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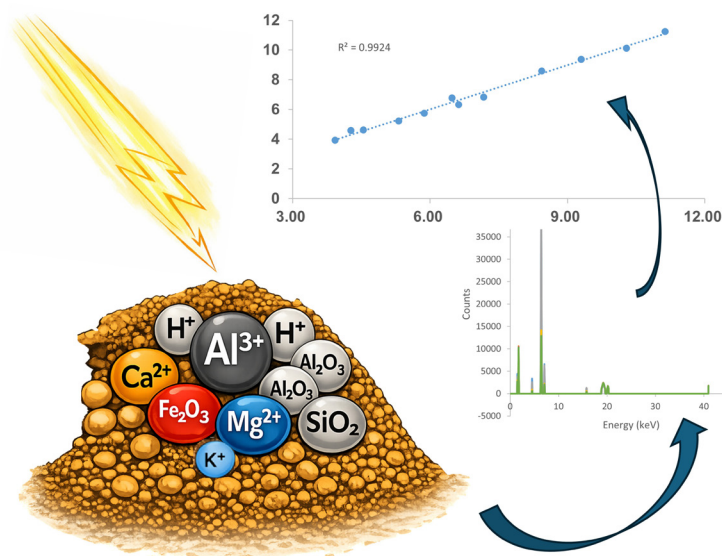
Integration of EDXRF and Chemometrics as a Fast and Green Alternative for Determining the Cation Exchange Capacity of Cerrado Soils Treated with Swine Manure

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Studies have shown that organic fertilizers derived from liquid swine waste (LSW) can improve several soil chemical properties, including cation exchange capacity (CEC). The determination of CEC is traditionally carried out using chemical methods based on cation extraction, followed by quantification through titrimetry, flame atomic absorption spectrometry (FAAS), or flame photometry. As an alternative to these classical methods, the present study aimed to evaluate energy-dispersive X-ray fluorescence (EDXRF) combined with chemometrics for the determination of CEC. For this purpose, multiple linear regression (MLR) was employed as the multivariate calibration method. The calibration model was built using X-ray intensities obtained by EDXRF and the CEC values determined by the chemical reference method (CEC at pH 7.0). The CEC values determined by the reference method ranged

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from 4.92 to 10.71 cmolc kg⁻¹. EDXRF analyses indicated a predominance of SiO₂ and Al₂O₃, reflecting the mineralogy of Cerrado soils, which are characterized by intense weathering and the presence of silicate and metal oxide minerals. The developed MLR model showed an adjusted R² of 0.97, indicating a strong correlation between the CEC values obtained by the reference method and those predicted by the model. The root mean square error (RMSE) of 0.40 cmolc kg⁻¹, approximately ten times lower than the lowest CEC value assessed, and the ratio of performance to deviation (RPD) of 5.97 demonstrate the high accuracy of the model. The characteristics of EDXRF, a rapid, non-destructive technique suitable for the analysis of solid samples, combined with MLR proved to be an efficient and environmentally friendly analytical strategy for determining CEC in Cerrado soils amended with LSW under different crops and application periods, in accordance with the principles of green chemistry.

Keywords: multiple linear regression, organic fertilizers, sustainable agriculture, tropical soils, green analytical chemistry

INTRODUCTION

Studies have shown that organic fertilization with animal manure improves several soil chemical attributes, including cation exchange capacity (CEC),¹⁻³ especially in the surface layers, due to the increase in soil organic matter (OM).³ The CEC represents the total amount of exchangeable cations that the soil can adsorb, which are retained by negatively charged clay and OM particles and can be readily exchanged and made available to plants.

The conventional method for determining CEC involves extracting cations using specific extractant solutions, KCl for Ca, Mg, and Al, and Mehlich-1 for Na and K, followed by the quantification of Al, Ca, and Mg by titration or flame atomic absorption spectrometry (FAAS), and of Na and K by flame photometry.⁴ Although widely employed, this procedure is time-consuming, requires chemical reagents, generates substantial post-analysis waste, and comprises labor-intensive laboratory steps.

