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Spatial and geostatistical distribution of arsenic and cadmium in soils of different geological formations and land uses in Southern Brazil[1]

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ABSTRACT

Soil contamination by potentially toxic elements (PTEs) poses risks to human health and ecosystems. This study characterized the spatial distribution and controlling factors of arsenic (As) and cadmium (Cd) in soils of southern Brazil. Forty-eight soil samples from different geological formations and land uses were analyzed for physicochemical attributes and pseudo-total As and Cd contents, using descriptive statistics, Pearson correlations, analysis of variance, and geostatistics. Mean levels were 7.85 mg kg^{-1} for As and 1.02 mg kg^{-1} for Cd, below CONAMA 420/2009 Prevention Values. Arsenic showed no significant correlations with the evaluated soil attributes ($p > 0.05$) but exhibited moderate spatial dependence ($r = 0.412$; range ~45 km), with kriging maps showing higher concentrations in the central area, suggesting control by regional geological and pedogenetic processes not fully captured by the analyzed attributes. Cadmium showed no significant correlations with soil attributes and exhibited poor spatial dependence ($r = 0.187$), suggesting diffuse anthropogenic influence from phosphate fertilizers. Identified hotspots approach legal limits and require monitoring. It is concluded that As distribution is influenced by regional geopedological factors, while Cd reflects diffuse anthropogenic inputs. The integrated approach effectively distinguished natural and anthropogenic patterns, providing support for environmental management and sampling planning.

Keywords: potentially toxic elements; spatial dependence; kriging; subtropical soils.

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INTRODUCTION

Soil contamination by potentially toxic elements (PTEs) represents a global environmental concern due to its toxicity, persistence, and potential for bioaccumulation.[1] Among these elements, arsenic (As) and cadmium (Cd) stand out for their adverse effects on human health and ecosystems, even at low concentrations.[2] Arsenic is a metalloid widely distributed in the Earth's crust and can occur naturally in association with sulfide minerals or be introduced by anthropogenic activities such as mining and pesticide use.[3] Cadmium is often associated with phosphate deposits and present as an impurity in phosphate fertilizers, which is its main source in agricultural soils.[4] The dynamics of these elements in the soil are controlled by factors such as pH, organic matter and mineralogy of the clay fraction,[5] as well as the charge/valence of the element, ionic radius and electronegativity are fundamental in its dynamics in the system.

In Brazil, CONAMA Resolution No. 420/2009 establishes guiding values for soil quality, defining Prevention Values (PV) of 15 mg kg^{-1} for As and 1.3 mg kg^{-1} for Cd.[6] Regional studies have shown significant variability in the natural contents of these elements as a function of the source material and pedogenetic processes acting in the environment of soil formation and weathering.[7] Understanding the spatial distribution of PTEs is essential for the management of contaminated areas. In this sense, geostatistics allows the description of spatial patterns, the estimation of values in unsampled locations and the quantification of uncertainties,[8,9] being fundamental for identifying zones with high concentrations (hotspots) and planning monitoring actions.[10]

The Northern Plateau of Santa Catarina was selected as the study area because it presents a unique combination of geological, pedological, and land-use characteristics that make it particularly relevant for understanding the spatial distribution of As and Cd in subtropical soils. Geologically, this region encompasses a transition zone between the Paraná Basin sedimentary sequences (Rio Bonito, Palermo, Teresina, and Rio do Rasto formations) and the volcanic rocks of the Serra Geral Formation, providing a natural laboratory to evaluate the influence of contrasting parent materials on PTE contents. The Rio Bonito Formation, in particular, hosts coal deposits with carbonaceous pelites and arsenic-bearing arsenopyrite (FeAsS),[11,12] while the Serra Geral basalts are rich in Fe and Mg, whose weathering products (goethite, hematite) exert strong control on arsenate adsorption.[13] Additionally, the region has been under intensive agricultural use for decades, with the application of phosphate fertilizers containing Cd as an impurity,[4] creating a scenario where natural and anthropogenic controls on PTE distribution coexist and may interact.

Despite the recognized importance of subtropical soils in southern Brazil for global food production and the known geochemical peculiarities of the Paraná Basin, there is a scientific knowledge gap regarding the integrated assessment of As and Cd distribution in soils of the Northern Plateau of Santa Catarina, particularly with respect to: (i) whether the spatial distribution of As is controlled primarily by lithological inheritance or by pedogenetic processes; (ii) whether the regional background of Cd has been altered by diffuse anthropogenic inputs from phosphate fertilizers; and (iii) how geostatistical tools can distinguish between natural and anthropogenic spatial patterns in this subtropical environment.

Based on this context, the present study was guided by the following research hypothesis: the spatial distribution of As in soils of the Northern Plateau of Santa Catarina is primarily controlled by geogenic factors (parent material and pedogenesis), resulting in moderate spatial dependence and regional patterns, whereas the distribution of Cd is predominantly influenced by diffuse anthropogenic inputs (phosphate fertilizers and agricultural practices), leading to weak spatial dependence and homogenized contents.

The present study aimed to statistically characterize the contents of As and Cd in soils of different geological formations and land uses in the southern region of Brazil; evaluate correlations with physicochemical attributes of the soil; analyze the spatial dependence of the contents by geostatistics; and generate kriging maps to identify hotspots, aiming to subsidize environmental monitoring and sustainable management of the studied areas.

MATERIALS AND METHODS

Soil Sampling

For this research, samples were collected at 48 points distributed along the Northern Plateau region of Santa Catarina (Figure 1), spaced 10 km apart. The study region has a Köppen Cfb climate classification. Detailed information on the geographic coordinates, geological formation, land use, and altitude of each sampling point is provided in the Supplementary Material (Table S1).

