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METAL CONTENTS IN HONEY AND MUSHROOMS FROM SERPENTINE SOILS IN THE MORAIS SITE, PORTUGAL.

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ABSTRACT:

Morais site, located in the northeast of Portugal, is known by its geology because it is one of the most representative areas of ultramafic rocks. This kind of soils has particular chemical characteristics, such as high levels of some heavy metals, namely chromium (Cr) and nickel (Ni). However, in Morais site several non-wood forest products (NWFP) are collected by the local community, and, so, it is of great importance to determine the contents of these metals in such food products. In this connection, in the present work three honeys of Morais site (additionally three commercial honeys – control), and nineteen mushroom species collected on four locals were analyzed in relation to calcium (Ca), magnesium (Mg), manganese (Mn), Cr and Ni contents.

The honeys of Morais site showed higher levels of Ni in relation to the control ones. For the other metals, no differences were detected between these two types of honeys. Even though Morais honeys showed higher Ni levels than the control ones, they do not put in danger human health.

Regarding mushrooms, the *Trametes* sp. (non-edible) was the one that showed always the highest metal concentrations. In relation to the edible species, the *Suillus* sp. was the one that had the highest levels of Ca, Mn, Cr and Ni. On the other hand, the *Agaricuscampestris* showed the highest Mg concentration. Nevertheless, the metal levels found in mushrooms collected on the Morais site were identical to those reported for other sites.

Keywords: Honeys; Mushrooms; Metals; Serpentine soils.

1. INTRODUCTION

Morais site is located in the northeast of Portugal and integrates theNatura 2000 conservationnetwork(PTCON0023), occupying an area of 12878 ha. This site has high geological and botanical interest because it is one of the few places in the world where it is possible to see the formation process of the Earth, being called the "navel of the world". This area has in its core the Morais Ophiolite Complex that is one of the most representative areas of ultramafic rocks, and the largest continuous serpentine unitin Portugal. Studies performed in serpentine soils have reporteddeficiencies in certain nutrients (P, N, K, Ca), imbalances in some elements (low Ca/Mg ratios) and high concentrations of Cr,NiandMn (Fernández et al 1999; Miranda et al, 2009).

In the Morais site several non-wood forest products (NWFP) are collected, consumed and, sometimes traded by the local community. These products contribute to the sustainable management of the world's forests, to preservetheir biodiversity, and to improve income generation and food security. However, as soils of Morais may have high contents on heavy metals, it is of great importance to analyze their contents in such food products. In the present study, to infer on the effect of soil chemistry on food security we analyzed the contents ofCa, Mg, Mn, Cr and Ni in three honeys from theMorais site and nineteen mushroom species collected in four locations within the serpentine unit.

2. MATERIALS AND METHODS

2.1 Sampling

The mushrooms were collected in late October and early November 2010in four locations in the Morais site. Plant cover was dominated by holm oak (*Quercusrotundifolia*). Undergrowth was comprised mostly of common gum cistus (*Cistusladanifer*). It was given particular attention to edible species indicatedby the local community.A total of nineteen mushroom species were collected, fiveof whichedible:*Agaricus* sp., *Bovista* sp., *Fistulina* sp., *Trametes* sp., *Hygrophorus* sp., *Lepiota* sp., *Lactarius* sp., *Russula* sp., *Suillus* sp., and *Xerocomus* sp. Three honey containers were purchased to beekeepers ofMorais Site. At the same time three commercial honeys were purchased to serve as control.

2.2 Chemical Analysis

Upon arrival at the laboratory, the mushrooms were washed with ultrapure water andthe excess of water was removed with absorbent paper. Afterwards, the samples were dried at 50-60 °C and subsequently ground. One gram of each sample was digested with concentrated nitric acid in amicrowave digestion system (MARS Xpress, CEM), applying the following program: 1600 W (100%), with a 15 minutes temperature ramp and holding at 200 °C for 15 minutes.

The honey samples were kept in the dark at ambient temperature. Ca, Mg, Mn, Ni, and Cr levels were determined by FAAS asdescribed byFrías et al. (2008).

