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ALTITUDINAL VARIATIONS IN H AND AL IONS INTERCHANGE ALONG WITH FE CONTENT IN AMAZONIAN RAINFOREST SOIL

VARIACIONES ALTITUDINALES EN IONES DE H Y AL EN EL CONTENIDO DE FE EN SUELOS DE LA SELVA AMAZÓNICA

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Abstract

Soils vary broadly across Amazonia having a large diversity of soil types, morphological characteristics and physical-chemical soil properties. Research that examines the soil properties of these areas improve the general knowledge of native, unexplored soils and provides promising control samples for soil science. There are important investigations in the literature that examine the Amazonian forests grow in a heterogeneous environment in relation to soil and topography. In this study soil samples of 3 depths and from 9 different altitudinal locations of Amazonian rainforest were collected. The present study provides the insight about the effects of soil depth as well as altitudinal variations on Fe content and interchangeable acidity (H-Al ion interchange). This study indicated that altitude compared to soil depth can play major role in Fe content and Interchangeable acidity.

Keywords: Rainforest, Control soil, Amazonian soil, Altitudinal variation, H ion, Al ion. Fe content.

Resumen

Los suelos varían ampliamente en la Amazonia mostrando gran diversidad, diferentes características morfológicas y propiedades físico-químicas del suelo. Las investigaciones llevadas a cabo en relación a las propiedades del suelo en estas áreas ayudan al conocimiento general de los suelos nativos e inexplorados y proporcionan muestras de control para el estudio del suelo. En la literatura existen importantes investigaciones que estudian los bosques amazónicos en un entorno heterogéneo en relación con el suelo y la topografía. En el estudio actual se recolectaron muestras de suelo de 3 profundidades, 9 localidades y altitudes diferentes en la selva amazónica; y proporciona la visión sobre los efectos de la profundidad del suelo así como las variaciones altitudinales sobre el contenido de Fe y la acidez intercambiable (intercambio iónico H-al). Los resultados indicaron que la altitud, en comparación con la profundidad del suelo, puede desempeñar un papel importante en el contenido de Fe y la acidez intercambiable.

Palabras clave: Selva tropical, control del suelo, suelo Amazónico, variación altitudinal, ion de H, ion del Al, contenido de Fe.

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1 Introduction

The study of soils requires an interdisciplinary approach involving geologists, physicists, chemists, biologists, amongst others (Brevik et al., 2015). Its importance cannot be emphasized enough as the soil is the basis for food and its properties are considered as indicators of numerous natural and artificial processes (Coyago and Bonilla, 2016; Ulloa et al., 2014; Yánez and Bárcenas, 2012) as well as the biodiversity (Guevara et al., 2018). Therefore, research that investigates the effects of organic versus conventional soil management has become increasingly important in sustainable agriculture (Bautista et al., 2017; Mátyás, Andrade, Chida, Velasco, Morales, Montero, Cando and Acevedo, 2018; Taipe Velasco, Lizano Acevedo and Mátyás, 2018). It should not be ignored either that great attention is on soil science in Ecuador lately thanks to another research area, the astrobiology, supporting research that seeks evidence of life-related molecules or traces of a former life on remote planets that is becoming increasingly important in the country due to its natural features that allow to analyze promising extraterrestrial analogue soils (Mátyás, Bautista, Szarka, Serrano, Arteaga, Loja, Yaguana, Gómez and Ramírez-Cando, 2018).

Both research areas require analyses of intact (uncultivated) soils as control samples, especially in astrobiology as the Earth soil samples having significant microbial activity, such as the one that the Amazonian rainforest provides, which can be considered as reliable control samples (Mátyás, Bautista, Szarka, Serrano, Arteaga, Loja, Yaguana, Gómez and Ramírez-Cando, 2018). Soils vary broadly across Amazonia having a large diversity of soil types, morphological characteristics and physical-chemical soil properties (Quesada et al., 2010). Research that examines the soil properties of these areas improves the general knowledge of native and unexplored soils (Quesada et al., 2011). There are important investigations in the literature that examine the Amazonian forests grow in a heterogeneous environment in relation to the soil and topography (de Castilho et al., 2006).

Soil acidification is a natural process conditioned by naturally acid parent rocks, high precipitations and slow organic matter decomposition producing various organic acids (Pavlu et al., 2007). The existence of high exchangeable acidity in a soil usually indicates the occurrence of exchangeable hydrogen (H), exchangeable aluminum (Al) as either free Al3+ ion or partially neutralized Al-hydroxy compounds (Hinrich, Brian and O'Connor George, 2001). It has also been observed that most of the stable carbon in acid subsoils was associated with polymeric Fe and Al hydroxides, ferrihydrite, and with crystalline Fe oxides (Mikutta et al., 2006; Spielvogel, Prietzel and Kögel-Knabner, 2008).

