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Trace Elements Reference Values for Soils from Santa Catarina, Brazil

Valores de Referência de Elementos-Traço Para Solos de Santa Catarina, Brasil

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Abstract

The presence of trace elements in the soils, above its natural concentrations, can indicate anthropogenic contamination. Therefore, knowing the natural level of trace elements contents in soils is extremely important in monitoring and remediating contaminated areas. The Brazilian National Environment Council (CONAMA) determines that the states and the Federal District establish the Quality Reference Values (QRV), based on the natural levels of inorganic substances content in soils. Thus, this study aimed to determine the QRV of barium (Ba), cadmium (Cd), nickel (Ni), copper (Cu), zinc (Zn), chromium (Cr), lead (Pb), manganese (Mn) and cobalt (Co) for soils from Santa Catarina. For such, the natural content levels of Cu, Zn, Cr, Pb, Ba, Cd, Ni, Co and Mn were obtained for 43 representative profiles from the state. The natural content and the Quality Reference Values determination for soils from Santa Catarina complied with that requested by the current legislation. The QRV (mg kg^{-1}) was determined based on the 75th percentile (upper quartile) and it was evident, due to the differences among the source materials in SC soils, the need in keeping it by soil groups with similar physical and chemical characteristics, in order to reduce the error possibility in future inspections.

Keywords: Natural Contents. Representative Soils. Environmental Monitoring. Environmental Pollution.

Resumo

A presença de elementos-traço nos solos acima das concentrações naturais pode indicar contaminação antrópica. Sendo assim, o conhecimento dos teores naturais de elementos-traço dos solos é de extrema importância no monitoramento e remediação de áreas contaminadas. O Conselho Nacional de Meio Ambiente (CONAMA) determina que os estados e o Distrito Federal estabeleçam os Valores de Referência de Qualidade (VRQ), baseados nos teores naturais de substâncias inorgânicas nos solos. Dessa forma, este trabalho objetivou determinar os VRQ de bário (Ba), cádmio (Cd), níquel (Ni), cobre (Cu), zinco (Zn), cromo (Cr), chumbo (Pb), manganês (Mn) e cobalto (Co) para solos de Santa Catarina. Para tanto foram utilizados os teores naturais de Cu, Zn, Cr, Pb, Ba, Cd, Ni, Co e Mn obtidos para 43 perfis representativos do estado. Os teores naturais e a determinação dos Valores de Referência de Qualidade para solos de Santa Catarina obedeceram ao preconizado pela legislação vigente. Os VRQ foram determinados com base no percentil 75 (quartil superior) e devido às diferenças entre materiais de origem nos solos de SC, viu-se a necessidade de manter os VRQ por grupo de solos com características físicas e químicas semelhantes, a fim de reduzir a possiblidade de erros em futuras fiscalizações.

Palavras-chave: *Teores Naturais. Solos Representativos. Monitoramento Ambiental. Poluição Ambiental.*

1 Introduction

Concentration of trace elements in the soils may be from natural causes, due to the source material, the weathering degree and the processes of natural deposition. However, these contents can be increased by anthropic sources, such as industrial, agricultural and mining activities, coal burning, vehicle emissions, as well as solid waste deposit or incineration, which can cause its entry into the food chain and consequent health damage (MARRUGO-NEGRETE *et al.*, 2017; MA *et al.*, 2018). Some trace elements are essential to living beings and some others are not, yet when in high concentrations, all of them can cause ecological imbalances. It is important to investigate the trace elements content in soils in order to protect both the environment and the human health (MAZHARI *et al.*, 2017).

Knowing the trace elements contents in soils with no or minimal human activity is important when verifying contamination in soils, since these values can be used in adopting preventive practices, control mitigation and in the identification, monitoring and the recovering of contaminated areas (SILVA *et al.*, 2017; NOGUEIRA *et al.*, 2018). All over the world, the comparison of trace elements content with the standard values established by legislation is often used for checking the soil contamination and thus characterize the potential risk (MAZHARI *et al.*, 2017).

Therefore, in 2009, the Brazilian National Environment Council (CONAMA) ratified the Resolution no. 420 (CONAMA, 2009) which determines that the competent environmental authorities of the states and the Federal District must establish the Quality Reference Values (QRV).

These values are based on the natural content assessment of elements in the soils and can be established based on the 75th or 90th percentile from the sample universe, with anomalies previously removed (CONAMA, 2009). This resolution also presents the terms: *Prevention Value (PV), as the limit concentration of a given substance in the soil, still capable of sustaining its main functions; and *Investigation Value (IV), as the concentration of a given substance in the soil, in which above this value there are potential risks to human health, considering a standardized exposure scenario (agricultural, industrial and residential).

