



Soil Ba, Cd, Co, Cr, Cu, Ni, Mn, Pb, and Zn contents in the Basaltic Hillsides of Santa Catarina, Brazil

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ABSTRACT: The Basaltic Hillsides region spans a vast area in western Santa Catarina State, Brazil, consisting of magmatic flows from the Serra Geral Group. This study analyzed soil levels of Ba, Cd, Ni, Cu, Zn, Cr, Pb, Mn, and Co in these hillsides, comparing them to the reference values set by current legislation for Santa Catarina. Pearson correlation analysis and hierarchical dendrogram were conducted based on results from multiple studies employing consistent methodologies. Nearly all trace elements showed levels above the Quality Reference Values (QRVs), except for Pb. The difference between current QRVs and natural background level highlights the need to update Ordinance IMA/SC n° 45/2021 to establish specific QRVs for the Basaltic Hillsides of Santa Catarina.

Key words: heavy metals, cluster analysis, mafic rocks, western region.

Teores de Ba, Cd, Co, Cr, Cu, Ni, Mn, Pb e Zn em solos de encostas basálticas de Santa Catarina

RESUMO: A região das “encostas basálticas” de Santa Catarina abrange uma área extensa no oeste do estado, composta por derrames magmáticos do grupo Serra Geral. Este estudo analisou os teores de Ba, Cd, Ni, Cu, Zn, Cr, Pb, Mn e Co nos solos dessas encostas, comparando-os com os valores de referência da legislação vigente para Santa Catarina. Com base em resultados de diversos estudos que utilizaram metodologias consistentes, foi realizada uma análise de correlação de Pearson e um dendrograma hierárquico. Exceto Pb, todos os elementos-traço apresentaram teores acima dos Valores de Referência de Qualidade (VRQ). A discrepância entre os VRQs atuais e os teores naturais (*background*) reforçam a necessidade de atualização da Portaria IMA/SC n° 45/2021 (IMA, 2021), visando à criação de VRQs específicos para as encostas basálticas de Santa Catarina.

Palavras-chave: metais pesados, análise de agrupamento, rochas máficas, região oeste.

INTRODUCTION

The Basaltic Hillsides region occupies just over a quarter of Santa Catarina State in Brazil, hosting small municipalities with predominantly small to medium-sized rural properties (ALMEIDA et al., 2018). Key economic activities in this area include beef cattle raising, pig and poultry farming, dairy production, cultivation of perennial pastures and annual crops, and preservation of permanent conservation areas (VEIGA et al., 2019).

Geologically, this region lies on the basic sequence flows, which formed between 120 and 135 million years ago, predominantly consisting of basalts and phenobasalts from the Serra Geral Group

(ALMEIDA et al., 2018). Geomorphologically, it corresponds to the Dissected Plateau of the Iguaçu and Uruguay Rivers, featuring deep valleys and gently sloping hillsides.

The soils in these basaltic hillsides are clay-textured, with high Fe₂O₃ content (POTTER et al., 2004) and elevated base saturation. Mineralogically, they consist of kaolinite, smectites, goethite, and hematite, with minimal to no gibbsite, and show substantial organic matter accumulation, supported by the region's mild climate (ALMEIDA et al., 2018).

Trace elements in these soils may originate naturally or from human activities (BOECHAT et al., 2020; ZHANG & WANG, 2020). Basalt weathering

naturally releases these elements into the soil (WANG et al., 2020), where some, like Cr (III), Cu, Fe, Mn, Zn, Ni, and B, are essential in small amounts for animals and plants. However, elements such as Cd and Pb lack biological roles, and their accumulation can be carcinogenic and lead to organ dysfunction (GEBREKIDAN et al., 2013; MUNIR et al., 2021; CHATHA & NAZ, 2023).