Keeping these points in view, soil samples of 3 depths and from 9 different altitudinal locations of Amazonian rainforest were collected. Thus, the present study will provide the insight about the effects of soil depth as well as altitudinal variations on Fe content and H-Al ion interchange. In addition were detected organic molecules in one of the samples collected providing control values for astrobiological research purposes.

2 Methods

A total of 27 soil samples were collected near Tena (Amazon Rainforest), Ecuador, on May 15, 2018, from upper layer at nine different altitudes of Hyperalic Alisol soil (Table 1). Soil pH in distilled water and in 1M NaF (soil/water, 1/2.5, w/w) were measured according to Buzás (1988). Soil moisture content was measured gravimetrically, drying the soil at 105 °C for 24 hours according to Díaz-Romeu and Hunter (1982) method. Allophane (Table 1) was detected according to Fieldes (1986) methods using 10g soil/water (1:2), soil/water + 20ml 1M NaF, soil/water (1:2,5) + 25ml 1M NaF, soil/water (1:2,5) + 25ml 0.5M NaF as described below. For the sample preparation 20ml of distilled water was added to 10g of soil sample. pH was measured and then 20ml of sodium fluoride (1M) was added to the solution. pH was measured again. Following this 25ml of distilled water was added to 10g of soil sample. pH was measured. 25ml of sodium fluoride (1M) was added to the solution and finally the pH was measured again. When the pH is greater than 9 during the measurement suggests allophane is present due to the volcanic origin of the sample (Table 1).

The Fe content was measured according to a modified (Blakemore, 1981) as follows: To prepare the samples 50ml of ammonium oxalate monohydrate (0.2 M, pH=3) was added to 1g of soil sample. The mixture was shaken to 4.5 hours at 150 rpms (using

NB-101M, N-Biotek Inc, Korea). To obtain the supernatant 12 hours later the mixture was centrifuged to 15 min at 3500 rpms (using Hermle Z400, Hermle AG, Germany). Following this a double filter process was carried out using Whatman No. 42 filter paper. To determine the concentration for the calibration curve (Table 2) extractant solution of oxalate ammonium acid (0.2M) was used as solvent. 2.5g of iron metal was added into 35 mL of 1:1 hydrochloric acid and then diluted to 1.5L adding 2500 µg/mL Fe. Finally the solution was measured using atomic absorption spectrophotometer (Wavelength: 392nm; Slit width: 0.2nm).

Table 1. Sampling sites and main physical-chemical soil properties.

ID	Latitude	Longitude	Altitude (m a.s.l.)	Depth (cm)	pH (H2O)	Moisture content (%)	Allophane
1	-77.2575327	-0.9765686	386	10	5.21	39.25	Not volcanic
2	-77.2575327	-0.9765686	386	20	4.87	38.15	Not volcanic
3	-77.2575327	-0.9765686	386	30	4.84	39.00	Not volcanic
4	-77.2575458	-0.9734722	369	10	5.23	40.06	Not volcanic
5	-77.2575458	-0.9734722	369	20	5.18	39.90	Not volcanic
6	-77.2575458	-0.9734722	369	30	475	39.11	Not volcanic
7	-77.2537563	-0.9763018	395	10	4.79	43.69	Not volcanic
8	-77.2537563	-0.9763018	395	20	4.68	39.15	Not volcanic
9	-77.2537563	-0.9763018	395	30	5.08	37.87	Not volcanic
10	-77.8857849	-0.9241473	911	10	5.06	55.04	Volcanic
11	-77.8857849	-0.9241473	911	20	5.15	47.02	Volcanic
12	-77.8857849	-0.9241473	911	30	5.29	43.91	Volcanic
13	-77.8839364	-0.9092520	1 006	10	5.11	54.41	Volcanic
14	-77.8839364	-0.9092520	1 006	20	5.32	46.51	Volcanic
15	-77.8839364	-0.9092520	1 006	30	5.46	42.48	Volcanic
16	-77.8908966	-0.9092071	1 181	10	5.56	54.22	Volcanic
17	-77.8908966	-0.9092071	1 181	20	5.72	52.16	Volcanic
18	-77.8908966	-0.9092071	1 181	30	5.82	51.43	Volcanic
19	-77.9082599	-0.9330021	1 444	10	5.28	64.84	Volcanic
20	-77.9082599	-0.9330021	1 444	20	5.35	60.56	Volcanic
21	-77.9082599	-0.9330021	1 444	30	5.48	58.77	Volcanic
22	-77.9283477	-0.9361859	1 564	10	5	70.14	Volcanic
23	-77.9283477	-0.9361859	1 564	20	5.50	64.03	Volcanic
24	-77.9283477	-0.9361859	1 564	30	5.57	61.16	Volcanic
25	-77.9361469	-0.9358267	1 800	10	5.02	61.24	Volcanic
26	-77.9361469	-0.9358267	1 800	20	5.30	63.59	Volcanic
27	-77.9361469	-0.9358267	1 800	30	5.47	58.92	Volcanic

Table 2. Calibration curve setup for Fe content determination.