The following Brazilian states and areas already have determined their own QRV values: São Paulo (CETESB, 2014), Espírito Santo (PAYE *et al.*, 2010)em âmbito mundial, são bastante heterogêneos. No Brasil, poucos estudos para estabelecer esses valores foram concluídos. Na ausência de VRQ para metais pesados em solos, estabelecidos para as condições do Estado do Espírito Santo, utilizam-se valores genéricos internacionais ou desenvolvidos para outros Estados. Entretanto, deve-se ressaltar que o uso desses valores pode levar a avaliações inadequadas, já que existem diferenças nas condições técnicas e variáveis ambientais de cada região, em especial das condições geológicas, hídricas e pedológicas. Essas diferenças justificam o desenvolvimento de uma tabela própria com VRQ para metais pesados em solos, adequada às condições do Estado do Espírito Santo. Nesse sentido, o presente estudo buscou obter os teores naturais de 10 metais pesados e verificar a distribuição desses elementos nos solos das bacias hidrográficas Riacho, Reis Magos e Santa Maria da Vitória, no Estado do Espírito Santo, tendo em vista o estabelecimento de Valores de Referência de Qualidade (VRQ, Mato Grosso and Rondônia (SANTOS; ALLEONI, 2013), Minas Gerais (COPAM, 2011), Rio Grande do Norte (PRESTON *et al.*, 2014), Paraíba (ALMEIDA JUNIOR et al., 2016), Rio Grande do Sul (ALTHAUS *et al.*, 2018), Pará (FERNANDES *et al.*, 2018), Paraná Lowland Coastal Plain (Melo *et al.*, 2017), Paraná river Watershed (BOCARDI *et al.*, 2020)and their extrapolation to different locations becomes inadequate. This research aimed to determine the natural concentrations of metals in soils (QRV and in Fernando de Noronha (FABRICIO NETA *et al.*, 2018).

Due to the geological, geomorphological and pedological diversity, the Quality Reference Values in different regions of the country, as well as around the world, may be different. Thus, the objective of this study was to establish the QRV of barium (Ba), cadmium (Cd), nickel (Ni), copper (Cu), zinc (Zn), chromium (Cr), lead (Pb), manganese (Mn) and cobalt (Co) for soils from the state of Santa Catarina, not only for the purpose of complying with federal legislation, but also and mainly to contribute with the Santa Catarina environmental authority in monitoring the elements in soils of the state.

2 Material and Methods

Santa Catarina state, located in southern Brazil, with 95.4 thousand km^2, corresponding to 1.1% of the total Brazilian area, has great geological diversity with recent sediments, a range of more ancient magmatic and metamorphic rocks, succession of Gondwana sedimentary rocks and basic, intermediate and acid lava spills (SCHEIBE, 1986).

The State University of Santa Catarina has a soil bank with samples from different soils of the state. Aiming to determine the natural levels and, consequently, the QRV for the trace elements content in soils from Santa Catarina, this bank was searched for soils that had been collected in places with absence or minimal anthropogenic activity. Hence, 43 profiles were chosen, representing the soils variability in the state (Table 1 and Figure 1). These samples had been collected and the profiles classified by Almeida et al. (2003, 2018), Almeida and Erhart (2009), Paes Sobrinho et al. (2009), Bringhenti et al. (2012), Costa et al. (2013), Ferriera (2013), Lunardi Neto and Almeida (2013), Teske et al. (2013).

Table 1 - Identification, soil class, source material, municipality of the sampling and geographical coordinates (decimals geodesics).

Profile	Soil Class	Source material	Municipality	Latitude	Longitude
1	Argissolo Amarelo Alítico típico	Mica schists	Botuverá	-27.190	-49.064
2	Argissolo Amarelo Distrófico latossólico	Migmatite	São Bonifácio	-27.939	-48.937
3	Argissolo Amarelo Distrófico típico	Granite e Granulite	Rancho Queimado	-27.697	-49.047
4	Argissolo Amarelo Distrófico típico	Hornblendite	Pomerode	-26.738	-49.228
5	Argissolo Bruno-Acinzentado Alítico típico	Argillite and Siltite	Alfredo Wagner	-27.668	-49.187
6	Argissolo Vermelho Distrófico	Siltite and Sandstone	Içara	-28.724	-49.289
7	Argissolo Vermelho Distrófico abrúptico	Siltite and Sandstone	Içara	-28.727	-49.295
8	Argissolo Vermelho Distrófico abruptico	Siltite and Sandstone	Içara	-28.727	-49.295
9	Argissolo Vermelho-Amarelo Alítico típico	Mafic Granulite	Luiz Alves	-26.682	-49.009
10	Argissolo Vermelho-Amarelo Alumínico típico	Metaarenite	Gaspar	-26.994	-48.903
11	Argissolo Vermelho-Amarelo Alumínico típico	Mafic Granulite	Blumenau	-26.798	-49.089
12	Argissolo Vermelho-Amarelo Distrófico latossólico	Sandstone and Siltite	Lauro Müller	-28.390	-49.368
13	Argissolo Vermelho-Amarelo Distrófico latossólico	Migmatite	Águas Mornas	-27.722	-48.936
14	Argissolo Vermelho-Amarelo Distrófico latossólico	Sandstone and Siltite	Lauro Müller	-28.390	-49.368
15	Argissolo Vermelho-Amarelo Distrófico típico	Granite	Treze de Maio	-28.583	-49.110
16	Cambissolo Háplico Alítico típico (Cambisol)	Riodacite	Lages	-28.268	-50.395