Younger soils, like those on the Basaltic Hillsides of Santa Catarina, generally contain higher levels of trace elements, with their mobility and bioavailability influenced by the soil's physical and chemical properties. Understanding the natural background levels of these elements is crucial for setting quality reference values and implementing control and mitigation strategies (SUPPI et al., 2022). Anthropogenic sources of trace elements include atmospheric deposition, industrial effluents, cemeteries, animal waste fertilizers, mining, and pesticides, making them significant and potentially toxic pollutants (GHOLIZADEH & HU, 2021).

Ordinance IMA No. 45 of 2021 (IMA, 2021) provides the Quality Reference Values (QRVs) for soils in Santa Catarina, as also reported by SUPPI et al. (2022). However, the soils examined in this study were not included in the database used to establish these QRVs. Therefore, this study is critical for reviewing and updating QRVs for Santa Catarina soils, ensuring that environmental legislation accurately represents the natural soil conditions in the region. The study aims to assess the natural trace element contents in soils from the Basaltic Hillsides of Santa Catarina.

MATERIALS AND METHODS

The study utilized 12 soil samples from the Santa Catarina State University's soil bank, collected from horizon A (0–20 cm) of soil profiles in the Basaltic Hillsides of Santa Catarina (Table 1). These samples are derived from basalt and phenobasalt rocks of the Serra Geral Formation, with context provided by ALMEIDA (2018); CORRÊA (2018); SCHMITT (2018), alongside chemical, physical, and mineralogical analyses. Table 2 summarizes these physical and chemical analyses. The soil samples were prepared by grinding in an agate mortar and sieving through a 145-µm mesh. Digestion followed the United States Environmental Protection Agency (EPA) method 3050B, as outlined by USEPA (1996). Digestions were performed in triplicate, with each batch including a reference sample, SRM 2709A (San Joaquin Soil), certified by the National Institute of Standards and Technology (NIST), and a blank sample to calculate the Qualitative Detection Limit (QDL) of the Analytical Method. Table 3 presents the recovery rates of the reference sample SRM 2709A for elements quantified after digestion by method 3050B and analysis via ICP–OES.

QDL was calculated using the equation $QDL = Fd \times (M \pm t \times s)$ (LIPPS et al., 2024), where Fd represents the sample dilution factor, M is the mean of the blank tests, t is Student's t -value for a 99% confidence interval based on the degrees of freedom from repeated measurements, and s is the standard deviation of the blank tests. Ba, Co, Cr, Cu, Mn, Ni, Pb, and Zn concentrations were measured using inductively coupled plasma–optical emission spectrometry (ICP–OES), while Cd content was

Table 1 - Classification, location, and altitude of the 11 soil classes analyzed in this study.

N	Soil classification ¹	Municipality	Latitude	Longitude	Altitude (m)
1	Cambissolo Háplico Tb Eutroférico típico (CXbef)	Riqueza	27°00'50.43"S	53°21'09.64"O	440
2	Chernossolo Argilúvico Férreo típico (MTf)	Ipira	26°57'16.61"S	53°20'32.20"O	480
3	Cambissolo Háplico Ta Eutroférico típico (CXve)	Descanso	26°52'39.72"S	53°26'03.26"O	510
4	Nitossolo Vermelho Eutroférico típico (NVef)	Descanso	26°52'01.56"S	53°29'46.26"O	580
5	Nitossolo Vermelho Eutroférico chernossólico (NVef)	Peritiba	27°22'19.17"S	51°50'07.58"O	690
6	Chernossolo Argilúvico Órtico típico (MTo)	Riqueza	27°23'41.49"S	51°48'25.57"O	585
7	Argissolo Amarelo Eutrófico típico (PAe)	Ipira	27°23'00.71"S	51°49'01.59"O	550
8	Neossolo Litólico Chernossólico fragmentário (RLm)	Ipira	27°23'37.76"S	51°48'29.37"O	485
9	Nitossolo Háplico Distrófico típico (NXd)	ÁguaDoce	27°02'39.74"S	51°32'06.17"O	785
10	Cambissolo Háplico Ta Eutrófico típico (CXve)	Luzerna	27°05'39.53"S	51°29'15.88"O	710
11	Nitossolo Vermelho Eutroférico típico (NVef)	Luzerna	27°06'43.20"S	51°28'40.80"O	575

¹Soil profiles collected and classified by ALMEIDA et al. (2018).

