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BIOGEOCHEMICAL ASPECTS OF SELECTED ELEMENTAL CONTENT IN *ILEX PARAGUAYENSIS* S.H FROM EASTERN PARAGUAY II BY X -RAY FLUORESCENCE

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Abstract. *Yerba mate,* Ilex paraguayensis*, is a plant used in infusions/macerations as a "reviver"/energy and mineral supplier beverage from historical times by the ancient originary inhabitants of Paraguay, to these days, almost worldwide; in regard to the mineral content of Ilex from Paraguay few studies are known, some of them by XRF (X-Ray Fluorencence). In this work, selected non-metallic, as well as some alkaline and alkaline earth elements contents in yerba mate from eastern Paraguay were studied by XRF techniques in order to determine their eventual correlation as well as provenance. The analysis of complex spectra was performed by the AXIL software and the quantitative analysis by the QAES software. The samples indicate that* Ilex paraguayensis *present in the aerial parts an important contents enrichment of Si,S,Cl, Br and I, some of them considered essentials. On the other hand, except K & Rb, the other cations are well below the line of reference when normalized to Upper Crust (UC) values.*

Keywords: *Eastern Paraguay, Ilex Paraguayensis, mineral uptake, Ilex infusion*

1. Introduction

Several studies on mineral content of Ilex paraguayensis, *Yerba Mate* (*Aquifoliaceae*), a tree from Paraguay, have been published [1-7]. They are mainly related to their multi-elemental contents including essential microelements, some REE (rare earth elements) and other refractory useful for provenance studies. Many of them, are related to healthiness [1,2]. Tree is a small one, of Paraguayan origin called *Ka'a* in Guaraní[**] or *yerba mate* in Spanish, which leaves and sticks were used as beverage in infusion in hot water (*mate* & *mate* tea) or as a maceration in cold water (*tereré*) by the Originary Population of Paraguay. Powerful in pharmacological properties as well as rich in mineral content, its consumption as "reviver" beverage, continues to these days especially in Paraguay, Argentina, Brazil and Uruguay; furthermore, it is used as the infusion almost worldwide [1].

Despite the importance of plant nutrition in ecology, geochemical approaches to yerba mate have limited coverage in the literature. In this regard, previous studies of Paraguayan *yerba mate* using XRF focused on the relationship between the element's oxidation state and its root uptake. In the case of 3D elements, uptake was favored when they acted with their lower valence and the stability (Ks) of their soluble complexes in the rhizosphere. Concerning the REE and some other refractory, their concentration show to be very low; on the other hand, elements as K and Mn [8] seem to be concentrated by the plants [2].

Non-metallic elements, as silicon, sulfur, halogens in Ilex from Paraguay are not mentioned in the resent literature, which mainly deals with metal ions.

In this work the concentration/presence of selected nonmetals as well as alkaline and alkaline earth metals, in *yerba mate* from Eastern Paraguay were studied, also by XRF techniques, to determine their correlation as well as provenance. It can be considered an extension of the above-mentioned previous efforts.

2. Experimental

2.1. Materials

The materials were from the north and the south of the Eastern Region of Paraguay main production areas of *yerba mate.* Two types of samples were analyzed:

A. Specimen of different commercial brands of *yerba mate*: for the analyzis, packages (pkg) of samples were selected from major production areas, that is, in the north: Nueva Germania, Azotey, Pedro J. Caballero and in the south, Itapúa, Capitan Miranda, Bella Vista in the Eastern Region of Paraguay. Thus, were analysed samples from different brands taken at random in several shops – four pkg of 0.5 and 1 kg packages, all of the same brand. Thus, the samples from different brands taken at random in several shops – four pkg of 0.5 and 1 kg packages, all of the same brand were analyzed. They are constituted by ground leaves and shoots mixed with small fragments of petioles and twigs, called usually sticks, whose presence in the product is admitted up to no more than 35% according to the art 1193 of the Código Alimentario Argentino. Moisture ranges from 8.3 to 12.5% [9,10].