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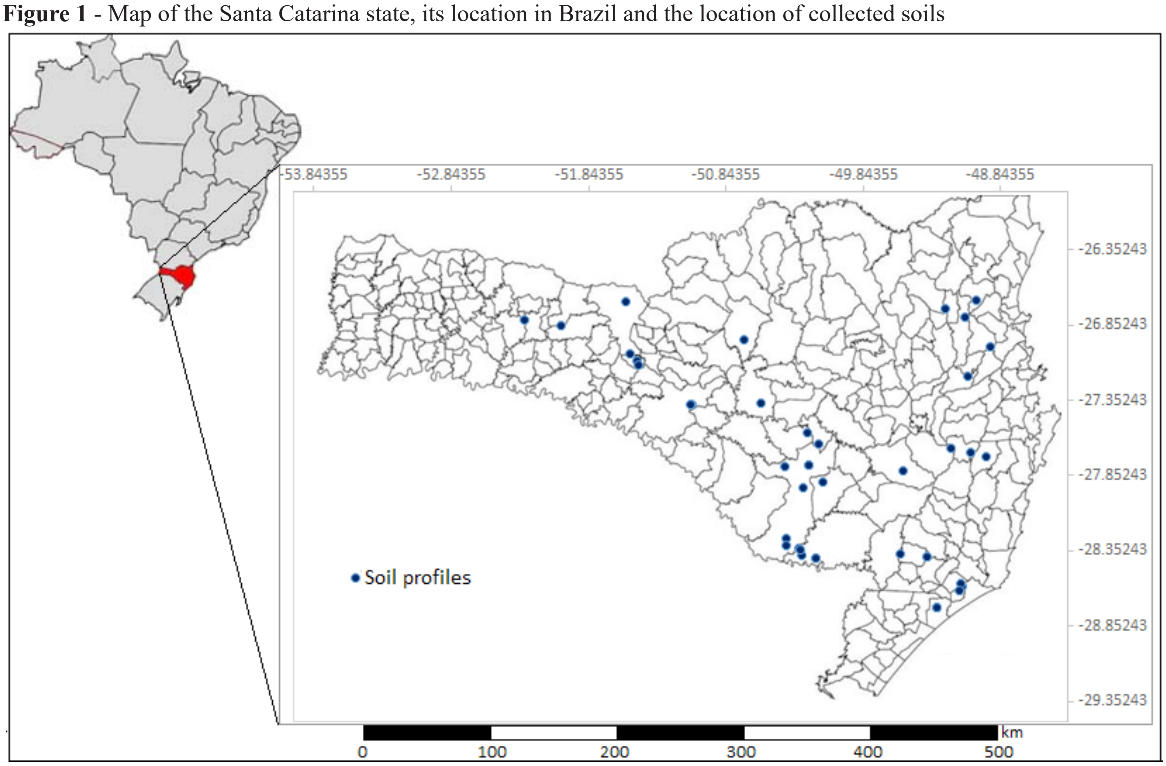
Profile	Soil Class	Source material	Municipality	Latitude	Longitude
17	Cambissolo Háplico Alítico típico	Riodacite	São Joaquim	-28.395	-50.177
18	Cambissolo Háplico Alítico típico	Riodacite	Lages	-28.395	-50.177
19	Cambissolo Háplico Alumínico típico	Porphyritic Phonolite	Palmeira	-27.564	-50.240
20	Cambissolo Háplico Alumínico úmbrico	Phonolite	Lages	-27.779	-50.232
21	Cambissolo Háplico Alumínico úmbrico	Riodacite	Lages	-27.930	-50.273
22	Cambissolo Háplico Alumínico úmbrico	Riodacite	Lages	-28.311	-50.396
23	Cambissolo Háplico Ta Eutrófico típico	Basalt	Luzerna	-27.091	-51.489
24	Cambissolo Háplico Tb Distrófico típico	Granite	Treze de Maio	-28.567	-49.117
25	Cambissolo hístico	Siltite	Bom Retiro	-27.815	-49.544
26	Cambissolo Húmico Alumínico típico	Porphyritic Syenite	Lages	-27.644	-50.164
27	Cambissolo Húmico Distróférrico típico	Basalt	Lages	-27.794	-50.403
28	Cambissolo Húmico Distrófico organossólico	Basalt	Bom Jardim da Serra	-28.372	-49.565
29	Cambissolo Húmico Distrófico típico	Riodacite	Lages	-28.331	-50.303
30	Latossolo Vermelho Distroférrico húmico	Basalt	Faxinal dos Guedes	-26.811	-52.306
31	Latossolo Vermelho Distrófico retrático úmbrico	Basalt	Campos Novos	-27.375	-51.085
32	Latossolo Vermelho Distrófico retrático úmbrico	Basalt	Campos Novos	-27.376	-51.091
33	Neossolo Regolítico Eutrófico típico	Granite	Sangão	-28.617	-49.131
34	Neossolo Regolítico Húmico típico	Phonolite	Lages	-27.779	-50.232
35	Nitossolo Bruno Distroférrico típico	Andesite Basalt	Água Doce	-26.691	-51.566
36	Nitossolo Bruno Distrófico húmico latossólico rúbrico	Riodacite	Ponte Serrada	-26.856	-52.042
37	Nitossolo Bruno Distrófico húmico latossólico rúbrico	Basalt	Curitibanos	-27.370	-50.579
38	Nitossolo Bruno Distrófico rúbrico	Basalt	Lebon Régis	-26.947	-50.706
39	Nitossolo Bruno Distrófico típico	Basalt	Painel	-27.895	-50.129
40	Nitossolo Háplico Distrófico típico	Basalt	Luzerna	-27.044	-51.537
41	Nitossolo Vermelho Alítico típico	Basalt	São Joaquim	-28.376	-50.286
42	Nitossolo Vermelho Distroférrico típico	Basalt	Lages	-28.345	-50.294
43	Nitossolo Vermelho Eutrófico típico	Basalt	Luzerna	-27.112	-51.478

Soil profiles collected and classified by Almeida et al. (2003, 2018), Almeida e Erhart (2009), Paes Sobrinho et al. (2009), Bringhenti et al. (2012), Costa et al. (2013), Ferriera (2013), Lunardi Neto e Almeida (2013), Teske et al. (2013).