As an alternative to conventional chemical methods, several spectrometric techniques have been investigated for the prediction of soil attributes, notably X-ray fluorescence (XRF),⁵⁻⁹ visible and near-infrared spectroscopy (Vis-NIR),¹⁰⁻¹⁴ gamma spectrometry (GR),¹⁵ diffuse reflectance spectroscopy (DRS),¹⁶ and laser-induced breakdown spectroscopy (LIBS).¹⁷ Additionally, data-fusion approaches combining spectral information, such as XRF with GR,¹⁸ XRF with Vis-NIR,¹⁹ and XRF, LIBS, and visible and near infrared diffuse reflectance spectroscopy (VNIR),²⁰ have shown promise for improving the accuracy of soil chemical property estimates. When integrated with chemometric methods, these techniques offer an efficient, rapid, and low-cost alternative, requiring minimal or no sample preparation.

However, to date, no studies have reported the use of XRF combined with chemometrics for determining CEC in soils amended with liquid swine waste (LSW). Considering that the addition of organic matter derived from this type of amendment can strongly influence CEC,²¹ investigating this relationship using advanced spectrometric and statistical methods becomes essential. In this context, the present study is the first to evaluate the application of EDXRF combined with chemometrics, through multiple linear regression (MLR), for determining the CEC of Cerrado soils amended with LSW.

MATERIALS AND METHODS

Sample collection and characteristics

The areas evaluated in this study encompassed six municipalities within the swine-producing region of the State of Mato Grosso, Brazil (Rondonópolis, Campo Verde, Lucas do Rio Verde, Sorriso, Tapurah, and Vera), with two sampling points in each municipality, totaling 12 samples. The sampled agricultural areas were cultivated with soybeans, corn, and pasture and had a history of fertilization with liquid swine manure for periods ranging from 5 to 10 years. Information on soil classes, sampling site locations, and the sampling procedures is provided in Silva et al.³ and Barros et al.²²

Briefly, within each property a 30-ha area was subdivided into two 15-ha plots. Soil sampling was performed following a zigzag pattern with five subsamples collected per plot using a Dutch auger at a depth of 0–0.20 m. The subsamples were combined and homogenized to form a composite sample for each plot. In the laboratory, the samples were oven-dried at 65 °C with forced air circulation, crushed, sieved through a 2 mm mesh, and manually ground using a mortar and pestle to ensure homogeneity.

Reference method

To obtain the reference CEC values required for constructing and validating the calibration model, the procedure described by Teixeira et al.⁴ was used. In summary, the extraction of Ca, Mg, and Al from soil samples amended with LSW was performed using 1 mol L⁻¹ KCl (Synth, Brazil) as the extracting solution, whereas the extraction of Na and K was carried out using the diluted acidic solution of HCl (Synth, Brazil) and H₂SO₄ (Éxodo, Brazil) (Mehlich-1 extracting solution: HCl 0.05 mol L⁻¹ and H₂SO₄ 0.0125 mol L⁻¹). Total acidity (H + Al) was extracted using a 0.5 mol L⁻¹ calcium acetate solution (pH 7.1–7.2; Synth-Brazil). The concentrations of Ca, Mg, Al, and H + Al were determined by complexometric and acid–base titration, whereas Na and K contents were quantified by flame photometry (ANALYSER 210).

EDXRF analysis

For the EDXRF chemical analysis, pressed pellets were prepared in triplicate (5–7 tons of pressure) were produced from the milled powder. A Shimadzu EDX-700HS spectrometer was employed, enabling quantitative measurements using the Fundamental Parameters (FP) approach implemented in the Qual-Quant FP[®] routine, including internal normalization and matrix correction procedures. A 10-mm X-ray beam and tube voltages of 15 and 50 kV were applied for detecting elements from sodium (Na) to scandium (Sc) and from titanium (Ti) to uranium (U), respectively. All spectra were collected under vacuum to enhance measurement accuracy for light elements, whose characteristic X-rays are strongly absorbed by matter, including air.

Data processing and model calibration (MLR)

To prevent systematic differences in the intensity levels of the spectra from affecting the performance of the multivariate calibration model, the data was autoscaled. Autoscaling consists of subtracting the mean of each variable from the dataset and dividing it by its corresponding standard deviation, resulting in variables with zero mean and unit variance.²³

After the data were preprocessed, multiple linear regression (MLR) was evaluated as the multivariate calibration model. Model performance was assessed using the root mean square error (RMSE), the adjusted coefficient of determination (adjusted R²), and the ratio of performance to deviation (RPD).²³ The RPD, defined as the ratio between the standard deviation of the reference values and the prediction error, is commonly used to evaluate the predictive ability of chemometric models.²⁴ In general, higher RPD values and lower prediction errors indicate better model performance. All calculations and modeling steps were performed using Microsoft Excel[®] and MATLAB[®] R2023a.