N°	Concentration µg/mL	Concentration in Percentage %
1	0	0
2	625	50
3	1250	100
4	2500	200

Interchangeable acidity was determined according to a modified Salinas and García (1979) method cited in Coleman and Thomas (1967); Lin and Coleman (1960); Pratt and Bair (1961) using 10 ml of extract obtained with 1N KCl, 10 ml of distilled water, 0.05 % phenolphthalein and 0.01N NaOH as follows: To prepare the samples 25 ml of potassium chloride (1N) was added to 2.5 g of soil sample. Then, was shaken (using NB-101M, N-Biotek Inc, Korea) for 15 minutes at 60 rpm. To filter the solution a Whatman No. 42 filter paper was used. 10ml of distilled water was added to 10 ml of filtrate. Approximately three drops of 0.05 % phenolphthalein indicator was than added. The solution was titrated by 0.01N NaOH. The following formula was used to calculate the results:

$$Interchangeableacidity(mEq/100gofsoil) = AmountofNaOH \times NNaOH \times (100/weightofthesoilsample)$$

where

Interchangeable acidity is (expressed in mEq/100g soil),
Amount of NaOH is the loss of NaOH during the titration (expressed in mL),
N NaOH is the concentration of NaOH used for the titration (expressed in N),
Weight of the soil sample is the weight of the soil sample used for the measurement (expressed in g).

Organic compounds were detected from dry and fresh soil sample (ID=10) via HPLC (Waters 1525 Binary HPLC Pump with Waters 2998 Photodiode Array Detector); spectrophotometry (Jasco V-730 spectrophotometer and PerkinElmer Spectrum BX) adn GC/MS (EVOQ Scion 436-GC, Bruker). SDS-VAGE was carried out according to Warrant el al. (2003) in Enduro ES vertical gel system. Results obtained from chromatography were matched with Wiley NIST 2014-11th edition GC/MS. Identifications of organic compounds were accepted when the probability of the similarity criterion was p>0.9 (Mátyás, Bautista, Szarka, Serrano, Arteaga, Loja, Yaguana, Gómez and Ramírez-Cando, 2018).

One way ANOVA model was applied for statistical analysis in order to understand whether there are differences within altitudes and depths in the examined parameters. Duncan test was used as post hoc analysis. To illustrate the results of Fe concentration and absorbency (ABS) within the different altitudes the Lagrange interpolation formula for the first derivative was applied which is suitable for examining unequally spaced data:

$$f'(x) = f(x_{i-1})\frac{2x - x_i - x_{i+1}}{(x_{i-1} - x_i)(x_{i-1} - x_{i+1})} + f(x_i)\frac{2x - x_{i-1} - x_{i+1}}{(x_i - x_{i-1})(x_i - x_{i+1})} + f(x_{i+1})\frac{2x - x_{i-1} - x_i}{(x_{i+1} - x_{i-1})(x_{i+1} - x_i)}$$

where
x is the altitude where the first derivative is calculated,
x_{i-1} ; x_i ; x_{i+1} are the known altitudes (the order is not relevant),
$f(x_{i-1})$; $f(x_i)$; $f(x_{i+1})$ are the concentrations of Fe linked to the altitudes, respectively.

note: for the Visual Basic for Applications (VBA) code please see Appendix.

For storing the experimental raw data and the evaluated results as well a non-relational data storage model JT (Mátyás, Bautista, Szarka, Serrano, Arteaga, Loja, Yaguana, Gómez and Ramírez-Cando, 2018; Mátyás et al., 2016*a*,*b*) was applied in an Oracle Application Express server (ORACLE, N.d.).

3 Results

Figure 1 corresponds to the first derivative of the Fe content (concentration and absorbency) within the altitudes. A fairly linear pattern can be observed within the depths (especially in 10 cm). In the three graphs it was found that the values of the derivatives around 1000 and 1200 masl are negative or similar. The highest Fe concentration, 222 mg/kg was observed at 1 564 masl in 20cm depth, while the lowest Fe concentration, 2.27 mg/kg was measured at 386 masl in 20cm depth. A clear decreasing tendency can be observed in the concentration values within the decrease of altitude.