Source: Resource data.

Figure 1 - Map of the Santa Catarina state, its location in Brazil and the location of collected soils



Source: Resource data.

With these soil samples, the natural contents of Cu, Zn (HUGEN *et al.*, 2013), Cr, Pb (HUGEN, 2010), Ba, Cd, Ni (SOUZA, 2015), Co and Mn (SUPPI *et al.*, 2018). In each digestion group (30 samples) a Standard Reference Materials (SRM) 2709A reference sample was included, San Joaquin Soil, certified by the National Institute of Standards and Technology (NIST), and a blank for calculating the Limit for Qualitative Detection of the Analytic Method (LDQM) (APHA, 2012). Table 2 shows the methodologies for determining the elements content, the recovery percentage and the LDQM of each studied element. All of them used glassware and reagents were certified.

Table 2 – NIST 2709A recovery percentage, LDQM, methodologies of extraction, reading and recovery percentage (NIST 2709A) of each studied trace element in this research

Elements	NIST Recovery[(1)] (%)	LDQM (mg kg^{-1})	Extraction Methodology	Reading Methodology
Cu Zn Cr Pb	71.02 54.21 83.46 70.55	0.86 2.37 10.64 3.18	Aqua Regia ($HCl+HNO_3$) ISO 11466	Atomic absorption spectrometry with flame atomization (FAAS)
Ni Ba	125 102	5.91 18.54	HNO_3 in microwave oven USEPA 3051A	Atomic absorption spectrometry with flame atomization (FAAS)
Cd	52	0.07	HNO_3 in microwave oven USEPA 3051A	Atomic absorption spectrometry with electrothermal atomization in a graphite furnace (GFAAS)
Co Mn	65 77	1.83 1.94	HNO_3 + H_2O_2 in digester block USEPA 3050B	Optical emission spectrometry with inductively coupled plasma source (ICP OES)

Natural contents determined by Hugen *et al.* 2013, Hugen, 2010; Souza, 2015, Suppi *et al.* 2018.

[(1)]Calculation of the recovery percentage: %recovery = [(recovery content * 100/certified content)].

Source: Resource data.

The natural contents of Cu, Zn, Cr, Pb, Ba, Cd, Ni, Co and Mn of the 43 soil profiles were evaluated by means of factor analysis and cluster analysis by using the R software (R DEVELOPMENT CORE TEAM, 2016).

For the factor and the cluster analysis, the data were standardized (mean = 0 and variance = 1). The used variables were the following: silt, contents of clay and organic carbon, cation exchange capacity (CEC), sum of bases (SB) and aluminum oxides, Al2O3 by sulfuric attack (Al) previously determined by Almeida *et al.*, 2003; Almeida & Erhart, 2009; Paes Sobrinho *et al.*, 2009; Bringhenti *et al.*, 2012; Costa *et al.*, 2013; Ferreira, 2013; Lunardi Neto & Almeida, 2013; Teske *et al.*, 2013with properties similar to the sombric horizon characterized by the USA Soil Taxonomy, are frequent in Southern Brazil. The genesis of this horizon is controversial and poorly understood. This study aimed to describe the occurrence of sombric-like horizons in Ultisols in the South of Santa Catarina State, at low altitudes, and suggest possible processes of humus transference, accumulation and persistence in these horizons. Physical, chemical and mineralogical properties of four Ultisols were evaluated; three were sampled in a toposequence, and another representative one in an isolated profile (RSP; Almeida *et al.*, 2018shallow soils are predominant in the Basaltic Hillsides of Santa Catarina State, in southern Brazil, but their agricultural use is restricted, either by excessive stoniness, low effective depth or steep slopes. Information about soil properties and distribution along the slopes in this region is, however, scarce, especially regarding genesis and clay fraction mineralogy. The objective of this study was to evaluate soil properties of 12 profiles distributed in three toposequences (T and, as a similarity measure, the Euclidean distance among the profiles. The agglomeration algorithm adopted was Ward's hierarchical method, in order to form groups that are more homogeneous. The values of physical chemical attributes of each soil profile are shown in Table 3.

