

Soil Characterization in a Subtropical Forest Crossed by Highways (Cantareira State Park, SP, Brazil)

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Foram analisadas onze amostras de solo do Parque Estadual da Cantareira para avaliar a influência do tráfego veicular. Determinou-se para todos os solos a concentração total, parcial e biodisponível de (Na, Al, Ca, Mg, K, Si, Ti, Mn, Cr, Ni, Cu, Zn, As, Cd, Pb). Até a data da amostragem não foram observadas influências das rodovias sobre a concentração dos metais no solo. A única exceção ocorreu no solo do ponto 3 (alta porcentagem de argila 64% e matéria orgânica 6,4%) onde se encontrou a mais alta concentração de Cr (74,5 e 94,5 mg kg⁻¹), Ni (22,5 e 54,8 mg kg⁻¹), Cu (83,8 e 121 mg kg⁻¹), Cd (1,28 e 1,74 mg kg⁻¹) e As (2,04 e 2,67 mg kg⁻¹) na fração A (0-20 cm) e B (20-40 cm) respectivamente, do que nos demais solos, provavelmente estes elementos provem de outra fonte poluidora. A seqüência dos microelementos biodisponíveis na fração A do solo foi As > Cd > Zn > Cu > Pb > Ni > Cr.

Eleven soil samples within the Cantareira State Park were analyzed to evaluate the traffic influence. For all soil samples total, partial and bioavailable concentration of (Na, Al, Ca, Mg, K, Si, Ti, Mn, Cr, Ni, Cu, Zn, As, Cd, Pb) were determined. No influence from the highways in metals concentration in the soil could be observed up to sampling date. The only exception occurred in soil point 3 (high clay 64% and organic matter 6.4%), that presented higher concentration of Cr (74.5 and 94.5 mg kg⁻¹), Ni (22.5 and 54.8 mg kg⁻¹), Cu (83.8 and 121 mg kg⁻¹), Cd (1.28 and 1.74 mg kg⁻¹) and As (2.04 and 2.67 mg kg⁻¹), in fraction A (0-20 cm) and B (20-40 cm) respectively than the others ones, probably these elements came from other pollutant source. The availability sequence of the microelements in fraction A of the soil was As > Cd > Zn > Cu > Pb > Ni > Cr.

Keywords: forest park, soil characterization, metals, highway influence

Introduction

The Cantareira State Park is one of the few subtropical forest ecosystems still preserved in the State of São Paulo, Brazil. This park plays an important role on city climate, avoiding the transference of heats and pollution from central area São Paulo city in the direction to the suburb. This park is located in the north of the city (latitude 23° 22" and longitude 46° 26") and occupies an area of 7900 m².

The Fernão Dias Highway (extension 14479 m), Sezefredo Fagundes Road (10510 m) and Nova Cantareira Road (8899 m) cross the park. These highways can cause

an environmental impact in the bordering areas. The drainage waters from the highways and winds drag pollutants containing toxic metals and organic compounds. The traffic, residues from the roads, car leaks and atmospheric deposition produce these pollutants.

Usually highways construction changes the landscape. Trombulak and Frissel¹ showed that the effects caused by construction of highways are associated to negative effects in biota integrity, *i.e.*, the terrestrial and aquatic ecosystems. The streets and highways traffic can cause several effects in the ecosystem, for example, mortality of species, modification of animal behavior and change in the soil characteristics (physical: soil density, temperature, soil water content and chemical: toxic metals, salts, ozone, nutrients).

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Munch ² investigated contaminations of polycyclic aromatic hydrocarbons (PAH) and metals (Pb, Zn, Cu, Cd) along the streets and highways of Dortmund (Germany) and found concentrations of 6.6-9.8 ppm for PAH; 58-330 ppm for Zn; 48-130 ppm for Pb and 0.6-1.4 ppm for Cd. Subsoil contamination of the streets and highways are about 26% for PAH, 36% for Zn, 43% for Pb and 78% for Cd smaller than in the surface soil. These results denote that in general, the soil tends to retain the pollutants in the upper layer.