B. Specimen of leaves from fresh plants: leaves, shoots, petioles and twigs were collected at

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** Paraguay is bilingual. Official languages are Spanish and Guarani.

localities of Azote'y in the North and of Capitán Miranda in the South (Itapua). Samples were taken at random from at least 12 plants in each cropping site. At the laboratory, materials were dried overnight under a fan at room temperature, crushed, dry again and ground.

Composite samples from each pkg were prepared by quartering, being then, dried at 105°C in an oven, ground and sieved. Samples from fresh plants were prepared in a similar way. For XRF measurements, the powdered samples were pressed into pellets of area weight of ~ 0.1 to 0.3 g.cm^{-2}. Samples from commercial products were analyzed in Asunción while those from fresh materials in Ljubljana.

C. Ashes samples: In order to verify the results, aliquots of A and B materials were reduced to ashes at 550°C in an oven. Ashes content ranges from ~4.3 up to 6.5 %.

2.2. X-Ray measurement and analysis

The XRF measurements and quantification were performed utilizing the facilities of the XRF laboratories at the Jožef Stefan Institute in Ljubljana and at the Atomic Energy Commission in Asunción. For the excitation of the fluorescence radiation the radioisotope sources of Cd-109 (30mCi) and Am^{-241} (100m Ci) were utilized. The energy dispersive X-ray spectrometer was based on a Si (Li) semiconductor detector (FWHM ≈140 eV at 5.9 keV). The analyses of complex spectra were performed by the AXIL software [11] which is based on iterative nonlinear least square fit of the spectra by the Gaussian shaped spectral lines. The resulting intensities of pure $K_{\alpha}$and L_{α} lines of measured elements were then utilized in quantitative analysis, employing the quantification software of QAES (quantitative analysis of environmental samples) designed by P. Kump [12]. This software utilizes the i.e. transmission-emission (TE method) for determination of the absorption in the sample and then iteratively finds the solution of the system of basic XRF equations (for each measured element there is one equation). The basic XRF equation namely relates the measured intensity to the respective concentration of the element in the sample. Since this relation is nonlinear and the intensities depend also on concentrations of all unmeasured elements, the information of the absorption in the total sample at single energy (Mo K_{α} line) obtained by the mentioned TE method is crucial in solving such a system of equations [13]. On the other hand, the quantification would be possible only if a set of standards very much resembling the unknown samples would be at hand to perform the necessary calibrations. The absorption measurement on the sample was in principle equivalent to additional measurements on a set of standards.

The uncertainties of elemental concentrations obtained by the QAES software were assessed to be between 5 % and 15 % which has been confirmed by the analysis of some standard reference materials (RM Soil-7 and Sediments SL^{-1}, SL^{-3}, V8 Flour rye from International Atomic Energy Agency, and Orchard leaves 1571 from NIST.

The preparation of the samples, were carried out at the Laboratory of Hydroconsult in Asunción.

3. Results and discussion

The materials analyzed were from the north and the south of the Eastern Region of Paraguay, main production areas of Ilex. They were constituted by commercial products and by fresh material.

Nonmetals elements analyzed in this work were Si, S, Cl, Br and I, while metals were selected alkaline and alkaline earth elements: K, Rb, Cs, Ca, Sr and Ba.

The result of the analysis of material samples are break down in Table 1.

For comparative studies, correlation and provenance, according to methods widely used in geochemistry, the content of mineral components in soils and plants (especially at trace level) must be standardized in relation to the recommended values for primordial materials such as chondrite, primordial mantle (PM), upper crust (UC), in the construction of arachnograms/multi-element diagrams.

Here we will refer to UC in relation to processes/products resulting from the major and the minor geochemical cycles.

