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Supplementary material

SUPPLEMENTARY MATERIAL TO

Unified method for multiresidue pesticide analysis in corn and sediment

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Sampling and Localization (Cont.)

Detailed maps illustrating the locations of the collection points for both matrices, corn and sediments, are provided in Fig. S-1 and S-2.

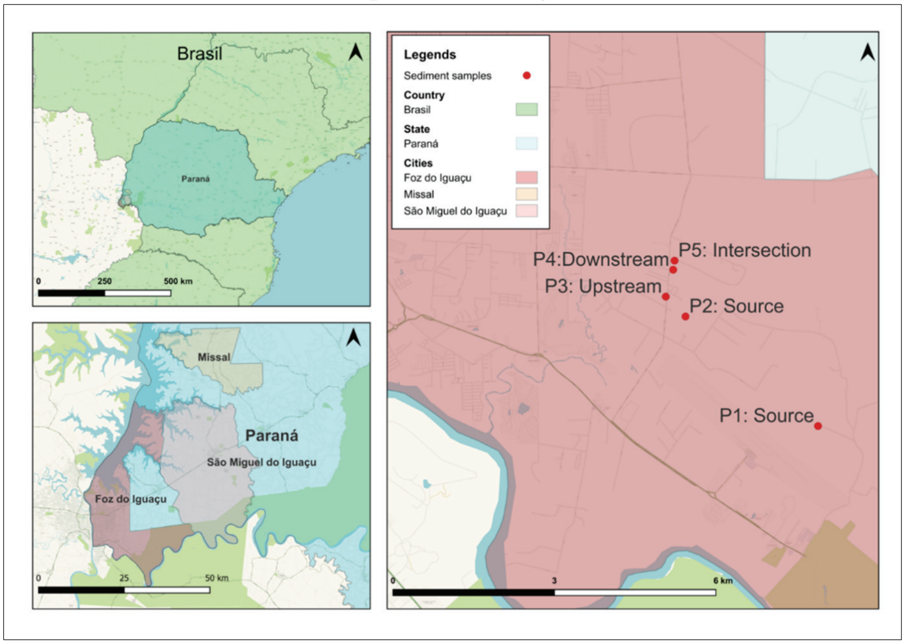

Fig. S-1. Spatial distribution of sampling sites selected for sediments samples collection using the modified QuEChERS/GC-MS method in Paraná State , Brazil.

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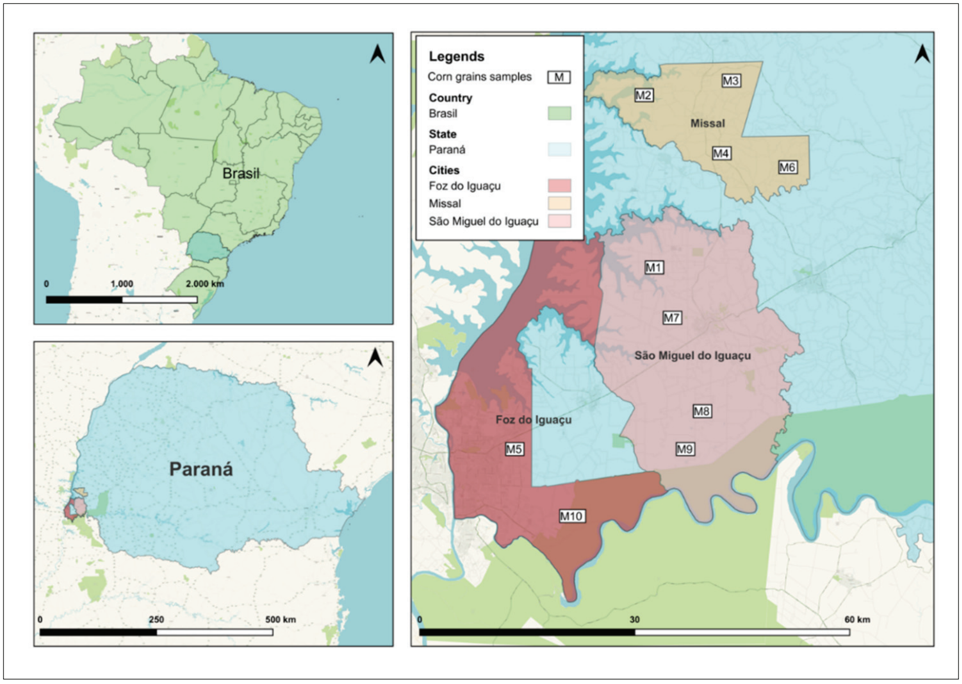

Fig. S-2. Spatial distribution of sampling sites selected for corn samples collection using the modified QuEChERS/GC-MS method in Paraná State , Brazil.

Method Validation (Cont.)