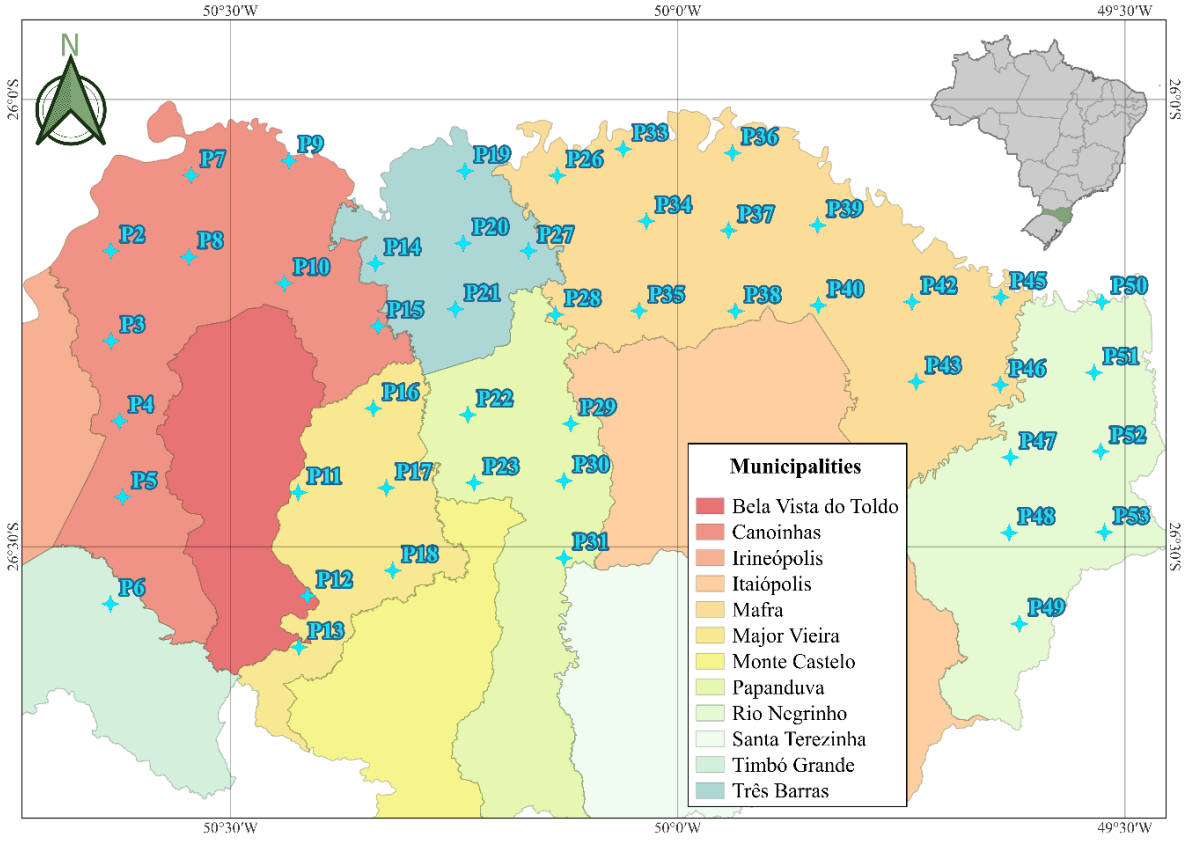

Figure 1. Location of the 48 sampling points in the Northern Plateau of Santa Catarina, southern Brazil.

At each sampling point, soil samples were collected at a depth of 0–20 cm after removal of the litter layer. The same sampling depth was used across all land-use types to ensure comparability among the different categories (agriculture, pasture, native forest, reforestation, and roadside). Each sampling point represents a composite sample obtained from three subsamples. The subsamples were homogenized in a plastic bag in the field to form a single composite sample.[14]

After collection, samples were identified, packed in plastic bags, and transported to the Laboratório de Levantamento e Análise Ambiental (Laboratory for Environmental Surveys and Analyses – LLAA) of the Centro de Ciências Agroveterinárias (Center for Agricultural and Veterinary Sciences – CAV) of the Universidade do Estado de Santa Catarina (State University of Santa Catarina – UDESC). Initially, the samples were subjected to air drying, followed by the disaggregation of the clods, grinding, and sieving in a 2 mm mesh, a procedure that resulted in obtaining the air-dried fine earth fraction (AFEF). In a later stage, in the laboratory environment, the collected samples were characterized by means of physical and chemical analyses.

Physical and Chemical Characterization of Soils

The samples from the 48 points collected were sent to the *Laboratório de Química do Solo* of the CAV-UDESC, with the purpose of evaluating the chemical attributes in the AFEF. pH measurements were performed in both water and in a 1 mol L^{-1} KCl solution, using the soil/solution ratio of 1:1, by means of potentiometry. The organic carbon content was quantified after wet oxidation, using potassium dichromate in acid medium, with subsequent titration.[14]

The contents of the exchangeable cations Ca, Mg and Al were determined after extraction with a 1 M KCl solution. K and Na were extracted with ammonium acetate and later quantified by flame photometry. The potential acidity (H+Al) was obtained by extraction with calcium acetate buffered at pH 7 and quantified by neutralization titrology. Based on the values obtained for these attributes, it was possible to calculate, according to the equations presented in the Liming and Fertilization Manual for the states of Rio Grande do Sul and Santa Catarina[15] the following quantities: sum of exchangeable bases (S), effective cation exchange capacity (effective CEC), cation exchange capacity at pH 7 (CEC pH 7), base saturation (V) and

aluminum saturation (m). The mathematical equations used for these calculations are provided in the Supplementary Material (Table S2).

Analysis of Trace Element Contents

The samples, ground and sieved in a 0.053 mm mesh, were sent to the *Laboratório de Análises ambientais* in *Fraiburgo-SC* (*Terranálise*) where they were extracted using U.S. Environmental Protection Agency (USEPA) method 3050B, whose detection limit and limits of quantification information are reported in Table 1.

Table 1. Detection and Quantification Limits for As and Cd Analysis

Analyzed standard	As	Cd
	mg kg^{-1}	
Limit of Detection	0.001	0.005
Limit of Quantification	0.02	0.02
Certified NIST[1]	6.4 - 10	0.33 – 0.66
NIST obtained	7.00	0.77
Recovery rate (%)	3.54	-----

[1] NIST SRM 2709a San Joaquin Soil.