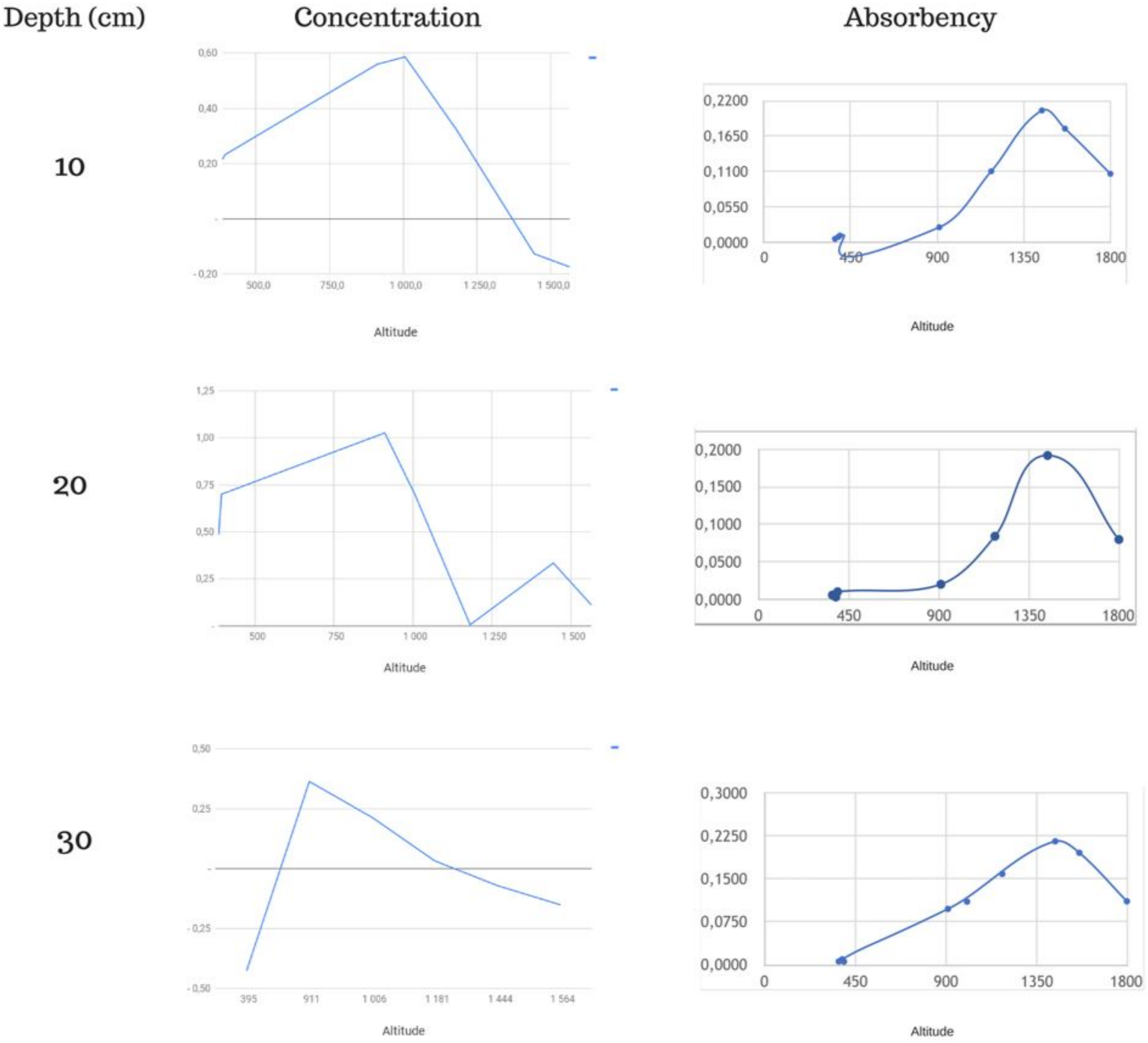

Figure 1. Fe concentration and absorbency in different altitudes and depths

The ABS graphics within the different depths are quite similar and linear. Inlet point around 1 444 masl can be observed where the slope of the curve becomes negative. The behavior in the three curves between 400 and 1 000 masl is quite similar in the first two graphs, is fairly smooth and ascending curve (up to 1 444 masl). In the third graph (corresponding to a depth of 30 cm) this section is rather linear and the aforementioned curvature is almost imperceptible.