Strnad *et al.* ³ evaluated 54 points of soil samples collected close to highways in Czech Republic. The average values found for Cd, Cr, Cu, Ni, Pb and Zn by the extraction with HNO₃ 2 mol L⁻¹ were 0.49, 6.7, 27.5, 8.0, 50 and 80 mg kg⁻¹, respectively.

Dierkes and Geiger⁴ had observed that highways drainage waters contain significant amount of toxic metals (Pb, Cu, Zn, Cd) and hydrocarbons that could leach through the soil and reach the groundwater. Usually, the contamination of Pb (5–11 mg L⁻¹) came from fuel and had decreased with the use of unleaded gas. High Zn concentrations (44–274 µg L⁻¹) could be related to guardrail and the Cd content (0.4 mg L⁻¹) to tire fragments. It was also observed that high amount of pollutants were in the upper layer of the soil and tend to decrease quickly with the soil depth and the distance from the highway. Usually, a drastic reduction of the metal concentration was observed after 20 m from the highway, but also high concentration could be found at 200 m depending on winds speed and direction.

Garcia *et al.* ⁵ found high concentrations of Zn, Pb and Cu in soils close to streets in Spain. Good correlations were observed for total and bioavailable concentration (extraction with diethylenetriaminepentaacetic acid (DTPA)) of Cd, Cu, Pb and Zn in soil samples. That fact indicates that the contamination could be from the same source, *i.e.*, the vehicles traffic.

Monaci *et al.* ⁶ determined several metals Al, Ba, Cr, Fe, Mn, Na, Ni, Pb, Ti and V in the Sena river and pointed out that the presence of those metals are due to soil resuspension and vehicular traffic. He also observed that Ba could be a substitute for Pb as fuel tracer.

Measurements of lead in agricultural soils of Illinois (USA) presented an increase in the Pb concentration from 12 µg g⁻¹ to 25 µg g⁻¹ between 1920 and 1960.⁷ A similar study carried out in soils close to highways with high vehicular traffic density, during 40 years, had increased Pb concentration from 17 µg g⁻¹ (1920) to 50 µg g⁻¹ (1967).⁸

The Forest Institute in São Paulo (Brazil), organization responsible for the control of Cantareira State Park, wished to evaluate the highway influence in the soil quality of

the subtropical forest. The aim of the present study is to determine the total, partial and bioavailable concentrations of metals in soils, as well as their mobility and availability to environment. This research will support the understanding of the impact traffic on the bordering soil of the Fernão Dias, Sezefredo Fagundes and Nova Cantareira highways.

Experimental

Soil samples were collected in 11 points along the Highway Fernão Dias (sampling date November 1999), Sezefredo Fagundes Road (sampling date November 1999) and Nova Cantareira (sampling date April 2000) inside and around of the Cantareira State Park. The collect points kept a distance of 5 km among them and a distance about 50 m from the highways. The Figure 1 presents the collect points in the park area. The sampling points 1, 2, 3, 4 and 5 were located along the Sezefredo Fagundes Road. The sampling points 6, 7 and 8 were sited along the Highway Fernão Dias and sampling points 9, 10 and 11 along the Nova Cantareira Road. The soils were collected in two different depths 0-20 cm (fraction A) and 20-40 cm (fraction B), using a special tube auger collector of stainless steel. The samples were kept in polyethylene bags. All samples were grounded to 2 mm, air-dried and carefully homogenized.

For all soil samples, total, partial and bioavailable concentration of Na, Al, Ca, Mg, K, Si, Ti, Mn, Cr, Ni, Cu, Zn, As, Cd and Pb were determined. Chemical (pH, cation exchange capacity (CEC), organic matter (OM) and physical (clay, silt and sand content) soil characterization was also carried out (Table 1).