Statistical Analysis

Statistical analyses were conducted in complementary stages to characterize the contents of As and Cd in the soil samples. Initially, descriptive statistics were performed with calculation of measures of central tendency (mean, median), dispersion (standard deviation, coefficient of variation) and position (quartiles, minimum and maximum values). Data normality was verified by the Shapiro-Wilk test ($p < 0.05$) and confirmed graphically by histograms and Q-Q plots.

To identify associations between metals and soil attributes (texture, pH, organic matter, CEC, bases and aluminum saturation), Pearson's correlation was applied, with significance evaluated at $p < 0.05$ and $p < 0.01$. The differences in the contents of As and Cd between geological formations and land uses were tested by means of one-way analysis of variance (ANOVA), preceded by the verification of the homogeneity of variances.

In addition, spatial exploratory analysis was used to identify the geographic distribution of the sampling points and locate potential contamination hotspots. All analyses were processed using Python as a general-purpose programming language, with statistical routines implemented through the NumPy, SciPy, and scikit-learn libraries, and data visualization through Matplotlib and GeoPandas.

RESULTS AND DISCUSSION

The concentrations of arsenic (average of 7.85 mg kg^{-1}) and cadmium (average of 1.02 mg kg^{-1}) in the soils of the Northern Plateau of Santa Catarina are below the CONAMA Prevention Values,[6] but the Cd exceeds the level of 0.8 mg kg^{-1} of IN MAPA No. 2/2025, indicating anthropogenic accumulation. Arsenic showed no significant correlations with the evaluated soil attributes but exhibited moderate spatial dependence ($r = 0.412$; range ~45 km), indicating control by regional geological and pedogenetic processes not captured by the analyzed attributes. Cadmium showed weak spatial structure ($r = 0.187$) and absence of correlations, compatible with diffuse inputs by phosphate fertilizers. The Pearson correlation matrix is provided in the Supplementary Material (Figure S1).

Descriptive Statistics and Data Distribution

The mean As (7.85 mg kg^{-1}) and Cd (1.02 mg kg^{-1}) levels were below the Prevention Values of CONAMA Resolution No. 420/2009 (15 mg kg^{-1} and 1.3 mg kg^{-1}, respectively).[6] However, the maximum As content (14.3 mg kg^{-1}, at P17) approached the regulatory limit, and the mean Cd exceeded the 0.8 mg kg^{-1} threshold established by Joint Normative Instruction SDA/SGA/MAPA No. 2/2025, indicating that the sampled agricultural areas already show Cd accumulation.[7]

The median values were 7.90 mg kg^{-1} for As and 1.00 mg kg^{-1} for Cd, closely matching the means, which indicates a symmetric distribution for both elements. The standard deviations were 3.24 mg kg^{-1} for As and 0.14 mg kg^{-1} for Cd. The interquartile ranges (Q1–Q3) were 5.30–9.50 mg kg^{-1} for As and 0.92–1.10 mg kg^{-1} for Cd. The minimum and maximum values were 1.60 and 14.30 mg kg^{-1} for As, and 0.70 and 1.30 mg kg^{-1} for Cd.

The contrast between the two elements is evident when analyzing their spatial variability. Arsenic showed a coefficient of variation of 41.27%, indicating moderate heterogeneity, which is consistent with the influence of multiple geological substrates and land uses across the study area. The highest As contents were observed at P17 (14.3 mg kg^{-1}, Teresina Formation, soybean), P33 (14.2 mg kg^{-1}, Taciba Formation, eucalyptus),

P39 (14.1 mg kg^{-1}, Campo Mourão Formation, native forest), and P47 (14.2 mg kg^{-1}, Taciba Formation, pine reforestation). These points are distributed across different geological formations and land uses, suggesting that As contents are not controlled by a single factor but rather reflect the complex interaction between lithological inheritance and pedogenetic processes.

Cadmium, in contrast, showed a low coefficient of variation (13.83%), indicating a homogeneous distribution across the study area. This homogeneity is characteristic of diffuse sources, such as the widespread application of phosphate fertilizers, rather than point sources or specific lithological controls.[20] The highest Cd content was observed at P31 (1.3 mg kg^{-1}, Rio Bonito Formation, banana cultivation), which may be related to the specific management practices of this crop, including frequent fertilization.

When comparing the two elements, the difference in their spatial behavior is striking. While As exhibits a wide range (1.6–14.3 mg kg^{-1}) and high variability (CV = 41.27%), Cd shows a narrow range (0.7–1.3 mg kg^{-1}) and low variability (CV = 13.83%). This contrast suggests that As distribution is primarily controlled by geogenic factors (parent material and pedogenesis), while Cd distribution reflects predominantly anthropogenic inputs that have been homogenized by agricultural practices across the region.

The mean As content (7.85 mg kg^{-1}) is within the range reported for the natural background of southern Brazil[7]. Although studies have reported that As contents in Santa Catarina soils are directly related to clay, organic carbon, CEC, and Al and Fe oxides, no significant correlations were observed between As and these attributes in the present study ($p > 0.05$), as discussed in the arsenic (As) section. This discrepancy may be attributed to the regional scale of sampling and the diversity of geological substrates, which may mask local pedological relationships.

Regarding Cd, the average (1.02 mg kg^{-1}) demands attention under Normative Instruction No. 164/2025 (MAPA), which limits Cd to 5 mg kg^{-1} in phosphate fertilizers (P_2O_5 basis). Joint Normative Instruction SDA/SGA/MAPA No. 2/2025 further establishes that soils exceeding 0.8 mg kg^{-1} Cd require monitored fertilization and may face restrictions in contamination-sensitive food production areas. The mean found here surpasses this 0.8 mg kg^{-1} threshold, signaling already elevated Cd levels in the sampled agricultural areas, likely from historical phosphate fertilization.