The limit of detection (LOD) refers to the smallest quantity of analyte in a sample that can be detected but not necessarily quantified under the conditions set for the assay conditions.[1] Estimating the limit of detection using parameters from the analytical curve provides greater statistical reliability, as it considers the confidence interval of the regression. In this context, the LOD is defined as the minimum concentration of a substance that can be measured and reported with either 99% or 95% confidence.

The estimation of the analytical signal from the regression equation introduces a standard error. By multiplying this error by the approximate value of t from Student's distribution, the confidence interval of the analytical curve can be calculated . This interval is represented by two hyperbolic lines surrounding the obtained curve, as illustrated in Figure S-3.[2]

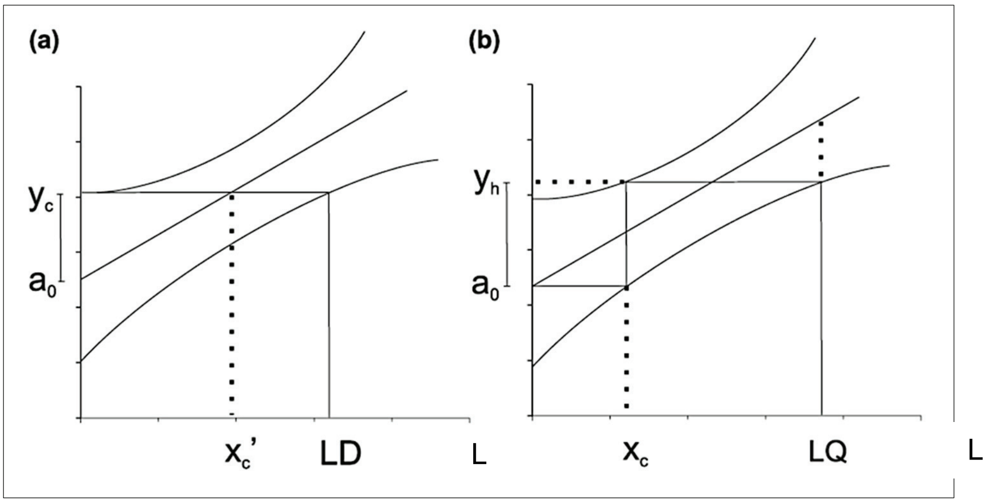

Fig. S-3. Calibration curve with illustration of the parameters used in the calculation of: (a) the limit of detection (LOD) and (b) limit of quantification (LOQ). Source: Ribeiro *et al.*[34]

The upper limit of the confidence interval is referred to as y_c (y - critical). Its projection onto the lower limit provides an estimate of the minimum concentration that can be measured with a statistically validated level of confidence, known as the limit of detection (LOD) of the method. This limit is determined by calculating the standard deviation s_y, for a linear fit, as described in Equation S-1.

$$s_y = \sqrt{\frac{\sum \left(y_i - \hat{y}_i\right)^2}{N - 2}} \tag{S-1}$$

Where N represents the number of measurements; y_i is the individual value of the instrumental signal (response); $\hat{y}_i$ is the value of the response predicted by the analytical curve equation.

$$y_c = a_0 + s_y . t \sqrt{\left(\frac{1}{N}\right) + 1 + \frac{\bar{x}^2}{\sum_{i=1}^{n}\left(x_i - \bar{x}\right)^2}} \tag{S-2}$$

On the other hand, the limit of quantification (LOQ) of an analytical procedure is the smallest amount of analyte in a sample that can be quantitatively determined with acceptable precision and accuracy.[33] The LOQ is calculated from the confidence interval of the analytical curve. Specifically, x_c represents the concentration value at the point where the value of a_0 intercepts the regression line down to the lower hyperbola. y_h corresponds to the intensity value of y, which is projected from x_c to the upper hyperbola. With these values, it is possible to calculate the LOQ using the following equations:

$$x_c = \frac{s_y \, . \, t}{a_1} \sqrt{\left(\frac{1}{N}\right) + 1 + \frac{\bar{x}^2}{\sum_{i=1}^{n}\left(x_i - \bar{x}\right)^2}} \tag{S-3}$$

$$y_h = a_0 + 2. \, s_y .t \sqrt{\left(\frac{1}{N}\right) + 1 + \frac{\left(x_c - \bar{x}\right)^2}{\sum_{i=1}^{n}\left(x_i - \bar{x}\right)^2}} \tag{S-4}$$

Matrix Effect (Cont.)

