experiment 4, and the addition of salt (0.2 g of sodium chloride) in experiments 5 and 6. The dinotefuran recovery percentages were lower and the RSDs were higher in these experiments.

The results showed that experiments 7 and 11 promoted greater dinotefuran recovery from soil samples. However, experiment 7 demands a longer freezing time and a greater number of solvents. Therefore, experiment 11 was chosen because it was simpler and more economical, using only ACN as the extractor phase and requiring only 1 h for complete freezing of the matrix.

The solubility of dinotefuran in water is 39.8 g $L^{-1}$ (Table S3, SI section), which contributes to the lower transfer of molecules of this insecticide from the soil matrix to the extracting phase. Therefore, it was observed in experiment 11 that the reduction in the amount of water (2 mL) added in the soil sample improved the analyte extraction. In addition, the reduction of the amount of water added to the sample increased the extracting phase/water ratio, which also helped in the extraction process.

The higher proportion of organic phase was also shown to be more efficient in the extraction of organochlorines in water samples by dispersive liquid-liquid microextraction,[35] for neonicotinoids, carbamates and phenyl pyrazole in plant extracts using the QuEChERS method,[36] and for drugs and pesticides from aquaculture products using the QuEChERS method.[37]

After optimizing the chromatographic and extraction conditions, the validation stage followed the recommendations of the SANTE Guidance.[34]

## Method validation

### Selectivity

The method was considered selective for the dinotefuran because no interference peaks were detected at the same dinotefuran retention time, i.e., in 4.62 min, as can be seen in Figure 4.

### LOD and LOQ

The LOD and LOQ values achieved in this study are presented in Table 3. The LOQ reached is within the range of (MRLs) allowed for dinotefuran by Brazilian legislation (10

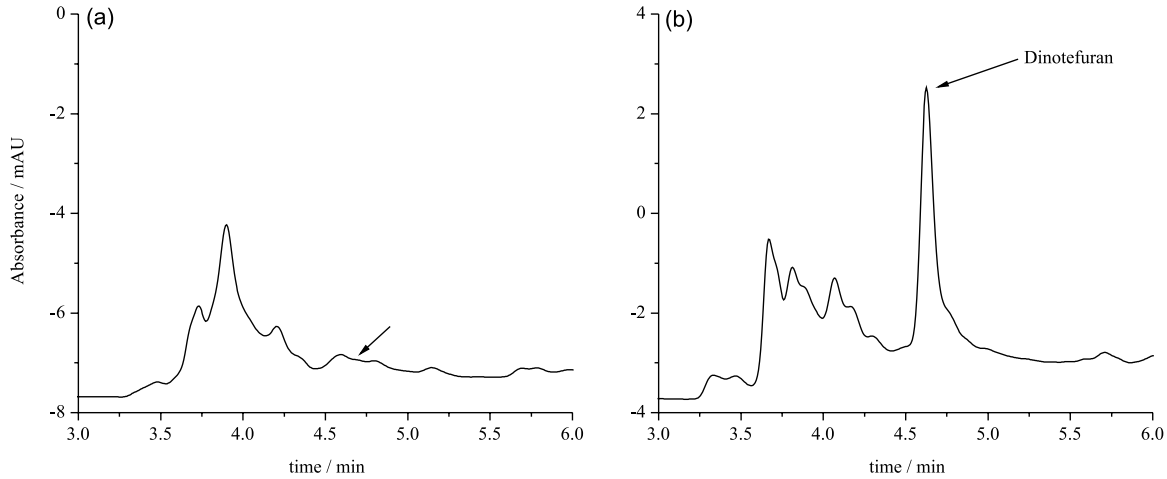


**Figure 4.** Chromatograms of dinotefuran-free soil matrix extract (a) and soil matrix extract spiked with dinotefuran at a concentration of 90 μg $L^{-1}$ (b). Chromatographic conditions: Kinetex (C18) (100 Å, 150 mm × 4.6 mm, 5 μm), flow rate 0.3 mL $min^{-1}$, temperature 20 ºC, λ = 270 nm, mobile phase: ACN with 0.1% (v/v) formic acid (A) and water with 0.1% (v/v) formic acid (B).

to 600 μg $kg^{-1}$) for several agricultural crops,[16] but national and international legislations have not yet established MRLs for dinotefuran in soil. However, the United States Environmental Protection Agency (US EPA)[38] admits the accidental and involuntary ingestion of soil and/or clay, with the maximum acceptable values being 50 and 200 mg *per* day for adults and children, respectively. In this scenario, a previous study[39] revealed that the maximum intake of dinotefuran via soil consumption would be 17.8 μg $kg^{-1}$ $day^{-1}$ for children and 4 μg $kg^{-1}$ $day^{-1}$ for adults based on maximum application dosages in household environments.

Previous studies[25,40] revealed that the daily neonicotinoid intake from regions of high agricultural applications, including food intake, soil particle ingestion and inhalation, were $1.2 \times 10^{-4}$ mg (kg live weight)$^{-1}$ $day^{-1}$ for adults and $2.2 \times 10^{-4}$ mg (kg live weight)$^{-1}$ $day^{-1}$ for children.