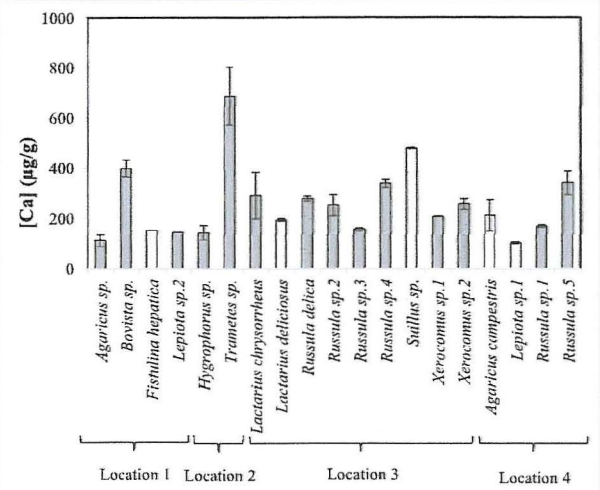
Internal matrix modifier, lanthanum nitrate hexahydrate, was added to the samples in which Ca and Mg were determined. The reliability of the method used inthe mushroomanalysis was tested with the NCS DC 73349certified reference material (Bush branches and leaves). The agreement between the analytical results for the reference material and the certified values wassatisfactory (recovery 77–110%).

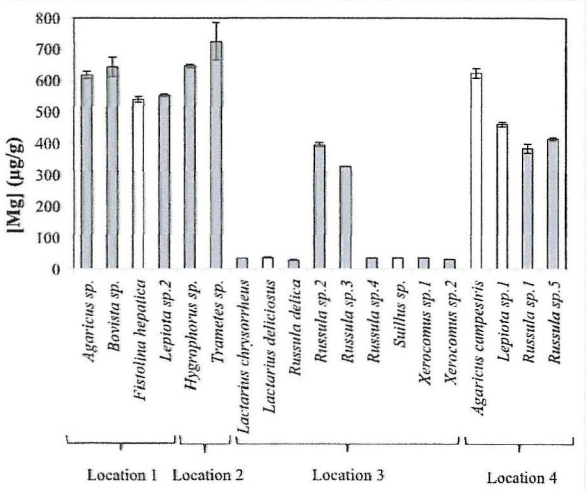
3. RESULTS AND DISCUSSION

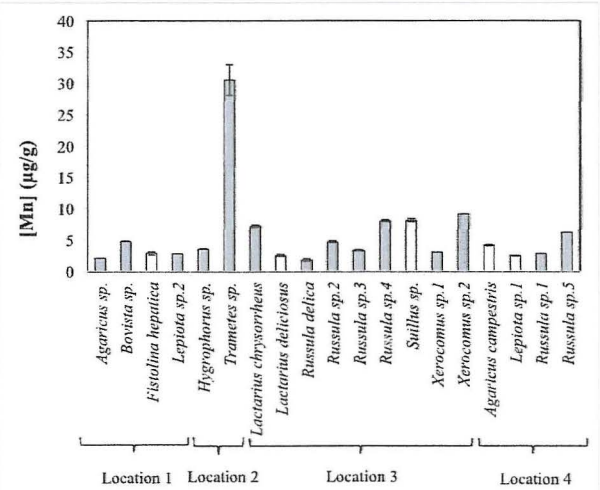
3.1 Mushrooms

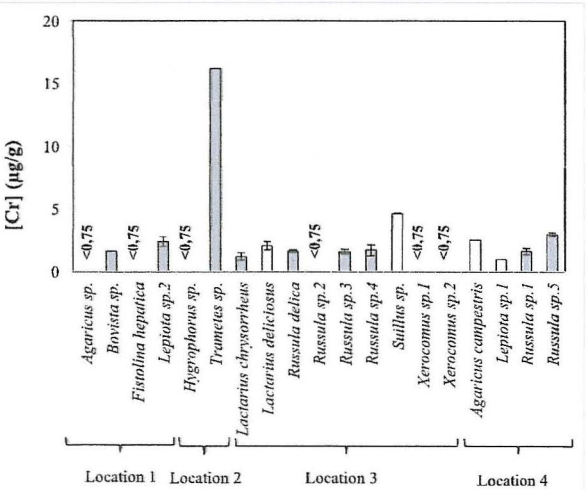
The Ca, Mg, Mn, Cr and Nicontents determined for mushrooms species are presented in Figure 1.Differences were detected amongmushroom species and collection sites. In general, it was observed that *Trametes* sp. was the speciesthat consistently presented the highest concentrations of all metals. This may be due to the fact that this speciesgrowsin decaying woodthat might have accumulated a higher amount of metals over time, passing for the mushrooms. Additionally, *Trametes* sp.are perennial allowing accumulation of metals in tissues.

In relation to the edible species, *Suillus* sp. presented the highest levels of Ca, Mn, Cr and Ni. On the other hand, *Agaricuscampestris* showed the highest Mg concentration, followed by *Fistulina hepatica* and *Lepiota* sp..*Lactariusdeliciosus* presented a lower Mg level than the speciesmentioned previously but a similar content to *Suillus* sp.; however, both mushrooms differed in other metal concentrations.