Table 2 - Physical and chemical analyses of the 11 studied soil classes.

No.	Sand	Silt	Clay	OC	Al ₂ O ₃	Fe ₂ O ₃	pH H ₂ O	T ¹	S ²	V ³
	-----g kg ⁻¹ -----							---cmol _c kg ⁻¹ ---	%	
1	270	230	500	40.7	138.6	259.4	4.98	15.3	10.7	69.0
2	220	360	420	30.0	114.1	321.9	5.64	20.2	18.0	90.0
3	320	370	310	53.6	158.8	253.9	6.04	27.1	24.6	91.0
4	180	270	550	45.1	140.7	259.5	5.71	17.5	15.9	91.0
5	170	460	370	51.4	132.7	209.6	5.90	19.3	15.3	79.0
6	330	440	230	31.5	149.6	206.1	6.00	27.0	23.1	86.0
7	250	420	330	55.9	140.8	221.7	6.30	23.4	21.4	92.0
8	140	580	280	32.8	172.1	304.5	5.50	23.2	19.1	83.0
9	70	260	670	46.5	140.7	144.5	4.73	15.3	7.1	46.0
10	330	190	480	34.3	162.7	189.7	4.90	14.3	4.0	28.0
11	210	370	420	27.9	147.0	194.7	5.40	12.0	8.1	68.0
Mean	226	359	415	40.9	145.2	233.2	5.56	19.5	15.2	74.8
Standard deviation	84	115	129	10.1	15.7	52.4	0.51	5.2	6.9	20.9

¹T value; ²Sum of bases; ³Base saturation.

quantified via graphite furnace–atomic absorption spectrophotometry (GF–AAS CONTRAA 700 ANALYTIK JENA).

Statistical analysis

Pearson correlation analysis was conducted to evaluate relationships among trace elements and their associations with soil physical and chemical properties (Table 2), taking into account altitude variations at each site. A hierarchical dendrogram was generated from standardized soil data on physical and chemical properties, using the Ward linkage method with Euclidean distance in Minitab 17 software. The Ward method, a hierarchical clustering technique,

calculates similarity by summing the squared differences between clusters across all variables, which typically yields clusters of similar sizes by minimizing internal variation (HAIR et al., 2009).

Additionally, an analysis of variance (ANOVA) was performed on each metal within the clusters to determine significant differences (P-value ≤ 0.05). The cluster analysis considered parameters such as particle size, organic carbon content, pH in H₂O, T value, sum of bases, base saturation, and aluminum and iron oxide contents. Each cluster variable was standardized relative to the global mean and standard deviation to ensure consistency across a common scale from –1 to +1.

Table 3 - Mean and standard deviation for the natural contents of the 11 soils, percentage of recovery obtained for NIST SRM 2709 A (NIST Rec.), Qualitative Detection Limit of the Analytical Method (QDLM) and QRVs published in CONAMA Resolution 420/2009, Ordinance IMA/SC No. 45/2021, Ordinance FEPAM/RS No. 85/2019, and by BOCARDI (2019).

	Ba	Cd	Cr	Cu	Mn	Ni	Pb	Zn
Mean (mg kg ⁻¹)	143.3	0.165	303.0	221.1	2590.4	41.5	10.4	103.5
Standard deviation (mg kg ⁻¹)	61.2	0.047	240.6	84.4	1451.8	19.8	4.1	16.7
Rec. NIST (%) ¹	102	52	83	71	77	125	71	54
LDQM (mg kg ⁻¹)	18.5	0.07	10.6	0.9	1.9	5.9	3.2	2.4
CONAMA (mg kg ⁻¹)	150	1.3	75	60	-	30	72	300
IMA(mg kg ⁻¹)	75	0.11	47.7	146.9	-	18.3	16.1	78
FEPAM(mg kg ⁻¹)	-	0.6	94	203	-	47	36	31
BOCARDI (2019) (mg kg ⁻¹) ²	148.5	0.8	39.1	103.8	-	7.7	15.0	62.3

¹Calculation of percentage recovery NIST SRM 2709 A obtained by: % recovered = [(certified content * 100) / recovered content];

²Reference values for soils in the State of Paraná.