Table 1. Selected mineral contents of yerba mate from Paraguay (mg Kg^{-1})

a) Nonmetallic elements					
Sites	**Si**	**S**	**Cl**	**Br**	**I**
Az	860	533	1370	10	16
Cap. M	743	1050	1060	80	3.6
BV	374.4	188.4	295	31.3	0.86
Nva. G	750	156	455.4	33.7	0.91
P.J.C	803	190	228	24.6	0.03
Itapua	940	156	534	25.5	0.11

b) Metallic elements						
Sites	**K**	**Rb**	**Cs ***	**Ca**	**Sr**	**Ba**
Az	6460	16.6	0.42	3860	46.5	25.7
Cap.M	25300	44.9	0.061	5450	42.7	56.1
BV	22132	29.6	0.009	3270	27.7	43.3
Nva.G	13920	27.2	0.02	2778	26.6	45.6
P.J.C.	15200	23.4	0.04	4273	45.3	30.13
Itapua	22107	21	0.03	6588	65	39

Relative SD range from 6 to 17%
* recalculated from ashes.
Az (Azotey), Cap. Miranda (Cap. M), Bella Vista (BV); Nueva Germania;
(Nva. G), Pedro Juan Caballero (PJC).

Silicon: in plants, it is beginning to be recognized as an essential/quasi essential element. After iron and oxygen, it is the most abundant element of the earth. It occurs in soils as in rocks forming minerals, mainly as silica and silicates strongly bonded to oxygen (E_b=193.5 Kcal M^{-1}).

It constitutes between 0.1 and 10% DW (drive weight) of higher plants. In this works it has been found that Si values range from 374,4 to 940 mg.Kg^{-1} in the Ilex samples.

In general, gymnosperms accumulate more Si than angiosperms, although differences may occur even at the variety level [14],[15] and that is also shown in a meta-analysis of 735 species including some of Ilex genus (*I. aquifolium, I. integra, I. latifolia*); the processes of absorption, transport and deposition of silicon are under genetic control. It is absorbed by the roots.

It is cited also, as a Si functions, its capacity of to strengthening the cell wall-lignin, providing structural support/tolerance to diseases, inter alia Mn, Fe and Al toxicity.

Sulfur: It is an essential nutrient of plants, widely studied but not yet in yerba mate. Its content in plants ranges between 0.1 to 6% DW in our samples concentration values ranges from 156 to 1050 ppm, although marked differences occur at species level [16].

It is up taken by the root as sulfate which is then reduced to sulfide at the root level through the plastids that contain all sulfate reductive enzymes; its further conversion to cysteine happens mostly at the shoots level in the chloroplast. It such be mentioned that plants contain a wide variety of organic thio-compounds; in the protein fraction.

The sulfate surplus is stored as it mainly in the vacuoles happens with other elements [2], often for any eventual requirement.

Chlorine: Average Cl^- content in plants varies in the range of 2.0 to 20.0 mg^{g-1} DW [17], in our samples concentration values ranges per 228 to 1370 ppm. The element is an essential nutrient for plants, usually as Cl^-, anion. Chloride participates in osmoregulation of cells. It is also an essential co-factor in enzymes involved in photosynthesis, e.g. PS_{II} photosystem oxidation, PS_{II} photosystem oxidation of water [18].

Cl is a critical plant nutrient. Although a large number of Chlorine organic compounds are anthropogenic; around 5000 Chlorine are natural produced by fungi, lichens, plants, insects, marine organisms, etc. although their role in biosphere are very little known. As mentioned, the Chloride anions dominate import and export from terrestrial ecosystems while soil Chlorine and biomass can dominate the standing stock [19].

Bromine, Iodine: This halogen trace element is often found in plants although it is not essential and is widely present in the biosphere; it is easily absorbed by plants that in their tissue can be found.

It has been studied profusely in grains, legumes and vegetables and distinguish in sensitive and resistant to the Br effects/presence. For example, potato, onion, are sensitive, while celery, tobacco, tomato as an example are resistant.

In soils and higher plants as there are in Japan, average of I-Br-Cl content in leaves (Chlorine 4200ppm; Bromine 12ppm; 0.60ppm Iodine), of large number of plants, trees such as orchards, red pine, cypress, oak, cedar, etc. In this works, it has been found that Br values range from 10 to 80 ppm; Iodine 0.03 to 16 ppm. Higher plants from overseas behave similarly [20].