Brazilian legislation through the Resolution 420 of 2009 from National Council for the Environment[41] has established the MRL for other insecticides such as dichloro-diphenyl-trichloroethane (DDT), dieldrin and endrin as between 200 and 5000 μg $kg^{-1}$ for soils. Therefore, the LOQ value found for dinotefuran is lower than that established for other pesticides, demonstrating the potential of this method to monitor dinotefuran in soil.

The LOD and LOQ values achieved in this study were similar to those found in other studies.[10,20,42] A previous study[42] using QuEChERS method followed by HPLC-DAD analysis for dinotefuran determination reached LOD values of 25 and 20 μg $kg^{-1}$ and LOQ values of 80 and 70 μg $kg^{-1}$ for cucumber and soil, respectively. In another similar study carried out in Egypt using the same extraction method followed by HPLC-DAD analysis for determining dinotefuran, LOD values of 10 and 3 μg $kg^{-1}$ and LOQ values of 30 and 10 μg $kg^{-1}$ were found for soil and cucumber, respectively.[20] On the other hand, a previous study[10] achieved a LOD of 0.03 μg $kg^{-1}$ and LOQ and 0.11 μg $kg^{-1}$ for the dinotefuran determination in soil, but it was used the QuEChERS method followed by LC-MS/MS analysis.

### Precision and accuracy

The precision and accuracy results achieved are shown in Table 3. Precision was confirmed by RSD values 3.6%, i.e., below the acceptability value of 20%. The accuracy was confirmed by the recovery values found between 83.4-92.9%, i.e., within the acceptable range of 70 to 120%, following the recommendations SANTE guidance.[34]

### Linearity

The method linearity was validated through the calibration curve of the soil sample extracts spiked with dinotefuran in six equidistant levels, with three independent repetitions in each level, with the first concentration being the LOQ value (Figure S3, SI section).

The linear regression values were estimated by the ordinary least squares method (OLSM), thus obtaining the slope, intersection and $R^2$ as may be seen in Table 3 and Figure S3a. Outlier values were analyzed using the Jackknife test, requiring the exclusion of one point (Figure S3b).

Linear regression residuals showed normal distribution by the Ryan-Joiner test, with a correlation coefficient (0.9886) greater than the critical correlation coefficient (0.9437) (Figure S4c, SI section). There was also homoscedasticity of the residues as confirmed by the Brown-Forsythe test, because $t_L$ (0.0693) was smaller than $t_{critical}$ (2.1200). The Durbin-Watson test demonstrated the independence of the regression residues which are randomly distributed in the four quadrants of the Figure S3d). ANOVA showed that the regression was significant, because the *p*-value was smaller than 0.01 and the deviation from linearity was not significant (*p*-value < 0.05), confirming that the ordinary least squares method was adequate to estimate the slope, intercept and $R^2$ coefficients. Statistical evaluation of linearity followed the recommendations of previous studies.[43,44]

### Matrix effect

The matrix effect was determined through the two calibration curves of dinotefuran prepared in acetonitrile (solvent) and in soil matrix extracts (Figure S3a). The calculated matrix effect was 14.18%, indicating an increase in the chromatographic response of dinotefuran caused by soil extract components. A similar work showed that soil

**Table 3.** Validation results of the SLE-LTP method in soil samples

| Linear range / (μg $kg^{-1}$) | $R^2$ | Mean recovery ± RSD / % | | | LOD / (μg $kg^{-1}$) | LOQ / (μg $kg^{-1}$) |
|---|---|---|---|---|---|---|
| | | 15.0 μg $kg^{-1}$ [a] | 90.0 μg $kg^{-1}$ [b] | 115.0 μg $kg^{-1}$ [a] | | |
| 15.0-140.0 | 0.9955 | 87.8 ± 1.4 | 92.9 ± 8.4 | 83.4 ± 1.3 | 10.0 | 15.0 |
| Equation | Y = 67980.8X – 132289.8 | | | | | |

[a]Mean of three repetitions; [b]mean of seven repetitions. $R^2$: determination coefficient; RSD: relative standard deviation; LOD: limit of detection; LOQ: limit of quantification; Y: chromatographic area of dinotefuran peak; X: concentration of dinotefuran in the spiked matrix extract.

matrix effects for dinotefuran and other neonicotinoids were close to those found in this study (–9.63%, at 9.81).[10,20,45]

Another previous study[20] has shown that matrix effect of 9.74% was observed in dinotefuran determinations in soil samples, and the soil matrix effect for neonicotinoid determinations was between 9.81 and 12.29%. However, in a study[10] carried out in China, the suppression of neonicotinoids peaks caused by the soil extract components was between –0.28 to –27.88%, with the matrix effect of dinotefuran being –9.63%.