RESULTS

Nearly all trace elements showed concentrations above the QRVs set by Ordinance IMA No. 45/2021 (IMA, 2021) for soils in Santa Catarina, except for Pb (Table 3). Additionally, Ba, Co, Cr, Cu, and Zn exceeded the limits established by Ordinance FEPAM/RS No. 85/2014 (FEPAM, 2014) for the state of Rio Grande do Sul. The concentrations of Cr, Cu, and Ni were also higher than those reported for basalt soils in western Paraná (BOCARDI, 2009).

The Cr, Cu, Pb, and Zn levels found in soils from the Basaltic Hillsides also exceeded the QRVs established by CONAMA Resolution No. 420/2009 (CONAMA, 2009). Manganese showed strong positive correlations with barium (Corr = 0.89), cobalt (Corr = 0.93), and chromium (Corr = 0.68) (Figure 1). This relationship may result from Mn oxides' capacity to act as geochemical barriers, retaining trace elements like Ba, Ni, Co, Cd, Zn, and Ce (MAYANNA et al., 2015).

The hierarchical dendrogram (Figure 2) identified two clusters with distinct soil weathering levels. Cluster 1, primarily composed of more weathered soils, showed lower trace element contents, such as Cu ($242.7 \pm 100.9 \text{ mg kg}^{-1}$), compared to Cluster 2 ($195.3 \pm 59.7 \text{ mg kg}^{-1}$), along with similar levels of Cd, Ni, Pb, and Fe_2O_3 . Cluster 1 also had a higher clay content ($506.7 \pm 94.2 \text{ g kg}^{-1}$) than Cluster 2 ($304.0 \pm 52.7 \text{ g kg}^{-1}$). However, Cluster 2 exhibited higher pH and base saturation than Cluster 1.

Correlations were observed between trace elements and both manganese and clay content. In Cluster 1, Mn correlated with Ba, Cd, Cu, Cr, and Co, while clay content correlated with Ba, Pb, Mn, and Co. In Cluster 2, Mn correlated with Ni, Cu, Cr, Pb, and Co, and sand correlated with Cd, Cr, and Fe. These relationships may be due to the reduced intensity of transformation and neogenesis processes in Cluster 1 soils, despite variations in weathering within the cluster.