Table 3 - Physical and chemical attributes of the 43 soil profiles

Profile	Silt (g kg^{-1})	Clay (g kg^{-1})	Organic Carbon (g kg^{-1})	CEC (cmolc kg^{-1})	SB (cmolc kg^{-1})	Al_2O_3 (g kg^{-1})
1	240.00	230.00	21.70	15.65	6.45	6.09
2	320.00	370.00	33.00	8.97	2.61	92.80
3	440.00	330.00	35.30	11.00	1.30	44.02
4	210.00	260.00	28.40	9.61	2.71	28.16
5	520.00	320.00	30.20	21.30	2.00	32.43
6	80.00	300.00	20.00	5.80	2.70	5.61
7	368.00	170.00	14.60	6.20	5.20	11.61
8	368.00	170.00	14.60	6.20	5.20	28.55
9	220.00	360.00	30.00	15.89	3.99	36.06
10	110.00	380.00	27.00	14.50	2.72	7.97

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Profile	Silt (g kg^{-1})	Clay (g kg^{-1})	Organic Carbon (g kg^{-1})	CEC (cmolc kg^{-1})	SB (cmolc kg^{-1})	Al_2O_3 (g kg^{-1})
11	180.00	240.00	24.90	15.07	5.30	7.15
12	126.00	157.00	12.80	5.80	2.70	5.81
13	180.00	450.00	21.00	6.65	0.69	34.90
14	140.00	180.00	17.00	6.21	5.18	31.40
15	80.00	300.00	9.00	2.68	0.36	92.03
16	260.00	640.00	33.00	25.50	2.60	132.37
17	328.80	610.00	32.70	26.30	3.90	93.82
18	330.80	570.00	33.00	23.40	3.70	126.94
19	240.00	500.00	20.80	12.40	1.60	149.03
20	240.00	550.00	22.20	13.20	3.00	159.47
21	240.00	620.00	43.30	19.60	7.00	100.76
22	360.00	580.00	33.70	23.90	1.80	99.39
23	190.00	480.00	34.30	14.28	4.03	38.61
24	170.00	300.00	14.00	5.71	0.95	97.16
25	207.00	481.00	33.00	22.12	0.30	93.39
26	360.00	460.00	39.00	17.40	2.80	104.35
27	220.00	540.00	31.80	11.30	1.50	51.34
28	239.00	485.00	52.10	17.80	0.80	102.77
29	208.00	600.00	39.10	19.00	0.90	108.43
30	190.00	736.00	26.40	25.60	14.00	98.82
31	210.00	774.00	22.00	15.52	1.45	70.82
32	227.00	754.00	40.20	17.00	2.40	60.26
33	210.00	140.00	7.00	2.24	0.69	2.75
34	230.00	540.00	29.60	15.30	4.30	155.57
35	390.00	446.00	38.07	16.60	4.00	56.74
36	284.00	614.00	32.70	19.00	11.70	127.00
37	294.00	684.00	38.30	18.90	4.40	101.90
38	313.00	641.00	46.50	20.00	1.20	40.96
39	316.00	578.00	33.90	15.50	2.80	46.13
40	260.00	670.00	46.50	15.29	7.06	24.11
41	152.00	680.00	16.40	21.00	8.50	49.85
42	261.20	590.00	32.40	23.60	10.00	46.89
43	370.00	420.00	27.90	11.96	8.10	11.06

These values were determined by Almeida et al. (2003, 2018), Almeida and Erhart (2009), Paes Sobrinho et al. (2009), Bringhenti et al. (2012), Costa et al. (2013), Ferriera (2013), Lunardi Neto and Almeida (2013), Teske et al. (2013).
Source: Resource data.

In order to group the samples by their degree of similarity, groups were built based on the joint contribution of the variables contents of silt, clay and organic carbon, CEC, SB and Al, in a way that the reference values could be estimated for each group. The dendrogram resulting from the cluster analysis (Figure 2, próxima página) presented six groups in accordance with the samples similarity (Group 1, Group 2, Group 3, Group 4, Group 5, Group 6). The connection distance delimitation was established based on a visual analysis.

Group 5 grouped three Nitossolos and a Latossolo with high levels of clay, SB and CEC (Profiles 30, 36, 41 and 42).

Group 6 is composed of Latossolos, Nitossolos and Cambissolos, all developed from basalt or andesite basalt of the highlands, west and midwest regions of Santa Catarina (Profiles 21, 23, 27, 28, 31, 32, 35, 37, 38, 39, 40 and 43), with high contents of clay and CEC.

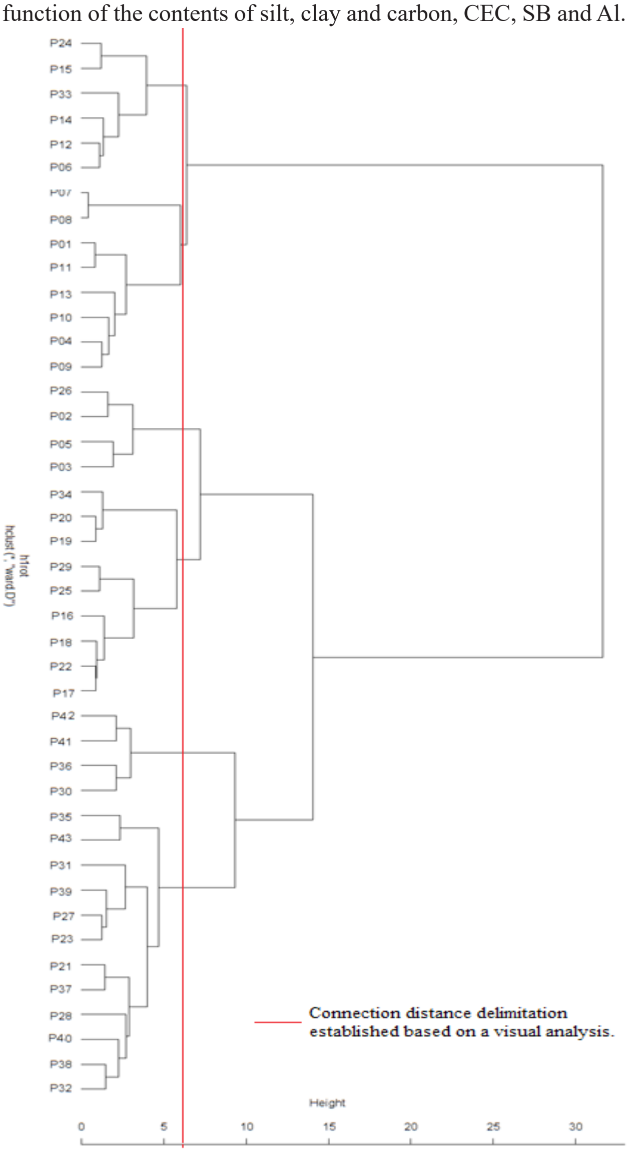
The QRV of Cu, Zn, Cr, Pb, Ba, Cd, Ni, Co and Mn were calculated from their natural contents, adopting the 75th percentile, or upper quartile (UQ). This percentile was chosen because it has less permissiveness than the 90th percentile, thus causing greater environmental security. For all the performed tests, the minimum significance level considered was 5%