Table 1. Soil characterization of the 11 samplings soils in fraction A (0-20cm) of the Cantareira State Park, SP, Brazil

| Soil | Sand (%) | Silt (%) | Clay (%) | CEC (cmol kg ⁻¹) | pH | OM (%) |
|------|----------|----------|----------|------------------------------|-----|--------|
| 1A | 56 | 16 | 28 | 18 | 4.1 | 4.5 |
| 2A | 56 | 14 | 30 | 24 | 4.4 | 5.4 |
| 3A | 22 | 16 | 64 | 30 | 4.1 | 6.4 |
| 4A | 39 | 20 | 41 | 23 | 3.6 | 6.2 |
| 5A | 41 | 13 | 46 | 26 | 3.4 | 6.7 |
| 6A | 48 | 18 | 34 | 21 | 3.7 | 5.5 |
| 7A | 53 | 10 | 37 | 24 | 3.3 | 6.4 |
| 8A | 48 | 21 | 31 | 24 | 5.7 | 6.5 |
| 9A | 56 | 8 | 36 | 27 | 3.7 | 6.7 |
| 10A | 55 | 11 | 34 | 22 | 3.7 | 6.4 |
| 11A | 45 | 14 | 41 | 22 | 3.7 | 5.6 |

The total metal content was determined by wavelength dispersive X-ray fluorescence spectrometer RIX 3000 (Rigaku Co, Osaka, Japan). Cd, Pb and As total content were not measured by this technique due to their low

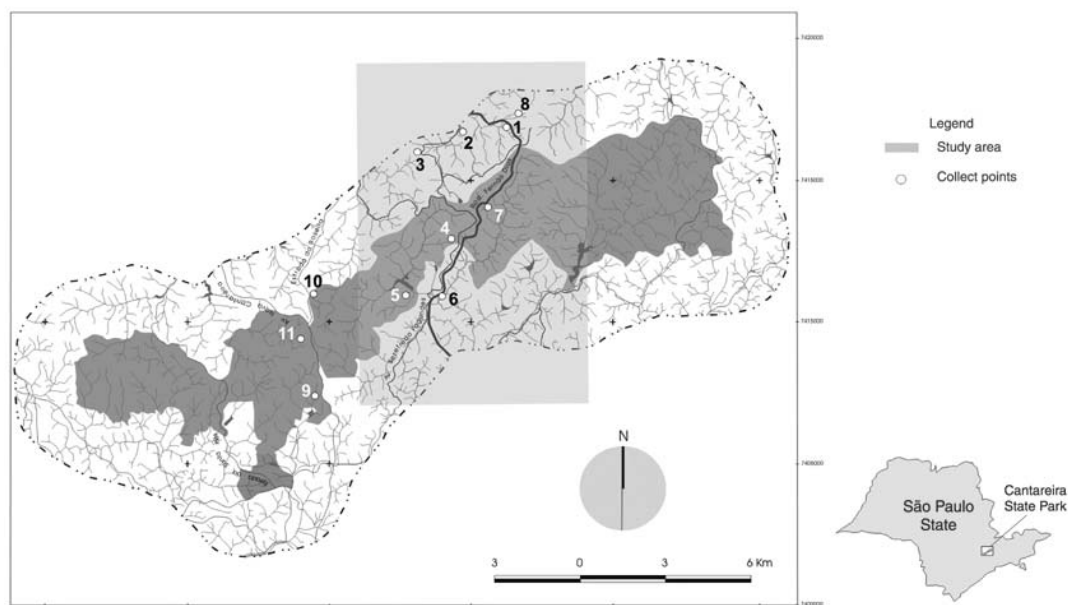


Figure 1. Cantareira State Park map and soil sampling points.

sensibility at trace level. Around 0.9g of soil samples were mixed with boric acid (9:1) and grounded carefully to 200 mesh. The powder was pressed with hydraulic press to obtain a double-layer pressed pellets. The results are

presented in Tables 2 and 3.