In the solution, rhizosphere absorption of Cl and Br is similar; however, Iodine is ten times lower [20].

It should also be mentioned that some studies suggest the leaves had higher bromine concentrations than in the roots.

The affected plants show higher iodine concentrations compared to normal plants. The toxicity is related to the availability of iodine bounding to a number of cellular components, including chlorophyll, consistent with intracellular oxidation of the iodide (possible by the plant peroxidase system) [20,21].

Potassium: Plants contain 1–6% of K^+ in the dry matter and is the most abundant cations in plants. It is absorbed easily by roots (rhizome). In the Ilex samples of this work, values of potassium concentration ranges from 6460 to 25300ppm. Uptake and distribution of potassium in plant cells are carried out by a variety of transporter proteins. As an essential macro-nutrient, it plays important roles in plant physiology *inter alia* water economy. Also very important, potassium is required in protein synthesis/ enzyme activation.

It must be mentioned that potassium also neutralizes various anions and other compounds within the plant.

In the case of *yerba mate*, the plant concentrates K and its recovery is high in the dissolution. This supports the explanation given in on the effect of K of the neutralization into the lactic acid/lactate/ $[H^+]$ system, which promotes muscular fatigue. This should explain why people drinking the beverage, gain/recover strength and their working yield improves [8].

Rubidium: There is a marked relationship between Rb and potassium. The element is taken up easily by plants; it substitutes K sites in them but does not substitute K metabolic function. At high concentration is toxic to the plants. Rb uptake as well as its transport in plants seems too different from that of K. The variation of the concentrations and different distribution of Rb and K ratio in organs of some plants can produce contradictory effects. That is to say, the behavior and healthy state of the plant *inter alia* depends on the Rb K ratios [22]. Rb in soils is closely connected to K. Its occurrence in soil is strongly related to the bed rocks.

Most of higher plants as the *yerba mate* show concentrations of rubidium ~ 20-70ppm, its concentration ranges from 16.6 to 44.9 ppm in our samples.

Calcium: essential macro nutrient for plants, it is taken up by roots from the rizome and delivered to the shoot via the xylem, and enters the plant cell through Ca^+ ion channels [23]. Ca^+ is an essential element for the plants and is fundamental in their nutrition.

It constituted around 0.5 to 6% of the dry matter of the higher plants, largely in the cell walls. And the Paraguayan samples analyzed values found range from 2778 to 6588ppm.

It promotes cell multiplication and ionic equilibrium. It plays an important role in the function of a variety of enzymes, delays senescence, leaf and affects the cotyledon. It increases the resistance to apical rot in the plants as well as physiological stress.

Strontium: Geochemical and biochemical properties of Sr are similar to those of Ca and very often are associated within the terrestrial environment. The interaction between them is complex; Sr usually cannot replace Ca in biochemical function. Its content in soils is mainly controlled by bedrock and climate: its concentration ranges from 26.6 to 46.5ppm in our Paraguayan Ilex samples; in sandstones in the areas of *yerba mate* production concentration of Sr ranges from ~15 to ~130ppm.

The contend of the elements in plants is very variable an is reported to range from < 1 to 10,000 (DW) and to 15,000 ppm (AW) [21].

The uptake of the elements is by both, leaves and roots. The ionic radius and charge of Strontium is closed to that of Calcium and its behavior follow to the latter. It is mentioned that the behavior of Calcium and strontium varied in forest ecosystems [20].

***Cesium*:** This element is not an essential one and there is little information on its presence and behavior. It is interestingly mentioned that it is present in flowering plants at average concentrations of 22 ppm; a concentration of 0.1 ppm is also mentioned in *Camellia sinensis* tea leaves, although this varies greatly depending on the type of tea. It also seems that cesium is relatively easy to take up by plants, although its absorption by the roots is not concurrent with the absorption of potassium [21].