Group 1 includes soils from southern Santa Catarina (Profiles 6, 12, 14, 15, 24 and 33), developed from sandstone and siltite or granite, with low silt and clay contents and lower CEC.

In Group 2 are the Argissolos) from cities with low altitudes, part of Florianópolis, Vale do Itajaí and southern SC (Profiles 1, 4, 7, 8, 9, 10, 11 and 13), with higher contents of silt, clay and CEC.

Group 3 concentrates Argissolos and Cambissolo from regions with higher altitude (Profiles 2, 3, 5 and 26), also having higher levels of clay and Al_2O_3 than the previous group.

Figure 2 - Dendrogram classifying samples into six groups, in function of the contents of silt, clay and carbon, CEC, SB and Al.



Source: Resource data.

In Group 4, Cambissolo and a Neossolo from the mountain region of Santa Catarina were included (Profiles 16, 17, 18, 19, 20, 22, 25, 29 and 34), developed from rhyodacite, phonolites or siltite and with high Al values.

3 Results and Discussion

Mean and standard deviation values regarding the contents of Cu, Zn, Cr, Pb, Ba, Cd, Ni, Co and Mn for the different soil classes from Santa Catarina are in Table 4 below.

The mean contents of Ba, Cd, Ni and Cr in Argissolos (37.12; 0.10; 10.8; 29.7 mg kg^{-1}) and Cambissolos (67.9; 0.10; 13.92; 27.29 mg kg^{-1}) from Santa Catarina were lower than the contents from Argissolos (133.12; 0.47; 22,55 72.97 mg kg^{-1}) and Cambissolos from Minas Gerais (231.67; 0.72; 26.47; 97.37 mg kg^{-1}) (CAIRES, 2009). The opposite occurred with the contents of Co, Pb and Mn (Acrisols: 9.55; 2.08 and 240.99 mg kg^{-1}; Cambisols: 14.76; 10.76; 337.12 mg kg^{-1}). These differences can happen due to lithological, topographic and climatic differences and, consequently, different degrees of weathering.

When observing the different soil classes, the highest contents of Ba, Ni, Cu, Zn, Cr, Mn and Co were found in Nitossolos. From the nine Nitisols evaluated in this study, eight are developed from mafic rocks. Although the highest contents were in the Nitossolosi, the soil classes do not seem to be a determinant factor for the trace elements concentration in this study. The regions of the state, and consequently the source material from the soils, seem to have greater importance on the element contents. The relation of trace element content with the source material (basaltic rock) and the absence of influence on the pedogenetic development degree were observed by Bocardi *et al.* (2020)and their extrapolation to different locations becomes inadequate. This research aimed to determine the natural concentrations of metals in soils

Table 4 - Characterization of the sampled soil classes based on the mean content and standard deviations from the concentrations of Ba, Cd, Ni, Cu, Zn, Cr, Pb, Mn and Co.

Element	Class [(1)]									
	Argissolos		Nitossolos		Cambissolos		Latosssolos		Neossolos	
	m[(2)]	s[(3)]	m	s	m	s	m	s	m	s
	mg kg^{-1}									
Ba	37.12	39.2	88.53	86.62	67.9	58.53	22.34	1.07	37.56	28.9
Cd	0.10	0.02	0.09	0.02	0.10	0.04	0.09	0.02	0.09	0.03
Ni	10.8	6.16	23.64	23.01	13.92	7.80	10.30	4.84	7.20	1.80
Cu	4.95	3.35	117.2	49.28	57.8	46.76	94.12	19.01	3.18	4.07
Zn	19.52	10.48	67.45	18.22	47.2	20.19	46.77	18.82	32.48	3.54
Cr	29.7	22.98	65.78	50.67	27.29	24.45	50.36	18.26	10.52	2.33
Pb	8.34	10.5	10.81	4.07	15.28	12.51	13.83	2.44	31.25	16.01
Mn	254.7	384	1033	1015	689.1	864.3	272.5	54.18	768.3	389
Co	10.23	7.13	47.28	44.2	23.27	28.17	13.56	2.27	9.22	0.15

[(1)]Classification of the first category level – Order, according to the Brazilian Soil Classification System and to the WRB international system; [(2)] Arithmetic mean; [(3)]Standard deviation.