The determination of partial concentration was made by inductively coupled plasma-optical spectrometer Spectro Flame (Spectro Analytical Instruments GmbH, Kleve,

Table 2. Total, partial, and bioavailable concentration range of the macro elements in soil sample fraction A (0-20 cm) and B (20-40 cm) in the state park Cantareira

| Elements | | Total (% m/m) | P3 | Partial (mg kg ⁻¹) | P3-P8 | Bioavailable (mg kg ⁻¹) | P3-P8 | Average value | | |
|----------|---|--------------------------------|---------------------------|-----------------------------------|-----------|--|----------|------------------------|-----------------------------------|--|
| | | | | | | | | Total (% m/m) | Partial (mg kg ⁻¹) | Bioavailable (mg kg ⁻¹) |
| Na | A | 0.25-0.41 | 0.074 | 27.2-694 | | <LOD | | ^a 0.32±0.05 | 284±258 | |
| | B | 0.28-0.69 | 0.075 | 27.4-814 | | | | ^a 0.37±0.12 | 349±289 | |
| Al | A | 8.4-12.2 | | 17121-52581 | | 420-1346 | P8=188 | 10.4±1.3 | 31951±10495 | ^b 672±313 |
| | B | 9.5-13.5 | | 23011-71799 | | 215-1023 | P8=89 | 11.4±1.2 | 38055±14528 | ^b 451±254 |
| Ca | A | 0.14-0.35 | | 126-872 | P8=1472 | 33-573 | P8=1462 | 0.22±0.07 | ^b 280±231 | ^b 209±187 |
| | B | 0.14-0.382 | | 88.9-566 | P8=1094 | 10-382 | P8=900 | 0.22±0.09 | ^b 238±155 | ^b 109±125 |
| Mg | A | 0.68-1.134 | 1.333 | 170-2489 | | 13.6-99.9 | P8=152.6 | ^a 0.85±0.12 | 1094±953 | ^b 41±31 |
| | B | 0.754-1.24 | 1.355 | 175-3588 | | 4.0-64.9 | P8=117.7 | ^a 0.94±0.15 | 1398±1400 | ^b 20±25 |
| K | A | 0.53-2.40 | 0.105 | 185-2295 | | 30.3-109.2 | P8=121.1 | ^a 1.48±0.63 | 1080±895 | ^b 52±24 |
| | B | 0.58-2.44 | 0.07 | 98.8-3473 | | 8.1-131.2 | P8=72.2 | ^a 1.66±0.63 | 1411±1319 | ^b 32±36 |
| Si | A | 27.4-39.3 | 8 | 57.1-246 | | - | | ^a 34.6±3.5 | 110±56 | |
| | B | 27.8-37.4 | 7.6 | 47.5-250 | | - | | ^a 33.9±3.1 | 113±70 | |
| Fe | A | 3.1-4.3 | 13.3 | 18954-37451 | P3=81133 | - | | ^a 3.7±0.5 | ^a 26158±5776 | |
| | B | 3.4-4.6 | 13.9 | 23479-36325 | P3=104736 | - | | ^a 4.1±0.4 | ^a 29123±4019 | |
| Ti | A | 0.50-0.80 | 1.25 | 602-3495 | P3=7798 | 0.96-7.98 | | ^a 0.68±0.10 | ^a 1481±888 | 2.6±2.2 |
| | B | 0.52-0.86 | 1.23 | 590-3132 | P3=3332 | 0.22-5.68 | | ^a 0.71±0.09 | ^a 1607±909 | 1.5±1.6 |
| Ba | A | 398-1138 µg g ⁻¹ | 115 µg g ⁻¹ | 31.3-122 | P3=19.7 | - | | ^a 806±258 | ^a 69±33 | |
| | B | 474-1119 | 91.4 | 46.7-120 | P3=34.4 | - | | ^a 833±228 | ^a 83±28 | |
| Mn | A | 19.3-716 | 1532 | 28.3-585 | P3=1152 | - | | ^a 309±244 | ^a 230±218 | |
| | B | 17.5-595 | 1525 | 54.2-522 | P3=234.2 | - | | ^a 251±187 | ^a 233±147 | |

(^a) Average values without sampling point 3=P3 or (^b) point 8=P8; LOD Na=0.0025 mg L⁻¹.