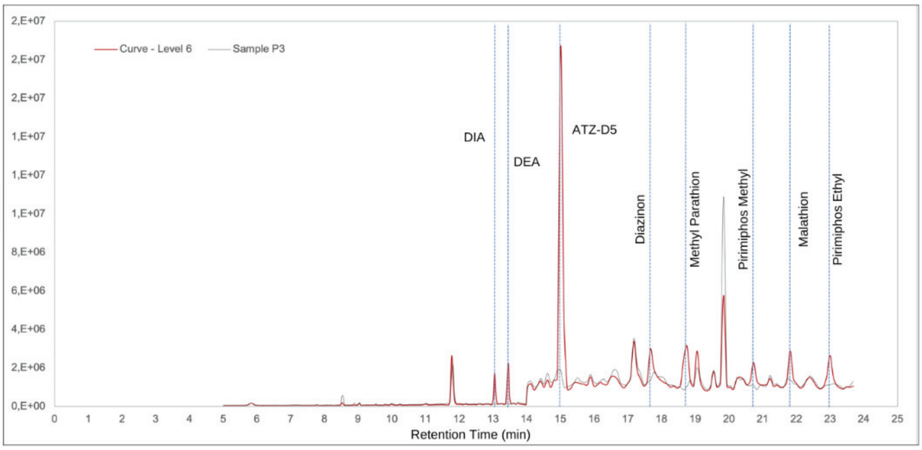

Fig. S-4. Total ion chromatogram (TIC) of pesticides obtained for a sediment sample (P3), and a calibration curve for Level 6 (42.50 μg kg^{-1}).

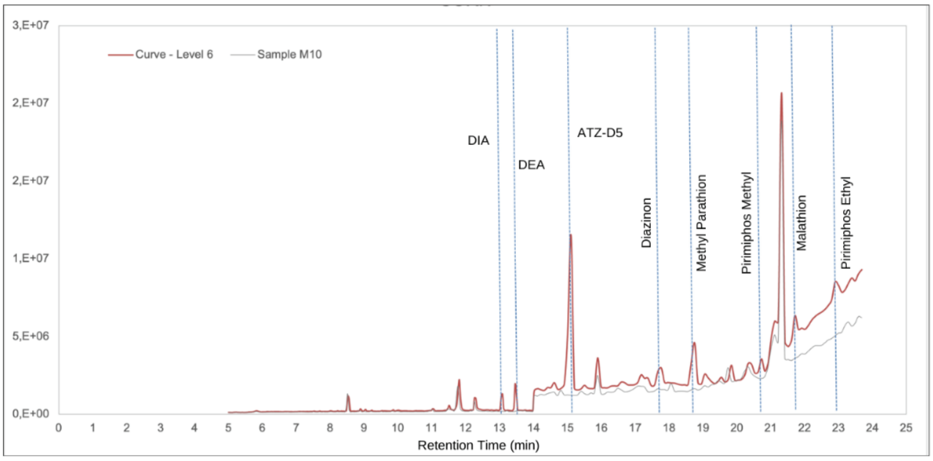

Fig. S-5. Total ion chromatogram (TIC) of pesticides obtained for a corn sample (M10), and a calibration curve for Level 6 (52.50 µg kg^{-1}).

Application of the proposed method to real samples (Cont.)

TABLE S-1. Results obtained using the linear equation derived from the modified QuEChERS/GC-MS method with sediment samples collected in the state of Paraná, Brazil.

Samples	SEDIMENTS				
	DIA	DEA	Diazinon	Malation	Pirimiphos Ethyl
P1	ND	ND	ND	ND	ND
P2	ND	ND	ND	ND	ND
P3	ND	ND	ND	ND	ND
P4	ND	ND	ND	ND	ND
P5	ND	ND	ND	ND	ND

ND: Not Detectable, below the LOD.

TABLE S-2. Results obtained using the linear equation derived from the modified QuEChERS/GC-MS method with corn samples collected in the state of Paraná, Brazil.

Samples	CORN				
	DIA	DEA	Diazinon	Methyl Parathion	Pirimiphos Methyl
M1	ND	ND	ND	ND	ND
M2	ND	ND	ND	ND	ND
M3	ND	ND	ND	ND	ND
M4	ND	ND	ND	ND	ND
M5	ND	ND	ND	ND	ND
M6	ND	ND	ND	ND	ND
M7	ND	ND	ND	ND	ND
M8	ND	ND	ND	ND	ND
M9	ND	ND	ND	ND	ND
M10	ND	ND	ND	ND	ND

ND: Not Detectable, below the LOD.

REFERENCES

1. Brazilian National Institute of Metrology, Quality and Technology (INMETRO), *Guidance on Validation of Analytical Methods DOQ-CGCRE-008*, 2020 (http://www.inmetro.gov.br/credenciamento/organismos/doc_organismos.asp?torganismo=calibensaios)
2. F. A. de L. Ribeiro, M. M. C. Ferreira, S. C. Morano, L. R. da Silva, R. P. Schneider, *Quim. Nova* **31** (2008) 164 (https://doi.org/10.1590/S0100-40422008000100029).