Source: Resource data.

(QRV).

Grouping samples according to the contents of silt, clay and organic carbon, CEC, SB and Al, enabled to know the contents distribution of Cu, Zn, Cr, Pb, Ba, Cd, Ni, Co and Mn at different levels. This can be seen in Table 5, where the proposed Quality Reference Values for soils from the State of Santa Catarina are displayed. For estimating the QRV, the value corresponding to the upper quartile (UQ) was adopted as the basis, equivalent to 75% of the data frequency distribution for each group.

Table 5 - Quality Reference Values(1) for contents of Ba, Cd, Ni, Cu, Zn, Cr, Pb, Mn and Co in soils from the state of Santa Catarina

Groups	Element								
	Ba	**Cd**	**Ni**	**Cu**	**Zn**	**Cr**	**Pb**	**Mn**	**Co**
	----Content(2) (mg kg^{-1})----								
1	23.52	0.11	10.52	3.58	27.59	24.48	34.36	506.79	8.80
2	19.62	0.1	14.23	6.94	23.07	48.27	3.73	99.11	8.92
3	90.01	0.12	13.07	6.40	41.10	21.63	22.8	325.6	15.06
4	57.99	0.12	10.69	66.58	48.11	13.83	18.09	963.25	12.01
5	167.81	0.11	18.54	117.93	75.40	45.24	16.82	2558.8	92.82
6	88.58	0.11	27.81	146.92	78.10	67.71	12.18	1303	54.28
UQm(3)	75.76	0.11	18.3	93.84	55.60	47.68	16.08	799.28	22.58

(1)Content for the soils belonging to each group, corresponding to the upper quartile value of the frequency distribution of the sample data in each group; (2)Upper middle quartile among the groups; (3) General upper middle quartile for groups.

Source: Resource data.

Regarding the evaluated mean trace elements contents, in each formed group, the highest contents of Ni, Cu, Zn, Cr, Mn and Co were found in groups 5 and 6. These are groups predominantly formed by soils developed from basalt and basalt andesite, mafic rocks. Generally, soils developed from mafic and ultramafic rocks have higher concentrations of trace elements than those from felsic rocks (Tiller, 1989). Fe, Co and Cr, for example, are concentrated in ultramafic rocks, Cu, Zn, Cd and Mn are concentrated in basalts and andesites (ALLEONI *et al.*, 2005). Biondi *et al.* (2011), Zinn *et al.* (2020), Caires (2009), and Althaus *et al.* (2018) when analyzing natural contents of trace elements in soils, also found higher contents of these elements in soils developed from rocks with higher Fe concentrations.

The mean contents obtained for Ba, Ni, Cu, Zn, Cr, Mn and Co in Groups 5 and 6, which have the highest clay contents and CEC, are higher than in Group 1, which also has the lowest clay contents and CEC. Adsorption processes on surfaces can explain the relation between trace elements and clay, or in other words, soils with higher CEC and clay contents are better chemical adsorbents of trace elements than soils with the sand fraction predominance, composed mainly of quartz and feldspars, minerals that have little adsorption capacity (dos SANTOS *et al.*, 2017)the local geological features may be so heterogeneous that global or even regional guideline values cannot be applied. The Greenstone Belts are worldwide geological formations of vast extension, containing mineralization of various metals (e.g., Au, Cr, Ni, and Ag. Xavier (2013), Costa (2013) and Fernandes *et al.* (2018) positively correlated the values found of trace element contents with the clay contents, CEC and organic matter. On the other hand, Almeida Júnior *et al.* (2016) related the low values found in his study with the source material (rocks with low iron content) and low values of pH, CEC and clay content.

The soil organic carbon also influenced the contents of Ba, Ni, Cu, Zn, Cr and Co. The trace elements, when released from the rocks by the weathering, can be adsorbed into the organic matter functional groups or then complex themselves with it, thus decreasing their soil mobility (ALLEONI *et al.*, 2005; FERNANDES *et al.*, 2018).

In Table 6 are the QRV for several regions of Brazil, as well as the mean contents of the studied elements for other regions of the world:

Table 6 - QRV comparison for the contents of Ba, Cd, Ni, Cu, Zn, Cr, Pb, Mn and Co in soils from Santa Catarina with the Reference or mean Values of soils from other regions of Brazil and the world

Locale	Element								
	Ba	**Cd**	**Ni**	**Cu**	**Zn**	**Cr**	**Pb**	**Mn**	**Co**
	----(mg kg^{-1})----								
SC*(1)	75.76	0.11	18.3	93.84	55.6	47.68	16.08	799.28	22.58
SP*(2)	75	<0.5	13	35	60	40	17	-	13
ES*(3)	-	<0.13	9.17	5.91	29.87	54.13	<4.54	137.8	10.21
MT and RO*(4)	-	<0.3	2.1	20.6	3	44.8	9	-	21.3
MG *(5)	93	<0.4	21.5	49	46.5	75	19.5	-	6
RN *(6)	58.91	0.1	19.84	13.69	23.85	30.94	-	-	15.41