DISCUSSION

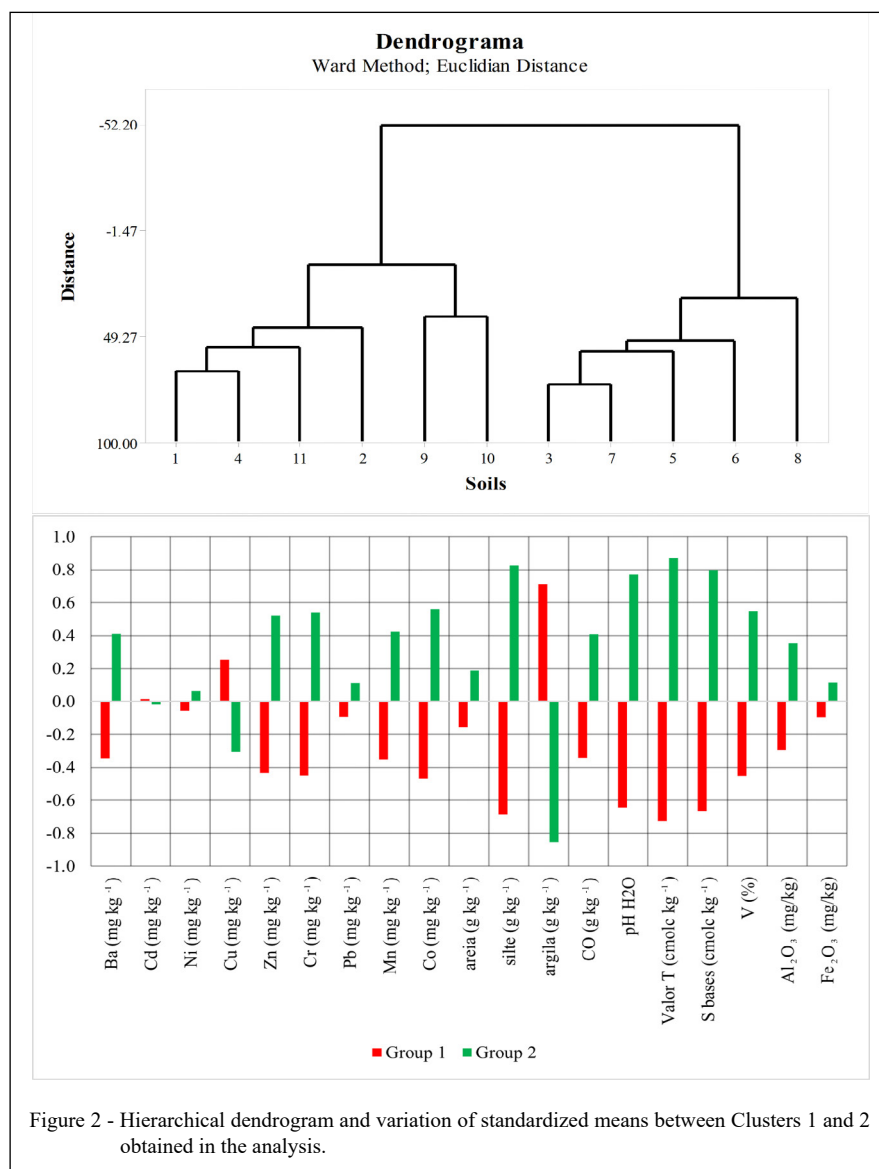
Soil characteristics like pH, organic matter, and specific physical properties influence nutrient availability, including manganese, which is vital for plant nutrition. Although this study found significant correlations between Mn and other trace elements, no direct correlations were observed with Ba, Cd, Cu, Cr, and Co. Lead and cadmium can compete with manganese, impacting its uptake by plants (LIU et al., 2020).

Older soils typically have lower trace element concentrations due to long-term geological and pedogenetic processes like weathering and leaching. Younger soils in Cluster 2 exhibit a higher silt-to-clay ratio, influenced by weathering, transport, and sedimentation, with this ratio affected by factors such as climate and local conditions (WILSON, 2019).

Soil differences in southern Brazil (Table 3) are likely due to variations in soil types, weathering