Compared to other Brazilian agricultural soils, this Cd mean (1.02 mg kg^{-1}) is medium to high. Studies reported 0.15–1.07 mg kg^{-1} in Oxisols under pasture-to-sugarcane conversion, with an estimated input of 9.54 mg ha^{-1} $year^{-1}$ via fertilizers; their maximum (1.07 mg kg^{-1}) closely matches the present maximum (1.30 mg kg^{-1}).[17] Authors found average Cd ten times above the local reference in intensive vegetable cultivation areas in Rio de Janeiro, averaging ~1.44 mg kg^{-1}, higher than in the Northern Plateau of Santa Catarina.[16] In contrast, a natural Cd background of only 0.1 mg kg^{-1} was reported in forest soils of Pará, confirming that levels near 1.0 mg kg^{-1} in agricultural soils are anthropogenically influenced.[18]

The As coefficient of variation (41.27%) indicates moderate heterogeneity, suggesting point sources or lithological variations.[19] The low Cd CV (13.83%) reflects a homogeneous distribution typical of diffuse sources, such as widespread phosphate fertilizer application.[20] The Shapiro-Wilk test showed normal distribution for both elements ($p > 0.05$), permitting parametric tests.[21]

Geostatistical Analysis and Spatial Dependence

The geostatistical analysis was performed to evaluate the existence of spatial dependence in the contents of Arsenic and Cadmium, as well as to generate interpolated maps (kriging) that allow visualizing the continuous distribution of these elements in the study area.

Exploratory Analysis of Spatial Data

The study area covers an approximate extent of 111 km in a east-west direction, with longitude coordinates ranging from -50.63° to -49.52° and latitude between -26.61° and -26.05°. The average distance between the sampling points is approximately 25.3 km, with a minimum distance of 2.1 km and a maximum distance of 98.7 km (Figure 2).

The spatial distribution of sampling points reveals that the area encompasses a transition zone between the sedimentary rocks of the Paraná Basin (Rio Bonito, Palermo, Teresina, and Rio do Rasto formations) in the eastern and central portions, and the volcanic rocks of the Serra Geral Formation in the western portion. This geological contrast is accompanied by differences in land use: the eastern portion is dominated by agriculture (soybean, corn, tobacco) and reforestation, while the western portion includes extensive areas of native forest and pasture. This spatial configuration allows the evaluation of how geological and anthropogenic factors interact to control the distribution of As and Cd.

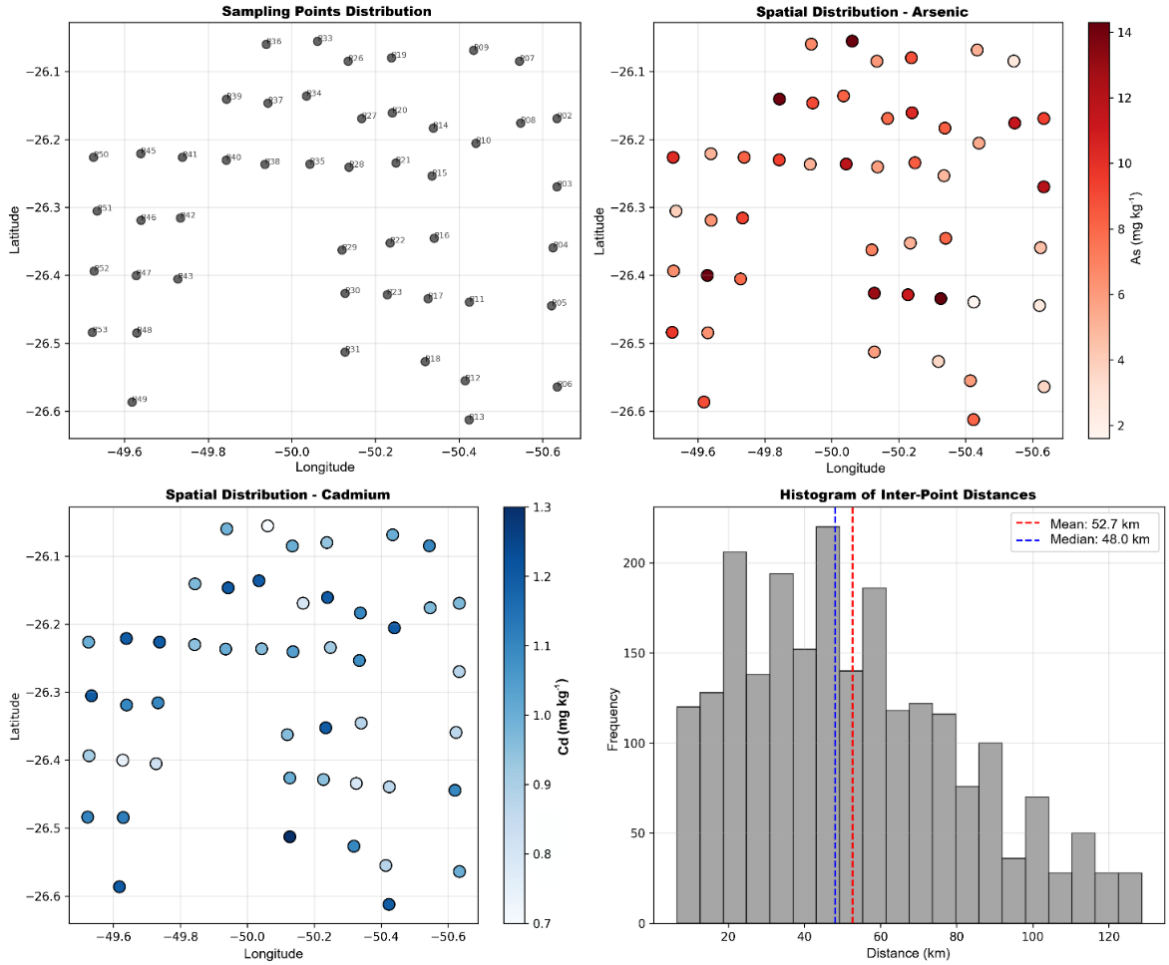

Figure 2. Spatial distribution and distance relationships among the 48 sampling points in the study area.