PB*(7)	87.96	0.06	-	11.22	23.46	28.81	10.01	350.83	-
Locale	Element								
	Ba	Cd	Ni	Cu	Zn	Cr	Pb	Mn	Co
	--(mg kg^{-1})------------------------------								
Coastal Plain - PR*(8)	111.4	1.02	17.22	17.8	52.5	48.7	16.9	-	<0.17
Paraná River Watershed *(9)	148.5	0.8	7.7	103.8	62.3	39.1	15.0	-	-
Pará *(10)	14.3	0.4	-	9.9	-	24.1	-	72	-
Fernando de Noronha*(11)	834.88	-	58.75	41.49	117.58	266.13	-	-	19.61
Cuba*(12)	111	0.6	170	83	86	153	50	1947	25
Florida **(13)	13.7	0.01	9.08	2.21	5.12	8.45	5.38	20.3	-
India**(14)	983.01	-	25.4	18.15	38.09	134.31	50.12	-	7.24
Cataluña, Spain **(15)	241	-	36.1	28.1	92.8	45.4	59.6	-	-

(VRQ; (4)(SANTOS and ALLEONI, 2013); (5)COPAM, 2011; (6)(PRESTON *et al.*, 2014); (7)(ALMEIDA JÚNIOR *et al.*, 2016); (8)(MELO *et al.*, 2017); (9) (Bocardi *et al.*, 2020) (QRV; (10) (FERNANDES *et al.*, 2018); (11) (FABRICIO NETA *et al.*, 2018); (12)(ALFARO *et al.*, 2015); (13)(CHEN *et al.*, 1999)As, Ba, Be, Cd, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Se, and Zn; (14)(DANTU, 2010); (15)(BECH *et al.*, 2005).

The QRV of Santa Catarina, for most of the analyzed trace elements, were greater than the QRV of Rio Grande do Norte, Paraíba, Espírito Santo, Mato Grosso and Rondônia and the mean contents of the state of Florida - USA. In SC, there is a large amount of soils developed from mafic and intermediate rocks, a material naturally rich in trace elements, which does not occur in the regions mentioned above.

The QRV generated in this study, with the exception of copper, were smaller than the QRV of Fernando de Noronha and Cuba. These regions showed high contents of trace elements and, consequently, high QRV due to their source material. In the case of Fernando de Noronha, the island is a volcanic archipelago, having from ultramafic rocks to intermediates resulting from volcanic events, with the presence of ankaratrites (FABRICIO NETA *et al.*, 2018). On the other hand, Cuba has soils developed on ultramafic rocks (ALFARO *et al.*, 2015).

The large variations among the QRVs determined in different states and in other countries consolidates that it is necessary to determine the QRV for each location, due to the great geological, geomorphological and pedological diversity of the country and the world. Thus, complying with the provisions of Article 8 of Resolution no. 420 of CONAMA for barium, cadmium, nickel, copper, zinc, chromium, lead, manganese and cobalt in Santa Catarina soils.

The determined cobalt Quality Reference Value for the state of Santa Catarina (22.58 mg kg^{-1}) is close to the Prevention Value (25 mg kg^{-1}) while that of the copper (93.84 mg kg^{-1}) is higher than the Prevention Value (60 mg kg^{-1}) established by CONAMA (2009). However, it is probable that the PV is underestimated, since they it was determined in soils different from those found in SC, showing the importance of also determining the PV and IV for trace elements in the state.

With the adoption of a single QRV for the state, most trace element contents in Groups 5 and 6 could be considered as hailing from anthropic contamination, when in fact they are natural for soils originated from mafic rocks. As for the soils of Groups 1, 2 and 3, the contents of most trace elements analyzed are much lower than the QRV suggested for the state, which would allow a future anthropic contamination.

Due to the diversity of soil source material in Santa Catarina, adopting a single QRV for the state can lead to inspection errors. Thereby, it is proposed in this study to use reference values by groups composed of soils with similar characteristics. This allows to reduce the error possibility at the inspection, by preventing a basalt-originated soil from being appointed as contaminated by trace elements, when it actually has only natural contents, or that soils originated from sandstone and siltite, for example, which are contaminated anthropically, to be considered as having a natural concentration.

Another important matter is that trace elements in uncontaminated soils have lower mobility when compared to the ones resulting from anthropogenic contamination, because the former are linked to silicates and minerals whereas the ones hailing from anthropic activities are in a less stable form and may be more easily available (BOTSOU et al., 2016) SUNGUR et al., 2014). That way, high natural trace element contents in soils do not necessarily indicate a risk for the living beings, due to their lower availability.

4 Conclusion

The Quality Reference Values of trace elements for soils in Santa Catarina are different from those in other regions, reinforcing the need of determining QRV for each state, as required by CONAMA.

Aiming at a greater representation, the 75th percentile values, determined for each group, can be used for soils that have similar characteristics.

The presence of source material from basalt and basalt andesite in soils from Santa Catarina resulted in QRV of trace elements generally superior to those from states where the soils do not have material developed from mafic source.

A higher CEC, clay content and organic carbon all contribute to a larger concentration of trace elements in the soil.

QRV from Cu exceeded and from Co was close to the PV adopted by CONAMA, illustrating the importance of determining this guiding value for trace elements in the states, considering the regional geology.

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