Germany). 0.5 g of soil (200 mesh) were treated with 10mL HNO_3 concentrated according to EPA 3051 methodology.⁹ The results are also presented in Tables 2 and 3.

The determination of bioavailable concentration was also carried out by ICP-OES technique. A sample of 2 g of soil, grounded to 2mm was extracted with 40 mL EDTA-NH_4 0.05 mol L^{-1} (pH 7) with 1 hour shake of 10 rpm, according to methodology proposed by Ure *et al.*¹⁰ The results are also presented in Tables 2 and 3.

The analytical methodologies were evaluated using certified reference materials (IAEA/soil-7 and NIST/soil-2709). The experimental results were in good agreement with the certified values, according to Table 4.

Table 4. Validation of analytical methodology. Reference material: Soil 2709-NIST (National Institute of Standards & Technology)

| Element | Certified values | Present work |
|---------------------|------------------|---------------|
| (% m/m) | | |
| Si | 29.66 ± 0.23 | 32.19 ± 0.08 |
| Al | 7.50 ± 0.06 | 6.7 ± 0.1 |
| Fe | 3.50 ± 0.11 | 3.70 ± 0.02 |
| K | 2.03 ± 0.06 | 1.95 ± 0.02 |
| Ca | 1.89 ± 0.05 | 1.85 ± 0.05 |
| Mg | 1.51 ± 0.05 | 1.48 ± 0.01 |
| Na | 1.16 ± 0.03 | 1.19 ± 0.01 |
| Ti | 0.342 ± 0.024 | 0.384 ± 0.002 |
| mg kg^{-1} | | |
| Ba | 968 ± 40 | 1019 ± 37 |
| Mn | 538 ± 17 | 548 ± 10 |
| Cr | 130 ± 4 | 130 ± 2 |
| Zn | 106 ± 3 | 104 ± 4 |
| Ni | 88 ± 5 | 86 ± 1 |
| Cu | 34.6 ± 0.7 | 36.0 ± 1.4 |

The determination of total, partial and bioavailable concentration in soil samples was carried out in triplicate and the analysis presented a variation coefficient smaller than 10% for macro elements and smaller than 15% for microelements determination.

Results and Discussion

The soil is an important compartment of the ecosystem. It makes possible the life of plants, animals and man on the earth surface. Due to anthropogenic sources (traffic, industries, agriculture, urban-residues etc) the soils can be polluted by toxic substances or acidified what can change their physical, chemical and biological properties. The soil tends to store trace elements from the environment, but its store capacity is finite. When that capacity is exceeded, an increase in metals mobility is observed. This phenomena cause environmental damage like contamination of plants, animals and also leach pollutant to groundwater and surface water.¹¹

The chemical kinetics balance of trace element between soil solution and soil solid phase is very complex and up now is few understood. The metals concentration in soil solution is usually considered as the balance of metals among clay mineral, organic matter and iron, manganese and aluminum hydroxides. This balance is strongly affected by the pH. The soil heterogeneity turns difficult to foresee the behavior of trace elements in the soil.¹¹

Metal polluted soils lead to human contamination, either by direct ingestion or through animals and plants. The total metal concentration in the soil is not the best way to express the risk of human exposure. The determination of partial concentration can be a better way to express the potential toxic concentration available to the environment. The combination of several natural processes as climatic conditions, atmospheric deposition (acid rain), erosion and other factors can change the chemical and physical soil characteristics and therefore causes a release of metals that up to moment were retained in the soil. To obtain a better evaluation of the soil contamination, the knowledge of the metal bioavailable concentration in soil is more interesting than the partial concentration. The metal bioavailability represents the mobility extension of the metals in soil and depends strongly on the physical and chemical soil properties. This is an important concept that represents the risk of human exposure to metal.¹¹

The results of total, partial and bioavailable concentration of metals in the Cantareira eleven (11) soil samples, their range and average values were presented in Table 2 (macroelements) and Table 3 (microelements). The results for the three metals concentration showed a similar profile, showing total concentration > partial concentration > bioavailable concentration for all metals. The samples were identified by point number *i.e.*, soil 1, soil 2 etc.