Experimental Semivariograms

For arsenic (As), the semivariogram (Figure 3) presents a well-defined structure, with an increase in semivariance with distance up to approximately 40–50 km, where a stabilization trend is observed. This behavior suggests the existence of moderate spatial dependence, with a practical range of around 45 km. This range is consistent with the scale of geological units in the study area, as the distance between the main geological boundaries (e.g., the transition between the Rio Bonito and Serra Geral formations) is on the order of tens of kilometers. The moderate spatial dependence observed for As suggests that its contents are controlled by regional processes, such as the distribution of As-bearing geological formations and the large-scale pedogenetic processes that govern the formation of Fe and Al oxides.

The semivariogram for Cadmium (Cd) (Figure 3) shows greater dispersion of the points and a less clear tendency to increase with distance. A more pronounced nugget effect is observed, indicating that a significant part of the variability occurs at distances shorter than the shortest sample distance (2.1 km). This short-range variability is consistent with the influence of diffuse anthropogenic sources, such as the application of phosphate fertilizers, which can vary in intensity and frequency even within the same land-use category. Additionally, agricultural practices such as plowing and harrowing promote the homogenization of soil properties at small scales, which can mask any regional-scale spatial pattern that might exist.

Kriging Maps

The kriging map (Figure 4) for Arsenic reveals areas of higher concentration (> 12 mg kg^{-1}) in the central and southwestern portions of the study area, coinciding with points P17, P33, P39 and P47. Zones of intermediate concentration (8-12 mg kg^{-1}) distributed more continuously and areas of lower concentration (< 6 mg kg^{-1}) on the northern and eastern borders.

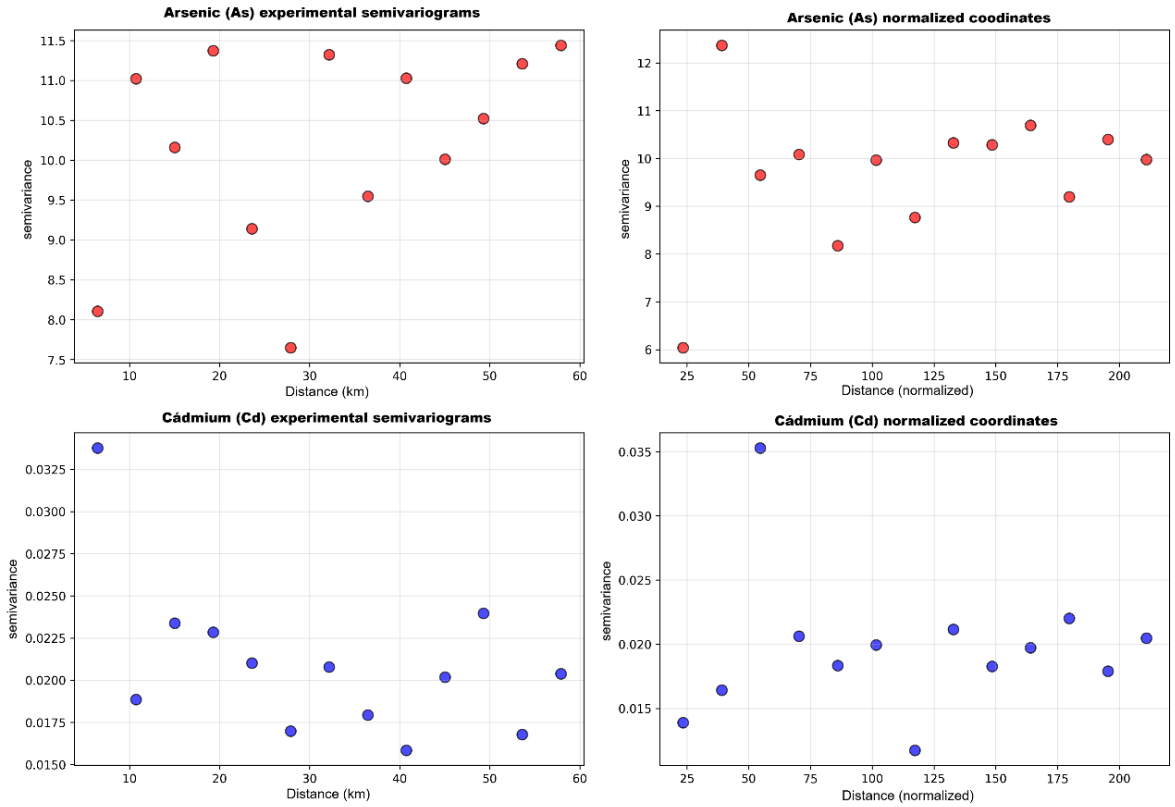

Figure 3. Experimental semivariograms of As and Cd, including normalized data.

The spatial pattern of As observed in the kriging map may be related to the occurrence of geological formations with higher natural As contents in the central and southwestern portions of the area. However, it is important to note that this interpretation is based on the spatial coincidence between the kriging map and the geological map, and not on a direct statistical test of the relationship between As contents and geological formations. The absence of significant differences between geological formations in the ANOVA suggests that the relationship between As and geology may be more complex than initially hypothesized, possibly involving the combined effects of parent material, weathering intensity, and secondary mineral formation.

Additionally, the higher As concentrations in the central portion of the area may be influenced by topographic factors, such as the accumulation of fine sediments in lower landscape positions. However, this hypothesis requires further investigation with detailed topographic data and soil profile descriptions, which were not available in the present study.[9]

The kriging map (Figure 4) for Cadmium shows a more homogeneous distribution, with most of the area presenting contents between 0.95 and 1.10 mg kg^{-1}; areas with slightly higher levels (> 1.15 mg kg^{-1}) in isolation, associated with points P31 and P48; high variance (uncertainty) throughout the extension, reflecting the low spatial structure identified in the semivariogram. The low spatial structure of Cd makes kriging maps less reliable for this element, and interpretation with caution is recommended.[10]

Geostatistical Interpretation

The geostatistical results indicate different behaviors for the two elements. The moderate spatial dependence observed for Arsenic (r = 0.412; range ~45 km) suggests that its contents may be controlled by regional processes related to geology and pedogenesis. However, the absence of significant correlations between As and the analyzed soil attributes and the absence of significant differences between geological formations indicate that this interpretation should be considered as a hypothesis rather than a conclusion.