RESULTS AND DISCUSSION

CEC determination by the reference method and qualitative analysis by EDXRF

The CEC of the soils amended with LSW, determined by the reference method, is presented in Table I. The CEC values ranged from 4.92 to 10.71 cmolc kg⁻¹. The oxide contents obtained by EDXRF indicated a predominance of SiO₂ and Al₂O₃, ranging from 30.12% to 70.26% and from 25.86% to 51.02%, respectively, whereas Fe₂O₃ exhibited lower levels, between 3.20% and 14.07%.

Table I. Cation exchange capacity (CEC at pH 7.0) of Cerrado soils amended with liquid swine waste and oxide concentrations obtained by EDXRF

Parameters*	City					
	Rondonópolis	Campo Verde	Lucas do Rio Verde	Sorriso	Tapurah	Vera
CEC (cmolc kg ⁻¹)*	10.71	8.87	6.24	4.92	4.09	6.82
Al ₂ O ₃ (%)	42.14	51.02	28.83	31.45	25.86	45.52
SiO ₂ (%)	41.74	30.12	63.71	61.90	70.26	45.49
Fe ₂ O ₃ (%)	12.59	14.07	5.22	4.51	3.20	5.59

*CEC – Cation exchange capacity

Although EDXRF-derived oxide data suggest an indicative trend—Al₂O₃-rich soils tend to exhibit higher CEC, whereas SiO₂-dominated soils present lower values—the observed patterns should be interpreted as indicative rather than conclusive. More robust explanations would require information on clay mineralogy, oxide crystallinity, specific surface area, and organic matter fractionation. Even so, integrating CEC with the oxide composition obtained via EDXRF reinforces the potential of EDXRF not only as a rapid preliminary tool for assessing soil properties, but also as a complementary approach for the indirect estimation of CEC in heterogeneous Cerrado soilscapes.

Spectral identification and data processing

EDXRF spectra were acquired for all soil samples amended with LSW from the evaluated cities. Figure 1 shows the EDXRF spectra for all sampling locations. Each energy peak corresponds to a specific chemical element present in the sample: the peak position reflects the energy of radiation characteristic of the element, while the peak intensity is associated with its relative concentration. This relationship enables both the qualitative identification and quantitative assessment of the detected elements (Table I). In Figure 1, characteristic peaks of Al, Fe, Si, Ti, and Zr are evident and were identified using the instrument's built-in software.