Soil characterization

Usually, the soil adsorption capacity to metals increase following the soil acidity, however exception to As, Mo and Se was observed by McBride¹², where their adsorption decreased with soil acidity. Among the 11 soils analyzed, the pH values varied between 3.3 and 4.4, characteristic of acid soils; only soil 8 presented a pH of 5.7.

The application of the Pearson correlation matrix ($p < 0.05$) for all results, showed a good correlations between pH and Mg, K, Ca and Al bioavailable concentration (+0.7). The soil 8 presented highest pH (pH 5.7), the smallest clay content (31%) and organic matter (6.5%), in comparison with the others ones, and showed an opposed behavior in the bioavailable concentration for Ca >> Al.

In the evaluated soils, the Ca content ranged from 34 to 573 mg kg⁻¹, exception for soil 8, where its concentration was 1462 mg kg⁻¹. In this soil, the bioavailable Ca content, in relation to partial concentration, was higher than other elements. Brady¹³ sustains this behavior, where the Ca cation is the most available element among the macro elements in soil solution. The K, Mg and Al content were smaller than 1%, but in the soil 8, the ratio Ca/Al presented an antagonist tendency, *i.e.*, when the concentration of Ca increased drastically Al concentration decreased abruptly, fact also had observed by Reuss *et al.*¹⁴ This behavior is responsible for less acidity in the soil 8.

The cation exchangeable capacity (CEC) in soil is strongly dependent on type of clay, organic matter (OM) and Fe, Mn and Al oxides amounts and is also influenced by the pH. The studied soils presented similar CEC (23.7±3.2 cmol kg⁻¹), OM (6.0±0.7 %) and pH (3.8±0.3), except for soil 8 (pH 5.7). The Pearson correlation matrix ($p < 0.05$) showed a good correlation CEC-clay (+0.7) and low correlation for CEC-OM (-0.3) and CEC-pH (+0.01). These results indicate that CEC is strongly influenced by clay content and less dependent by OM and pH. The Pearson correlation showed good values for clay-Fe correlation (+0.9) and moderate for clay-Al (+0.6) and clay-Mn (+0.6). These values showed that trace metals retention are highly influenced by the presence of iron oxide. The clay percentage in the 11 soils presented an average value of 35.8%, except soil 3 where it value was 64%.

The Si average concentration in the studied soils was 32%, except for soil 3A and 3B, where theirs content were much lower, 8.0 and 7.6%, respectively. The average value for Fe was 3.2%, and for soil 3A and 3B it was much higher than the average, 13.3% and 13.9%, respectively. This knowledge was very important for the understanding of the trace metals retention behavior, where the presence of iron oxide plays a very important role on the adsorption of trace metals in soil.

Microelements

In spite of the variability of the metals concentrations found in the sampling points, it was possible to observe that the soil 3 and 8 presented different concentration for microelements (Table 2 and 3). Cr, Cu, Ni, Cd and As presented a similar profile for all sampling points. However, Zn and Pb presented a very different behavior.

Soil 3 presented high clay content 64%, pH 4.1 and organic matter 6.4%. Moreover, it presents the lowest total concentrations of Si (8%) and Ba (155 mg kg⁻¹) and the highest Fe and Mn concentrations, 13% and 1532 mg kg⁻¹, respectively. This fact evidences an association of Fe

and Mn in soil clay minerals. Soil 3 also presented highest values of partial concentration of Cr (74.5 and 94.5 mg kg⁻¹), Ni (22.5 and 54.8 mg kg⁻¹), Cu (83.8 and 121 mg kg⁻¹), Cd (1.28 and 1.74 mg kg⁻¹) and As (2.04 and 2.67 mg kg⁻¹) for fraction A and B respectively. These values were above the average for the others soils, showing a tendency of retention of these metals in soil 3. The Pearson correlation matrix confirms this tendency resulting good correlation of clay with Cd (+0.9), Cu (+0.8), Cr (+0.8), Ni (+0.8) and As (+0.8).