The hypothesis that As distribution is controlled by regional geological and pedogenetic processes is supported by the moderate spatial dependence observed (range ~45 km), which is consistent with the scale of geological units in the study area. The lithologies potentially

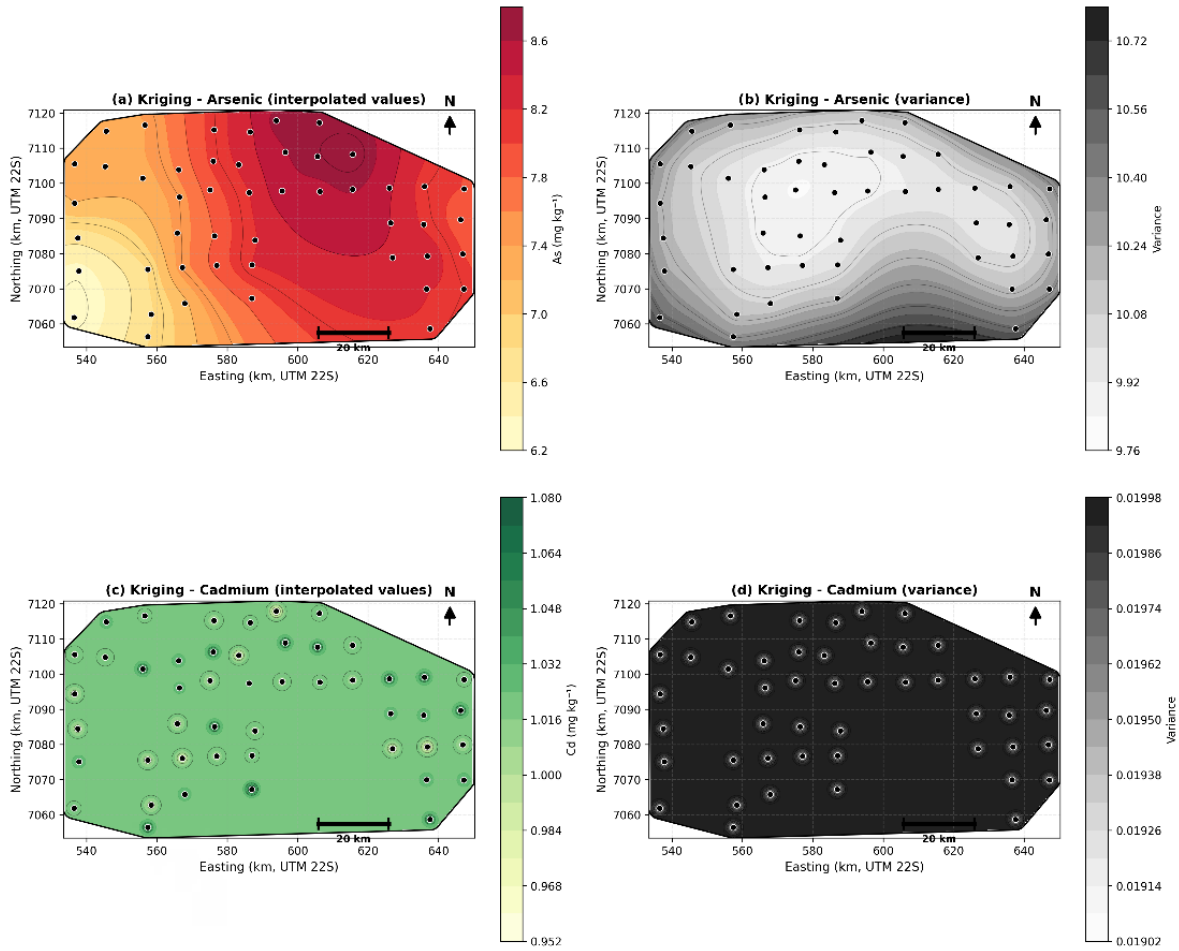

Figure 4. Spatial distribution maps of arsenic As and Cd obtained by ordinary kriging.

bearing As are the carbonaceous pelites of the Rio Bonito Formation – which contain arsenopyrite (FeAsS) – and the basalts of the Serra Geral Formation, whose secondary Fe oxides may act as arsenate adsorbents. However, direct evidence linking As contents to these specific lithologies was not obtained in the present study, as the sampling design was not specifically designed to test this hypothesis (e.g., by sampling along geological transects or by mineralogical analysis of the soil fractions).

The low spatial dependence for cadmium (r = 0.187) indicates the absence of a defined regional pattern, a typical behavior of elements with a strong diffuse anthropogenic influence, such as the application of phosphate fertilizers.[4] However, the absence of significant differences between agricultural and non-agricultural areas suggests that this hypothesis also requires further investigation, possibly involving the analysis of fertilizer application history and Cd inputs at the farm scale.

Correlations with Soil Attributes

The Pearson correlation matrix (Figure S1, Supplementary Material) revealed no significant associations between As or Cd and the evaluated pedological attributes ($p > 0.05$).

Arsenic (As)

Contrary to expectations based on the literature, Arsenic did not show significant correlations with any of the evaluated soil attributes ($p > 0.05$), including Al^{3+} (r = 0.05), Al saturation (r = 0.15), pH (r = -0.07), organic carbon (r = 0.16), base saturation (r = 0.09), sand (r = -0.22), silt (r = 0.15), and clay (r = 0.08) contents. This absence of significant correlations may indicate that As contents in the studied soils are controlled by factors not captured by the analyzed physicochemical attributes, such as specific mineralogical phases (e.g., poorly crystalline Fe and Al oxides), which were not directly quantified in this study.