Absorption of cesium in grains seems to be easy according to studies with Cs-137. In our samples, after recalculated from ashes, values are from 0.009 to 0.061 ppm.

***Barium*:** is a non-essential element in plants and other terrestrial organisms although it is one of the higher abundant in the earth. It is known to be toxic at elevated concentrations. The toxicity of a Ba compounds is significantly related to its solubility in water [24]. In soil, the presence of these elements ranges from 19 to 2,300 mg/kg [21,24]. In plants tissue, the elements contend range from 1 to 198 ppm (DW). In trees of the forests of Russia were reported values >10,000 ppm. In our samples, their ranges were from 25.7 to 56.1 ppm.

There for some of the essentials here analysed as K, S, Ca, Cl, have well known function in the development of plants. Others as Rb, Sr, Ba, Cs seem to follows the movements and distribution of K and Ca although not their function. We must also mention the role of K contents in the reviver properties of beverage of *mate* tea, infusion and cold water maceration [8].

On the other hand, *mate* tea, [3] has, due to some components, important pharmacological properties. Chlorogenic acid and caffeoyl derivatives, polyphenols contribute for its antioxidant capacity. Xanthines, as theophilline, theobromine and caffeine account for diuretic, CNS stimulant, hepatoprotective as well as other biological/ pharmacological properties. Saponins in addition to their role in the flavor, have hypocholesterolemic, anti-inflammatory properties; some of them have antiparasitic effects [1].

4. Multielement diagrams

The multi elemental diagrams is used for comparison the values resulted from the XRF analysis. Considering that plants usually take up minerals elements from the Continental shelf soils for baseline, it is customary to normalized them using the Upper Crust recommended values [25], they are present in Figures 1 and 2 that show the distribution of not metallic and metallic elements.

In regard to the negative effects of the cropping on the environment, they are not significant. *Yerba mate* plantations are located in open areas that have long been used. In addition, care is taken to get healthy and well-developed plants and they are ready for processing in about 3 years.

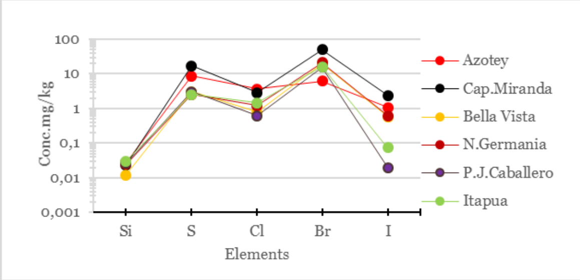

Figure 1. Diagrams of non-metal content of *Paraguayan Ilex*

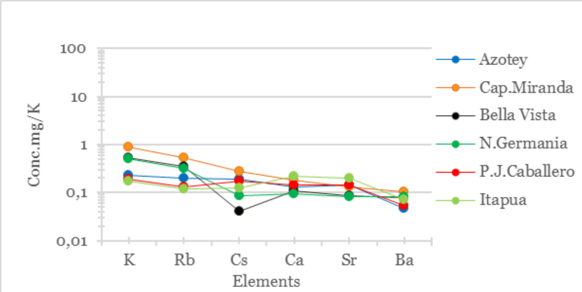

Figure 2. Diagrams of metallic element content of *Paraguayan Ilex*

5. Conclusion

The diagrams indicate that the *Ilex paraguayensis* present in their aerial parts an important content/ enrichment of S Cl Br some of them considered essentials; in addition, diagrams show, that the enrichment, *inter alia*, of the *Ilex* fractions in K.

On the other hand, Si are well below the line of reference when normalized to UC, *Ilex* follows in some way the cations content/distribution of the sedimentary environment. Besides, K plays a prominent role in the “reviver” property of *mate* beverages.

The result of from north and south samples are close in both distribution and values. Them asper themselves do not differentiate north/south provenance.

The diagrams suggest concentration of S and Br by *Yerba Mate* as well as K.

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