	Cd	Ni	Cu	Zn	Cr	Pb	Mn	Co	Sand	Silt	Clay	OC	pH	T value	Bases sat	V (%)	Al	Fe	Altitude
Ba (mg kg^{-1})	0.25	-0.1	0.11	0.13	0.49	-0.01	0.89	0.85	0.23	0.57	-0.66	-0.3	0.51	0.56	0.59	0.54	-0.25	0.64	-0.54
Cd (mg kg^{-1})		-0.14	0.25	0.09	0.13	-0.24	0.43	0.37	0.63	-0.25	-0.19	-0.23	0.07	0.32	0.21	0.02	-0.14	0.14	-0.06
Ni (mg kg^{-1})			-0.4	-0.24	0.19	0.24	0.05	0.07	-0.29	0.17	0.03	0.01	0.19	-0.05	0.03	0.14	-0.38	-0.54	0.35
Cu (mg kg^{-1})				0.29	-0.15	-0.55	0.15	0.22	-0.1	-0.17	0.21	0.01	-0.05	-0.09	0.08	0.34	-0.41	0.68	-0.49
Zn (mg kg^{-1})					0.68	-0.23	0.33	0.45	0.41	0.12	-0.37	0.62	0.6	0.51	0.59	0.57	0.04	0.28	-0.45
Cr (mg kg^{-1})						0.15	0.68	0.63	0.4	0.25	-0.48	0.4	0.75	0.66	0.72	0.63	-0.21	0.14	-0.34
Pb (mg kg^{-1})							-0.01	-0.12	-0.34	0.14	0.1	0.00	0.01	0.09	-0.02	-0.16	0.25	-0.36	0.52
Mn (mg kg^{-1})								0.93	0.37	0.42	-0.62	-0.08	0.71	0.61	0.68	0.65	-0.42	0.51	-0.42
Co (mg kg^{-1})									0.34	0.56	-0.72	-0.07	0.73	0.61	0.7	0.7	-0.31	0.52	-0.49
Sand (g kg^{-1})										-0.18	-0.49	-0.09	0.29	0.33	0.26	0.05	0.2	0.08	-0.32
Silt (g kg^{-1})											-0.77	-0.03	0.61	0.61	0.65	0.6	0.2	0.34	-0.29
Clay (g kg^{-1})												0.09	-0.74	-0.76	-0.74	-0.56	-0.31	-0.36	0.47
OC (g kg^{-1})													0.36	0.28	0.29	0.22	-0.08	-0.2	0.18
pH H_2O														0.75	0.87	0.84	-0.1	0.31	-0.35
T value (cmolc kg^{-1})															0.94	0.67	0.19	0.36	-0.36
Base Sat (cmolc kg^{-1})																0.88	0.01	0.5	-0.53
V (%)																	0.26	0.62	-0.65
Al (ppm)																		-0.13	0.04
Fe (ppm)																			-0.83

Figure 1 - Correlation matrix of trace element contents and soil attributes.



levels, and lithochemical differences in the Serra Geral Formation. Soils derived from mafic and ultramafic rocks generally show higher trace element concentrations, whereas those from felsic rocks have lower levels (TILLER, 1989). The elevated base saturation and pH in Basaltic Hillside soils may influence trace element retention without necessarily indicating contamination (MEDEIROS et al., 2020).

Distinguishing soils derived from the effusive rocks of the Serra Geral Formation from other Santa Catarina soils is crucial for monitoring purposes due to the differing trace element contents related to basalt rock and pedogenetic development stages (BOCARDI et al., 2019). This differentiation

highlights the need to consider spatial variations in Quality Reference Values (QRVs) across different geological provinces and geographic areas.

CONCLUSION

Soils from the Basaltic Hillsides in Santa Catarina were grouped into two clusters based on varying weathering levels, leading to significant differences in barium, chromium, and manganese contents. These findings underscore the need to revise Ordinance IMA/SC No. 45/2021 (IMA, 2021) to establish specific QRVs for basaltic provinces, addressing the discrepancy between legislated

values and the natural levels observed in these areas. Implementing these QRVs would be crucial for enhancing the monitoring of soil contamination by trace elements in the regions studied.

ACKNOWLEDGMENTS

The authors would like to thank the Fundação Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), Programa de Apoio à Pós-graduação (PROAP), Fundação de Amparo à Pesquisa e Inovação de Santa Catarina (FAPESC), Programa de Bolsas Universitárias de Santa Catarina (UNIEDU), to the Universidade do Estado de Santa Catarina (UDESC) for financial support. They would also like to thank the Instituto do Meio Ambiente de Santa Catarina (IMA-SC) for technical assistance. And was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), Brasil – Finance code 001.

DECLARATION OF CONFLICT OF INTEREST

The authors declare no conflict of interest. The founding sponsors had no role in the design of the study, the collection, analysis, or interpretation of data, the writing of the manuscript, and the decision to publish the results.

AUTHORS' CONTRIBUTIONS

All authors contributed equally to the conception and writing of the manuscript. All authors critically reviewed the manuscript and approved the final version.

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