The lack of correlation between As and soil attributes contrasts with findings from other studies in Santa Catarina[7] and other regions,[5] which reported significant relationships between As and clay, organic carbon, CEC, and Fe and Al oxides. Several factors may explain this discrepancy. First, the regional-scale sampling design (48 points across 111 km) integrates multiple geological formations and land uses, potentially masking local pedological relationships that would be evident at a more detailed scale. Second, the high variability of As contents (CV = 41.27%) and the diverse geological substrates sampled may contribute to the absence of a single dominant pedological control. Third, the analytical method used (USEPA 3050B) extracts only a fraction of the total As, which may not fully represent the geochemical associations of the element in the soil.

The mechanisms by which soil attributes control As retention are well documented in the literature. Arsenate ($H_2AsO_4^-$ and $HAsO_4^{2-}$) is strongly adsorbed by Fe and Al oxides through ligand exchange with surface hydroxyl groups.[3,5] Organic matter can both retain As through complexation with functional groups (–COOH, –OH, phenolics) and compete with As for adsorption sites.[22] Soil pH influences As speciation and adsorption, with maximum retention occurring under acidic conditions (pH 4–6) and decreasing mobility at alkaline pH.[1,3] Clay minerals provide additional adsorption sites, while sandy soils have lower retention capacity due to their smaller specific surface area.[23]

Although these mechanisms are well established, the absence of significant correlations in the present study suggests that they may not be the dominant controls on As distribution at the regional scale evaluated. Alternatively, relationships may exist but be masked by the high spatial variability of As and the confounding effects of multiple geological substrates and land uses.

The mean As content (7.85 mg kg^{-1}) is within the range expected for the natural background of southern Brazil. Studies have identified areas with naturally high As levels associated with specific geological formations in the State of Paraná,[24] evidencing the variability of background on a regional scale. Additionally, in weathered soils derived from diabase in the Paraná Basin, authors demonstrated that geochemical inheritance of the parent material is a determining factor for soil elemental composition, without significant differences being attributed exclusively to agricultural use.[16]

Thus, the absence of correlations with soil attributes does not preclude the interpretation that As contents reflect natural geochemical inheritance. Rather, it suggests that the scale of sampling and the attributes analyzed may not fully capture the pedogeochemical processes controlling As distribution in these subtropical soils. The moderate spatial dependence observed (r = 0.412; range ~45 km) supports the influence of regional geological and pedogenetic processes on As distribution, as discussed in the Geostatistical Interpretation section.

Cadmium (Cd)

Cadmium did not show significant correlations with the soil attributes analyzed ($p > 0.05$). The highest correlation observed was with pH (r = 0.18), followed by base saturation (r = 0.16), but neither reached statistical significance. This result can be explained by the diffuse anthropogenic influence, since Cd in agricultural soils often originates from phosphate fertilizers, which contain Cd as an impurity.[4,25] The intrinsic properties of Cd also contribute to this behavior: Cd^{2+} has low electronegativity (1.69) and a relatively large ionic radius (0.97 Å), reducing its affinity for adsorption sites in Fe and Al oxides, with a low tendency to form stable complexes with organic matter.[26] This high mobility, combined with the homogenization promoted by agricultural practices (plowing, harrowing), explains the absence of correlations with soil attributes and the weak spatial dependence observed.

This pattern is characteristic of elements whose distribution is strongly influenced by diffuse anthropogenic inputs, particularly in agricultural environments. In the Brazilian context, several studies point to phosphate fertilizers as the main anthropogenic source of Cd in agricultural soils, since this element occurs naturally as an impurity in rock phosphates used in the production of these inputs. Authors demonstrated that natural phosphates used as raw material for fertilizers in Brazil contain measurable concentrations of Cd, in addition to other potentially toxic metals, showing that the continuous application of these products can promote the gradual accumulation of the element in the soil, even in the absence of point sources of contamination.[25] This mechanism explains the relative spatial homogeneity of the Cd contents observed in this study, with mean values close to 1.0 mg kg^{-1}, compatible with those reported for Brazilian agricultural soils under intensive use. Thus, the results reinforce the

interpretation that the Cd present in the soils of the study area predominantly reflects diffuse anthropogenic sources associated with agricultural management, corroborating the behavior described in the literature for this element.[27,28]

Although Cd occurs naturally in all agricultural soils and in phosphate fertilizers, its behavior in the soil and accumulation by crops is a complex process influenced by several factors such as soil pH, organic matter content, salinity, plant species and cultivar, and management practices.[4]

Variation by Geological Formation

The ANOVA test did not reveal significant differences between the geological formations for As ($F = 0.462$; $p = 0.893$) or for Cd ($F = 0.392$; $p = 0.931$) (Table 2).

However, this result should be interpreted with caution due to the unequal number of samples among geological formations. Some formations (Botucatu, Gramado, and Serra Geral) are represented by only one sample, making it impossible to assess their within-formation variability or determine whether the observed values are representative of these geological units. Additionally, the high intralithological variability observed in Santa Catarina soils[29] and the advanced weathering of subtropical soils may homogenize geochemical signatures across different parent materials, reducing the power of the ANOVA to detect significant differences.

Therefore, the absence of statistically significant differences for As and Cd does not necessarily indicate the absence of lithological influence. It may instead reflect the limited sampling representativeness of some formations and the high natural variability of the elements. Studies in Santa Catarina have also observed high intralithological variability, with greater homogeneity in plateau areas due to advanced weathering.[29] Authors found that As contents are more related to pedological attributes than to geological formation itself.[7] Studies in the Carajás Province, demonstrated that local pedogenetic processes (formation of Fe and Al oxides) can overlap with lithological control in the retention of trace elements.[30]

Thus, the results suggest that pedogeochemical control may predominate over direct lithological control in subtropical weathered soils, but this conclusion should be considered as a hypothesis rather than a definitive conclusion, given the limitations of the sampling design. Future studies with balanced sampling across geological formations and mineralogical analysis of the soil fractions would be necessary to definitively test this hypothesis.