Statistical results show that there are no significant differences in Fe concentration and interchangeable acidity within the different depths (p=0.85). On the other hand, strong differences can be observed applying ANOVA on the altitudes (p =0.00005). Duncan test in Figure 2 resumes groups for the parameters evaluated regarding different altitudes. This information presents the mean and the confidence intervals for any single altitude in trials. The values of Fe concentration decrease in line with the decrease of the altitude (Figure1.A).

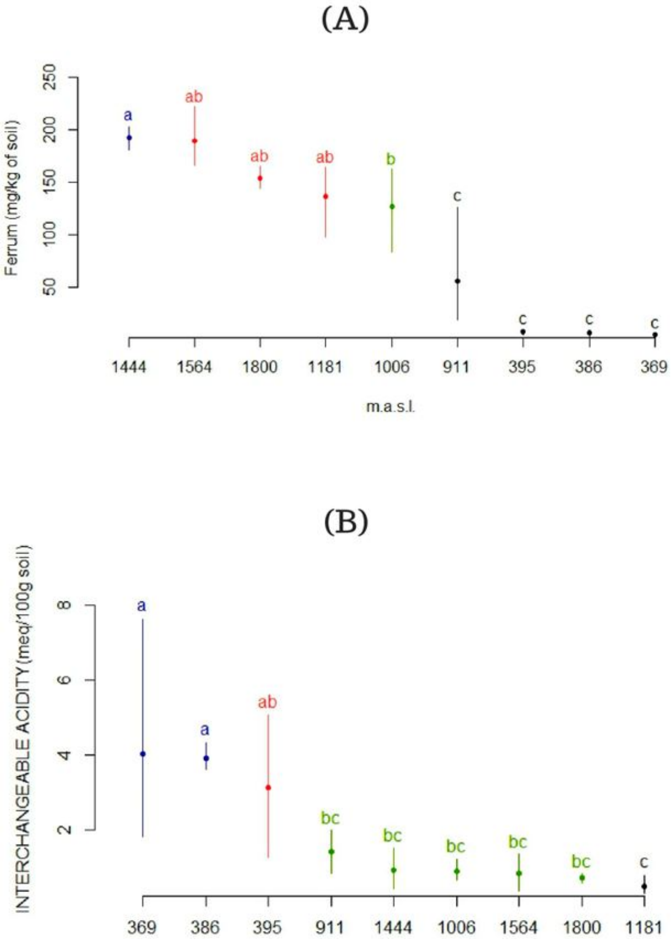

Figure 2. Differences in Fe concentration and values of Interchangeable acidity within the different altitudes

Sugar alcohols, anhydrosugars, hydroxy acids and oxoacids were detected by using HPLC. Carbon (48.1%), nitrogen (7.6%) and amino acids (7.9%) were found via electrophoresis. Glycerol, oxalic acid, masonic acid, glutaric acid, glycolic acid, 4-hydroxybenzonic acid and 3.4-dihydroxybenzonic acid were detected by GC/MS (Mátyás, Bautista, Szarka, Serrano, Arteaga, Loja, Yaguana, Gómez and Ramírez-Cando, 2018)).

4 Conclusions

It was concluded that depth of soil did not significantly affect Fe content and interchangeable acidity; while altitude affected both. This study indicated that altitude, compared to soil depth, can play major role in Fe content and interchangeable acidity. Moreover, the high amount of organic molecules that could be detected by analytical instruments suggest that the selected sampling sites could provide promising control samples for evaluating extraterrestrial analogue soils for further analyses.

Competing interests

No competing interests were disclosed.

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Appendix

Lagrange interpolation formula for the first derivative programmed in VBA:

```
Public Function DIFF1_LAGRANGE_ORDEN2(x, x0, x1, x2, f0, f1, f2)
If (x0 = x1) Then DIFF1_LAGRANGE_ORDEN2 = "Div. por 0. Verifique que los valores de las x’s son todos distintos."
If (x0 = x2) Then DIFF1_LAGRANGE_ORDEN2 = "Div. por 0. Verifique que los valores de las x’s son todos distintos."
If (x1 = x2) Then DIFF1_LAGRANGE_ORDEN2 = "Div. por 0. Verifique que los valores de las x’s son todos distintos."
DIFF1_LAGRANGE_ORDEN2 = _
f0 * (2 * x - x1 - x2) / ((x0 - x1) * (x0 - x2)) + _
f1 * (2 * x - x0 - x2) / ((x1 - x0) * (x1 - x2)) + _
f2 * (2 * x - x0 - x1) / ((x2 - x0) * (x2 - x1))
End Function
```