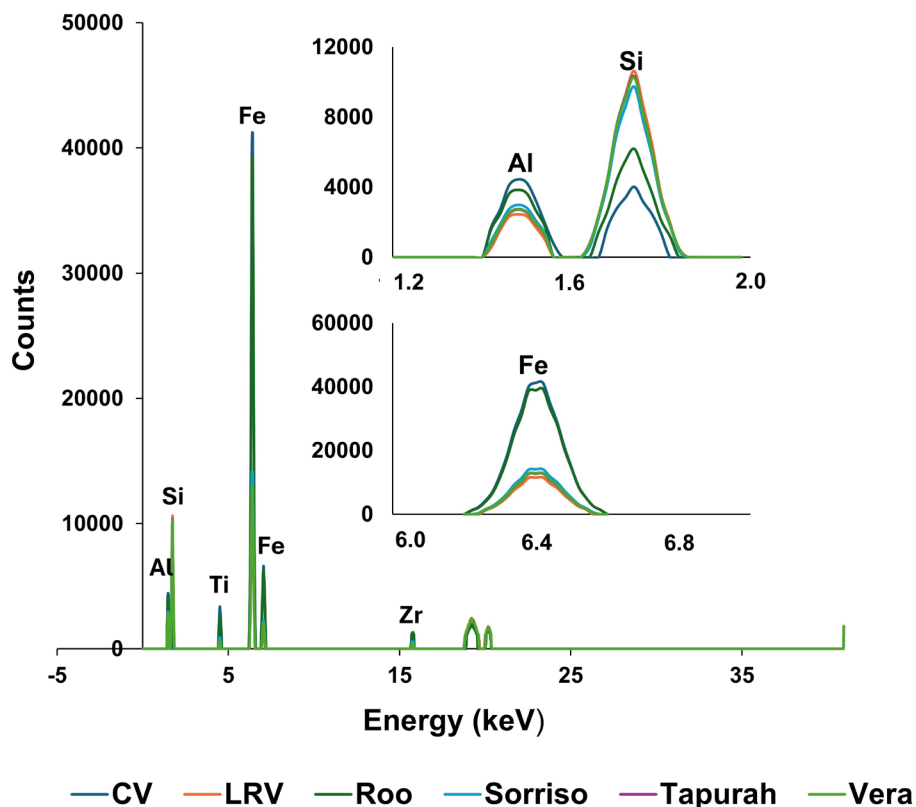


Figure 1. Energy-dispersive X-ray fluorescence (EDXRF) spectra obtained in the Ti–U channel for soil samples from the cities of Campo Verde (CV), Lucas do Rio Verde (LRV), Rondonópolis (Roo), Sorriso, Tapurah and Vera.

Figure 1 shows the raw spectra used for peak identification, without any preprocessing treatment. To prevent systematic differences in spectral intensity from affecting the performance of the multivariate calibration model, autoscaling was applied only to the variables used in the MLR model, as described in the Materials and Methods section. This preprocessing step ensures that differences in signal magnitude among the selected peaks do not bias the regression model.²³

Multivariate calibration model

The intensities obtained for $TiK\alpha$, $FeK\beta$, $ZrK\alpha$, $AlK\alpha$, $SiK\alpha$, $SK\alpha$, $KK\alpha$, and $CaK\alpha$, together with the CEC values determined by the reference method, were used to construct the data matrices for the multivariate calibration model based on MLR. The performance of the developed model was evaluated using the adjusted coefficient of determination (R^2), root mean square error (RMSE), and the ratio of performance to deviation (RPD). The corresponding values obtained for the model are presented in Table II.

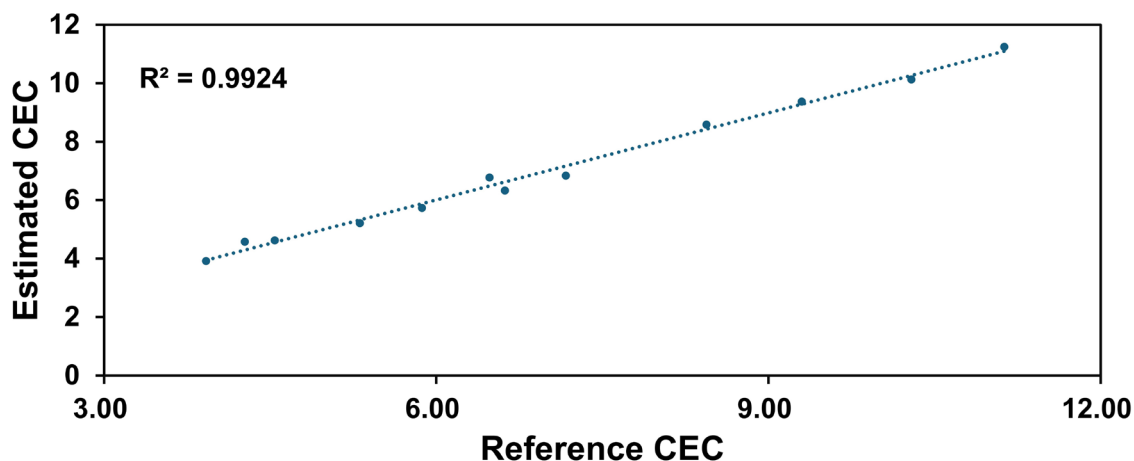
Table II. Multivariate multiple linear regression (MLR) calibration model for determining cation exchange capacity (CEC) using energy-dispersive X-ray fluorescence (EDXRF)

Parameters*	CEC
Sample concentration range (cmolc kg ⁻¹)	3.92 – 11.13
R ² _{adjusted}	0.97
RMSE (cmolc kg ⁻¹)	0.40
RPD	5.97

*Sample concentration range – concentration range of the samples used for model calibration; RMSE – root mean square error; RPD – ratio of performance to deviation.