The Pearson correlation did not presented satisfactory values for relation clay-Pb (+0.5) and clay-Zn (-0.35), indicating that these metals have low association to clay. Good correlations were obtained for the relation OM-Pb (+0.6) and for pH-Zn (+0.7) among all microelements. These results showed that the adsorption of Pb depends on the OM amount. Suduan *et al.*¹⁵ observed that Pb presented greater affinity to organic matter and the Zn adsorption is influenced by the soil pH. Moreover, *ca.* of 100% of Zn content, in partial fraction A, was available in low soil pH condition. Anderson and Christensen¹⁶ observed that metals adsorption is influenced by soil pH and Zn is highly influenced by pH variation.

The fraction A and B partial concentration of Cu 83.8-121; Cr 74.5-94.5; Ni 22.5-54.8 mg kg⁻¹ (Table 3) in soil 3, is higher than the values observed in USA soils by McBride¹² (Cu 14-29; Cr 20-85; Ni 13-30 mg kg⁻¹). The same results were overcome of the Alert Values for Protection Areas established by CETESB¹⁷, São Paulo State Environmental Agency, (Cu 60; Cr 75; Ni 30 mg kg⁻¹). Moreover, Cu and Ni fraction B values also overcome the Intervention Values (Ni 50 and Cu 100 mg kg⁻¹) established by this agency.

The ratio $K = [\text{bioavailable}] / [\text{partial}]$ for microelements were calculated. A graphic representation was used to evaluate the availability for several microelements. This methodology allows a visualization of the metals availability among different sampling location, the range of ratio K, average and median values as well as comparison among them.

The results presented in Figure 2 show that metals present in fraction A were more available than in fraction B. A comparison of the average of the K values shows the following availability sequence for the microelements present in fraction A:

As > Cd > Zn > Cu > Pb > Ni > Cr

This result indicates that arsenic is the most available and chromium is the less available among microelements. To observe the individual data of the K ratio for the 11 soils, they were split in three columns, where (a) the more

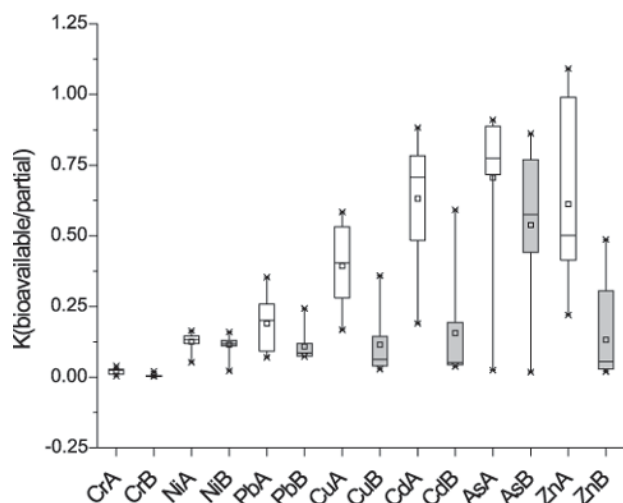


Figure 2. Graphic representation of soil ratio (K) metal concentrations (mg kg^{-1}) of all soil sampling points in fraction A (0-20 cm)-[empty box] and B (20-40 cm)-[full box] of the Cantareira State Park.

available, (b) the moderate available and (c) the less available (Table 5). As, Cd and Zn appear in more frequency class (a), Cu in moderate (b) and Pb, Ni and Cr in the less available column (c). Arsenic, in soil 8, had unusual behavior, *i. e.*, different available sequence (Table 5-column c) that could be related with the pH value 5.7.