The exact mechanism of suppression or enhancement caused by the matrix components is still not completely elucidated.[45] However, this phenomenon has been believed to be associated with the type of matrix and the efficiency of the sample preparation step. In this sense, the presence of endogenous, organic or inorganic substances present in the sample and recovered together with the extract and the possible contamination of the sample in the preparation steps are identified as causing the matrix effect.[46]

The type of texture (clay, silt and sand content) and organic matter content for the soil matrix are closely linked to the presence of unknown compounds that can have a great influence on the matrix effect.[47] However, the matrix effects found for soil matrix in this study may be considered low.[48]

### Comparison between extraction methods

Until now, the solid-phase extraction and QuEChERS methods have been applied to determine dinotefuran in soil samples. Therefore, a comparative study of these extraction methods with optimized and validated SLE-LTP is shown in Table 4.

The data presented in Table 4 revealed that SLE-LTP used less adsorbent in the clean-up stage compared to the QuEChERS method, but SPE did not have a clean-up stage. In relation to the number of steps in the extraction method, SLE-LTP had fewer steps than the QuEChERS and SPE methods. However, the main advantages observed for SLE-LTP in relation to the other two methods were the smaller volume of organic solvent in the extraction phase and the smaller amount of sample for extraction, as SLE-LTP used almost ten times less organic solvent and five times less sample mass than SPE.

### Dinotefuran determination from real samples

Dinotefuran residues were not detected in the 19 soil samples collected in the city of Poço Fundo, Minas Gerais. Dinotefuran and your metabolites have a low octanol/water partition coefficient, Kow (0.283) and Log Kow (–0.549), suggesting a low interaction of this insecticide with different types of soil.[39,49] Therefore, it is improbable that dinotefuran remains retained in any kind of soil. Furthermore, SLE-LTP followed by HPLC-DAD analysis showed recovery rates close to 85.4%. This scenario proves that the soil samples analyzed did not contain dinotefuran residues or had concentrations below the LOQ achieved in this study, i.e., 15 μg $kg^{-1}$. Another factor that may have contributed to the non-detection of dinotefuran residues in soil samples may have been the half-life of this insecticide. A previous study[49] revealed that the dinotefuran has medium half-life of 50 to 100 days protected from light, and 7 to 8 days in the presence of sunlight.

A recent study[10] which conducted an investigation of several neonicotinoid insecticides in soils in urban areas in China reported that only flonicamid and nitenpyram were not detected, and the authors attributed this fact to the non-use of these insecticides in the test areas and the lower registration of this product in the country.

**Table 4.** Comparative study of extraction methods for determining dinotefuran in the soil matrix

| | Present study | Farouk *et al.*[20] | Zhou *et al.*[10] | Gu *et al.*[25] |
|---|---|---|---|---|
| Analysis technique | HPLC-DAD | HPLC-DAD | LC-MS/MS | UPLC-MS/MS |
| Extraction method | SLE-LTP | QuEChERS | QuEChERS | SPE |
| Cleaning step / mg | 50 PSA | 400 C18 | 200 PSA | – |
| Number of steps | 7 | 9 | 9 | 12 |
| Solvent volume / mL | 8 | 25 | 10 | 70 |
| Sample mass / g | 4 | 10 | 5 | 20 |
| Recovery rate / % | 85.4 | 99.00 | 85 | 78 to 103[a] |
| RSD / % | 5.8 | 1.97 | | 3.6 |

[a]Dinotefuran and seven more nicotinoids: acetamiprid, thiamethoxam, imidacloprid, clothianidin, thiacloprid, dinotefuran, nitenpyram and imidaclothiz. HPLC-DAD: high performance liquid chromatography with diode array detection; LC-MS/MS: liquid chromatography with detection by tandem mass spectrometry; UPLC-MS/MS: ultra-liquid chromatography with detection by tandem mass spectrometry; SLE-LTP: solid-liquid extraction with low temperature purification; QuEChERS: quick, easy, cheap, effective, rugged, and safe; SPE: solid-phase extraction; RSD: relative standard deviation; PSA: primary-secondary amine; C18-reversed phase silica gel.

On the other hand, dinotefuran residues were the most detected neonicotinoid in the flowers of cotton crops in China in the years 2020 and 2021, with a frequency of 24.5% of the samples, and a mean concentration of 25.7 μg $kg^{-1}$ in the flower stamens.[11]

In a study carried out in France,[12] where the use of dinotefuran is only allowed in veterinary products, this insecticide was detected in birds in the order of 2.14 to 9.10 ng $L^{-1}$ in the winter of 2020/2021 and 3.32 to 16.6 ng $L^{-1}$ in the winter of 2021/2022.

For soils in urban areas in China, dinotefuran residues were only detected in one sample collected in a green belt park, at a concentration of 1.35 μg $kg^{-1}$.[10]

## Conclusions

The SLE-LTP followed by HPLC-DAD analysis may be considered an efficient method for monitoring dinotefuran in soil samples because it met all validation parameters; in addition, the method proved to be easy to execute due to the reduced number of steps, fast and economical when compared to other extraction methods already used for this insecticide in soil. Dinotefuran residues were not detected in soil samples collected in agricultural production areas, which may be attributed to the reduced use of this product due to the recent authorization of this pesticide in Brazil.

## Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br as a PDF file.

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