An adjusted R² of 0.97 was obtained, indicating a strong correlation between the CEC values determined by the reference method and those estimated from the EDXRF-derived signal intensities using the MLR calibration model. The RMSE of 0.40 cmolc kg⁻¹ was well below the lowest CEC value observed in the samples, indicating good model performance within the studied concentration range. In soil science, models with RPD values > 2 are considered to exhibit excellent predictive ability.²⁴ In the proposed method, an RPD > 5 was obtained, indicating that CEC estimation using EDXRF spectral information presents high modeling capability.

Additionally, the CEC values estimated by the MLR calibration model showed strong agreement with the reference measurements, with a linear correlation coefficient (R²) greater than 0.99, as illustrated in Figure 2.

**Figure 2.** Relationship between the CEC values estimated by the EDXRF–MLR calibration model and the reference CEC measurements.

Comparing the results obtained in this study with those reported in the literature (Table III) is challenging due to several factors: (i) the type of instrumentation employed, since benchtop EDXRF systems generally provide higher energy resolution and lower noise than portable devices such as portable X-ray fluorescence (pXRF), (ii) the pedological heterogeneity of the sample sets, which reflects textural and mineralogical variability, (iii) differences in modeling approaches, including the use of linear or nonlinear models and the presence or absence of data fusion strategies, and (iv) the diversity of units used to express CEC (cmolc kg⁻¹ vs. cmolc dm⁻³) and the wide range of error metrics reported, such as RMSE, root mean square error of prediction (RMSEP), residual prediction deviation (RPD), ratio of performance to interquartile distance (RPIQ) and mean absolute error (MAE), which makes direct comparisons across studies difficult.

Table III. Comparison of models and methods for determining soil cation exchange capacity using X-ray fluorescence

Country – States*	Soil Type	Method**	Best Model***	R ² ****	Erro*****	Number of Sample (N)	Data Fusion	Ref.
Brazil – MT	Dystric and Rhodic Ferralsol Arenosol	EDXRF	MLR	0.97 R ² _{adj}	RMSE = 0.4 cmolc kg ⁻¹ RPD = 5.97	12	No	This work
United States – CA, NE	Hastings Filmore Butler Wasco	pXRF	MLR	0.908	RMSE = 2.498	360 – calibration 90 – validation	No	8
China – Yunnan	Agricultural and Forest Soils	pXRF + Vis-NIR	SVMR	0.82	RMSE = 3.02 RPIQ = 2.31	378 – calibration 194 – validation	Yes	19
Brazil – ES, BA, MG	Ultisols Oxisols Spodosols Entisols	pXRF	RF	0.75	RMSE = 0.89 cmolc dm ⁻³	197 – calibration 88 – validation	No	5
Brazil – SP, MS	Ultisol Inceptisol Entisol Oxisol Alfisol Entisol	XRF	XGB	0.78	RMSE = 12.12 MAE = 9.34 RPD = 1.94 RI = 0.00	~143 – calibration ~61 – validation	No	9
Brazil – PR	Rhodic Ferralsol Rhodic Nitisol	pXRF	PLS	0.9 - 1.0	RPD >2.0	~276 – calibration ~118 – validation	No	6
Brazil – PR (Cambé, Toledo)	Eutrophic Red Latosol	pXRF	PLS	Cambé – R ² = 0.68 Toledo – R ² = 0.69	RMSEP Cambé = 0.79 RPIQ Cambé = 2.95 RMSEP Toledo = 0.96 RPIQ Toledo = 2.28	calibration Cambé – 136 validation Cambé – 110 calibration Toledo – 100 validation Toledo – 65	No	7
Brazil – PR	Rhodic Ferrasol	XRF + GR	RF	0.70	RMSEP = 0.51 RPIQ = 2.83	64 – calibration 16 – validation	Yes	18
Brazil – MT, SP	Lixisol Ferralsol	VNIR + XRF + LIBS	GR	0.86	RPD = 2.63 RMSE = 9.95 mmolc dm ⁻³	68 – calibration 34 – validation	Yes	20