The chemistry of arsenate is similar to phosphate. Generally, in aerobic soil environments arsenic species are present mainly as arsenate As (V). Arsenate, like phosphorus, tends to accumulate into Al and Fe hydrous oxides, although in neutral or alkaline soils arsenate is commonly associated with calcium minerals like calcite (lime). In this condition, arsenate sorbed and supplies Ca^{2+} to form Ca arsenate precipitates, reducing the availability of arsenic in soil solution.¹² The availability of arsenic in soils is affected by changes in pH. In general, there is an increase in As toxic effects on plants when the soils became more acid, particularly at pH below 5. In that condition,

Table 5. The availability ($K = [\text{bioavailable}] / [\text{partial}]$) of the microelements in the different soils points. The columns (a) express the more available, (b) moderate and (c) the less available

| Points | ↑ available (a) | (b) | (c) available ↓ |
|--------|-----------------|----------|-----------------|
| 1 | As Cu Cd | Pb Zn Ni | Cr |
| 2 | As Cd Zn | Cu Ni Pb | Cr |
| 3 | Zn As Cd | Cu Pb Ni | Cr |
| 4 | As Zn Cd | Cu Pb Ni | Cr |
| 5 | Zn As Cd | Cu Pb Ni | Cr |
| 6 | As Cd Zn | Cu Ni Pb | Cr |
| 7 | Zn As Cd | Cu Pb Ni | Cr |
| 8 | Cd Cu Zn | Pb Ni Cr | As |
| 9 | Zn As Cd | Cu Ni Pb | Cr |
| 10 | As Cd Cu | Zn Pb Ni | Cr |
| 11 | As Cd Zn | Cu Pb Ni | Cr |

the binding between Fe and Al compounds with As become more label.¹⁸ In acid medium (pH 3-4) Fe and Al arsenates are more stable than Ca arsenates.¹⁹ The soil 8 showed high pH characteristic (5.7) and the highest Ca concentration (Table 1) that removed arsenic as Ca arsenate and reduces its availability.

The Pearson correlation for partial and bioavailable concentration of Cd, Pb, Cr, Zn, Ni and As showed a very low correlations (<0.3), suggesting that these metals present different behaviors in each one of the soils. Probably, the chemical form of the pollutant are different and their assimilation unequal, that cause different metal availability. Cu presented good correlation ($+0.9$) indicating that this element presents the same behavior in all soils.

Conclusions

The 11 soil samples along the Highway Fernão Dias, Sezefredo Fagundes Road and Nova Cantareira Road inside the Cantareira State Park presented a great variability in total metal concentrations, and wide variation were observed for the partial and bioavailable concentrations.

Usually, highways boundary soils were contaminated with metals like Pb, Cd, Zn and Ba.¹¹ In this study, in spite of the difference in the vehicular traffic density (Highway Fernão Dias > Sezefredo Fagundes Road > Nova Cantareira Road) and also the soil characteristics, none of them presented disturbing values, according to the Alert and Intervention Values established by CETESB.¹⁷

Therefore, no influence from the highways in the metals concentration in soil could be observed up to sampling date.

The soil 3 presented total and partial concentration of Cu, Cr and Ni higher than others ones. These concentrations were above the Alert and Intervention Values established by CETESB.¹⁷ The Cu, Cr and Ni values suggest other pollutant source or a natural accumulation of these metals due to the high Fe and clay contents of this site.

The leaching of toxic metals is limited to fraction A for most of the analyzed elements and not represents an environmental problem. The exception occurred in soil 3 for Cu, Cr and Ni partial concentrations in fraction B. A possible reason for metal availability of those elements could be the characteristics of the own soil and the chemical species of each metal.

Besides that, at soil 3, Cu, Cr and Ni metal leaching is not expected in short term due to its high cation exchange capacity. As observed in this study, soil-3 has a clay and oxide ferric high content, that will increase metal retention. Otherwise, if the soil buffer capacity decline, for instance,

due to the acid deposition (acid rain), the metal mobility will become an environmental problem. Therefore, it is important to keep monitoring this site in near future.

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