Table 2. Mean Concentrations of As and Cd by Geological Formation (mg kg^{-1})

Geological Formation	n	Arsenic (mean ± SD)	Cadmium (mean ± SD)
Botucatu	2	8.40	0.92
Campo Mourão	9	7.14 ± 3.15	1.08 ± 0.12
Depósitos aluvionares	4	7.60 ± 2.40	0.98 ± 0.07
Gramado	1	3.60	1.00
Palermo	6	8.18 ± 2.41	1.00 ± 0.15
Rio Bonito	8	8.06 ± 3.39	1.00 ± 0.18
Rio do Rastro	9	7.16 ± 3.48	0.98 ± 0.10
Serra Alta	2	10.65 ± 4.60	1.00 ± 0.14
Serra Geral	1	8.10	1.20
Taciba	6	7.25 ± 4.52	1.00 ± 0.18

Variation by Land Use

The ANOVA test for simplified land uses revealed no significant differences for As ($F = 0.618$; $p = 0.687$) or Cd ($F = 0.712$; $p = 0.618$) (Table 3). This result presents an apparent contradiction with the hypothesis that Cd contents are influenced by phosphate fertilization, since agricultural areas would be expected to show higher Cd levels than non-agricultural areas.

Several factors may explain this apparent contradiction. First, the native forest areas sampled in this study are often secondary forests *(capoeiras)* in regeneration, which may have been under agricultural use in the past and thus maintain a geochemical signature of previous fertilization.[31] Second, the regional scale of sampling and the high natural variability of soil attributes may mask the effects of land use, which operate at smaller scales. Third, the history of phosphate fertilization may vary considerably among agricultural areas, depending on crop type, management practices, and time since conversion, introducing additional variability that is not captured by the simplified land-use categories.

Although the statistical analysis did not reveal significant differences, it was observed that agriculture presented higher average levels for both As (8.28 mg kg^{-1}) and Cd (1.06 mg kg^{-1}). However, these differences were not statistically significant, and the observed pattern should be interpreted with caution. The literature documents the cumulative effect of agricultural practices on PTE levels in soil,[32,33] but in the present study, the high natural variability and the regional scale of sampling may have masked potential land-use effects.

Alternative sources and processes controlling Cd distribution should also be considered. Atmospheric deposition, irrigation water quality, and the use of other agrochemicals (e.g., fungicides containing Cd) may contribute to Cd inputs in agricultural soils.[4] Additionally, the natural geochemical background of Cd in the study area may be higher than the global average, as suggested by the mean content of 1.02 mg kg^{-1}, which exceeds the 0.8 mg kg^{-1} threshold established by MAPA.

Thus, the results indicate that, although agricultural management, particularly phosphate fertilization, may contribute to Cd enrichment in cultivated soils, the present dataset does not provide sufficient statistical evidence to confirm this effect. Continuous monitoring is recommended, especially in areas with higher Cd levels.

Table 3. Mean Concentrations of As and Cd by Land Use (mg kg^{-1})

Land Use	n	Arsenic (mean ± SD)	Cadmium (mean ± SD)
Agriculture	12	8.28 ± 3.32	1.06 ± 0.12
Roadside	7	7.61 ± 3.04	1.00 ± 0.13
Native Forest	11	8.29 ± 3.62	1.00 ± 0.14
Pasture	3	5.93 ± 2.05	1.00 ± 0.10
Reforestation	15	7.18 ± 3.59	0.97 ± 0.15

Environmental and Agronomic Implications

The results obtained have important implications for the management of the areas studied. The absence of significant correlations between As and soil acidity attributes in this study suggests that liming practices may not have a predictable effect on As availability in these soils, although this hypothesis requires further investigation with controlled experiments. The maximum Arsenic content (14.3 mg kg^{-1}) is close to the prevention value (15 mg kg^{-1}),[6] indicating the need for monitoring, especially in areas with a history of pesticide application or irrigation.

For Cadmium, the average (1.02 mg kg^{-1}) is below the PV of CONAMA, but the anthropogenic influence, probably associated with phosphate fertilizers, deserves attention in soil quality monitoring programs.

CONCLUSIONS

The mean concentrations of Arsenic (As) and Cadmium (Cd) in soils of the Northern Plateau of Santa Catarina were 7.85 mg kg^{-1} and 1.02 mg kg^{-1}, respectively, remaining below the Prevention Values established by CONAMA Resolution No. 420/2009. The normal data distribution indicates relatively homogeneous geochemical behavior at the regional scale evaluated.

Arsenic did not show significant correlations with the evaluated physicochemical attributes (Al^{3+}, Al saturation, pH, organic carbon, base saturation, and texture), suggesting that its distribution is controlled by factors not captured by the analyzed attributes, such as specific mineralogical phases. However, the moderate spatial dependence observed (r = 0.412; range ~45 km) indicates the influence of regional geological and pedogenetic processes on As distribution.

In contrast, Cadmium displayed no significant correlations with the evaluated physicochemical attributes and showed reduced spatial dependence. This behavior suggests a predominance of diffuse anthropogenic inputs, likely related to the historical use of phosphate fertilizers, in line with observations reported for intensively managed Brazilian agricultural soils.

Geostatistical analysis revealed moderate spatial dependence for Arsenic, with a range of approximately 45 km, indicating the influence of regional processes associated with geology and pedogenesis. For Cadmium, the absence of a defined spatial structure limits the reliability of continuous interpolation, suggesting that sampling strategies based on land use and management history are more appropriate for this element.

No statistically significant differences were observed in As and Cd contents between geological formations or land use categories, possibly due to homogenization promoted by intense pedogenetic processes, high intralithological variability, and the regional character of the sampling scale. Even so, specific points with concentrations close to legal limits (P17 for As and P31 for Cd) require attention in environmental monitoring programs.

Overall, the results reinforce that Arsenic exhibits predominantly natural behavior linked to the regional geochemical background, while Cadmium reflects diffuse anthropogenic influences related to agricultural practices.

The study contributes to understanding the distribution of potentially toxic elements in subtropical agricultural soils in southern Brazil and provides technical support for monitoring, environmental planning, and sustainable soil management.

SUPPLEMENTARY MATERIAL

Supplementary data is available at: https://doi.org/10.5281/zenodo.23702908

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DATA AVAILABILITY STATEMENT

All datasets supporting the findings of this study are included in this article.

AUTHOR CONTRIBUTIONS

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