* MT – Mato Grosso; CA – California; NE – Nebraska; ES – Espírito Santo; BA – Bahia; MG – Minas Gerais; SP – São Paulo; MS – Mato Grosso do Sul; PR – Paraná. EDXRF – Energy-Dispersive X-ray Fluorescence Spectrometry; pXRF – Portable X-ray Fluorescence Spectrometry; GR – Gamma-Ray Spectrometry; VNIR – Visible and Near-Infrared Diffuse Reflectance; LIBS – Laser-Induced Breakdown Spectroscopy. ** MLR – Multiple Linear Regression; SVMR – Support Vector Machine Regression; RF – Random Forest; XGB – Extreme Gradient Boosting; PLS – Partial Least Squares Regression; GR – Granger and Ramanathan. ***R² – coefficient of determination; R²_{adj} – adjusted coefficient of determination. ****RMSEP – root mean square error of prediction; RPD – residual prediction deviation, RPIQ – ratio of prediction to interquartile range; RMSE – root mean squared error; MAE – mean absolute error.

Despite these limitations, the model developed in this study exhibited strong performance even with a reduced number of samples ($N = 12$). For comparison, Sharma et al.,⁸ using pXRF in soils from the United States ($N = 360$), reported $R^2 = 0.91$, whereas Andrade et al.,⁵ working with Brazilian soils, obtained $R^2 = 0.75$ with 197 samples. Silva et al.,⁹ using XRF and an Extreme Gradient Boosting (XGB) model ($N = 143$), reported $R^2 = 0.78$, and Ribeiro et al.,⁶ using 276 soil samples, reported R^2 values ranging from 0.90 to 1.00. More recent studies that incorporated spectral data fusion or advanced machine learning algorithms, such as Ribeiro et al.¹⁸ (XRF + GR, Random Forest (RF), $N = 64$, $R^2 = 0.70$), Wan et al.¹⁹ (pXRF + Vis-NIR, Support Vector Machine Regression (SVMR), $N = 378$, $R^2 = 0.82$), and Tavares et al.²⁰ (VNIR + XRF + LIBS, Granger and Ramanathan (GR), $N = 68$, $R^2 = 0.86$), reported results comparable to those observed in the present work. Overall, these findings highlight the potential of the proposed approach, particularly considering the limited sample size and the methodological simplicity adopted.

From the perspective of green analytical chemistry, the proposed EDXRF-based approach presents important advantages compared with conventional methods used for CEC determination. The reference method requires chemical extraction steps involving reagents and generates liquid waste during the analytical procedure. In contrast, the EDXRF technique allows the direct analysis of solid samples without the use of chemical reagents, minimizing waste generation and reducing the environmental impact of the analysis. In addition, the method is non-destructive, requires only simple sample preparation, and provides rapid measurements, which significantly reduces analysis time. These characteristics highlight the potential of EDXRF combined with multivariate calibration as a more sustainable analytical strategy for soil evaluation.

CONCLUSIONS

The association between EDXRF and MLR proved to be an efficient, rapid, and sustainable alternative for the indirect determination of CEC in Cerrado soils fertilized with LSW. The developed model exhibited excellent performance (adjusted $R^2 = 0.97$; RPD = 5.97; RMSE = $0.40 \text{ cmolc kg}^{-1}$), demonstrating a strong correlation with the reference method.

Even with a reduced number of samples ($N = 12$), the results were consistent, highlighting the potential of the proposed approach for exploratory applications. The samples analyzed were collected from agricultural areas cultivated with soybeans, corn, and pasture, where liquid swine manure has been applied as fertilizer for periods ranging from 5 to 10 years, reflecting real field conditions. The use of EDXRF combined with MLR proved to be a rapid and environmentally friendly strategy for estimating soil CEC. Furthermore, the method requires no chemical reagents, reduces analysis time, and preserves the samples, thereby aligning with the principles of green chemistry. Future studies including a larger number of samples and a broader range of soil conditions will be important to further validate and expand the applicability of the model.

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Conflicts of interest

The authors declare that there are no financial or personal conflicts of interest that could have influenced the work reported in this paper. This includes all affiliations, funding sources, and financial or management relationships.

Use of Artificial Intelligence (AI) tools

The authors declare that they have used ChatGPT for language editing and to improve the clarity of the manuscript. The authors take full responsibility for the accuracy, integrity, and originality of the article

content, and confirm that no AI tool was used to generate novel scientific ideas, analyze data independently, or replace the critical role of the authors.

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