[Ca] (µg/g)
1000
800
600
400
200
0
Agaricus sp.
Bovista sp.
Fistulina hepatica
Lepiota sp.2
Hygrophorus sp.
Trametes sp.
Lactarius chrysorrheus
Lactarius deliciosus
Russula delica
Russula sp.2
Russula sp.3
Russula sp.4
Suillus sp.
Xerocomus sp.1
Xerocomus sp.2
Agaricus campestris
Lepiota sp.1
Russula sp.1
Russula sp.5
Location 1
Location 2
Location 3
Location 4


[Mg] (µg/g)
800
700
600
500
400
300
200
100
0
Agaricus sp.
Bovista sp.
Fistolina hepatica
Lepiota sp.2
Hygrophorus sp.
Trametes sp.
Lactarius chrysorrheus
Lactarius deliciosus
Russula delica
Russula sp.2
Russula sp.3
Russula sp.4
Suillus sp.
Xerocomus sp.1
Xerocomus sp.2
Agaricus campestris
Lepiota sp.1
Russula sp.1
Russula sp.5
Location 1
Location 2
Location 3
Location 4


[Mn] (µg/g)
40
35
30
25
20
15
10
5
0
Agaricus sp.
Bovista sp.
Fistolina hepatica
Lepiota sp.2
Hygrophorus sp.
Trametes sp.
Lactarius chrysorrheus
Lactarius deliciosus
Russula delica
Russula sp.2
Russula sp.3
Russula sp.4
Suillus sp.
Xerocomus sp.1
Xerocomus sp.2
Agaricus campestris
Lepiota sp.1
Russula sp.1
Russula sp.5
Location 1
Location 2
Location 3
Location 4


[Cr] (µg/g)
20
15
10
5
0
<0.75
Agaricus sp.
Bovista sp.
Fistolina hepatica
Lepiota sp.2
Hygrophorus sp.
Trametes sp.
Lactarius chrysorrheus
Lactarius deliciosus
Russula delica
Russula sp.2
Russula sp.3
Russula sp.4
Suillus sp.
Xerocomus sp.1
Xerocomus sp.2
Agaricus campestris
Lepiota sp.1
Russula sp.1
Russula sp.5
Location 1
Location 2
Location 3
Location 4

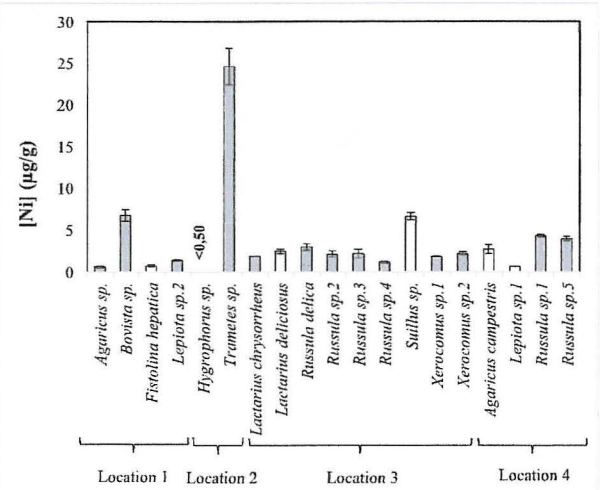

[Ni] (µg/g)
30
25
20
15
10
5
0
<0.50
Agaricus sp.
Bovista sp.
Fistolina hepatica
Lepiota sp.2
Hygrophorus sp.
Trametes sp.
Lactarius chrysorrheus
Lactarius deliciosus
Russula delica
Russula sp.2
Russula sp.3
Russula sp.4
Suillus sp.
Xerocomus sp.1
Xerocomus sp.2
Agaricus campestris
Lepiota sp.1
Russula sp.1
Russula sp.5
Location 1
Location 2
Location 3
Location 4

Figure 1 - Ca, Mg, Mn, Cr and Ni contents (μg/g) inmushroomsanalyzed from the Morais site (white bars – edible species; grey bars –non-edible species).

In terms of locations, the lowest Mg contentswere determined in edible mushrooms fromlocation 3. No differences were detected in other metal levels. Similar results were obtained for non-edible species. The metal levels found in edible mushroom species collected in the Morais site were identical or lower to those reported by other authors such as Siobud-Dorocant et al. (2011) for *Agaricus*sp., *Lepiota*ps. and *Fistulina hepatica*collected in several locations in Paris (France) orIsologlu et al. (2001) and Dermibas (2001) for *Lactarius*sp. in north western Turkey and in the East Black Sea region, respectively.

3.2 Honey

Ca, Mg, Mnand Ni contents determined for the honey samplesstudied in this work, are presented in Figure 2. We found that chromium concentration was lower than 0.060 μg Cr/g in all cases.

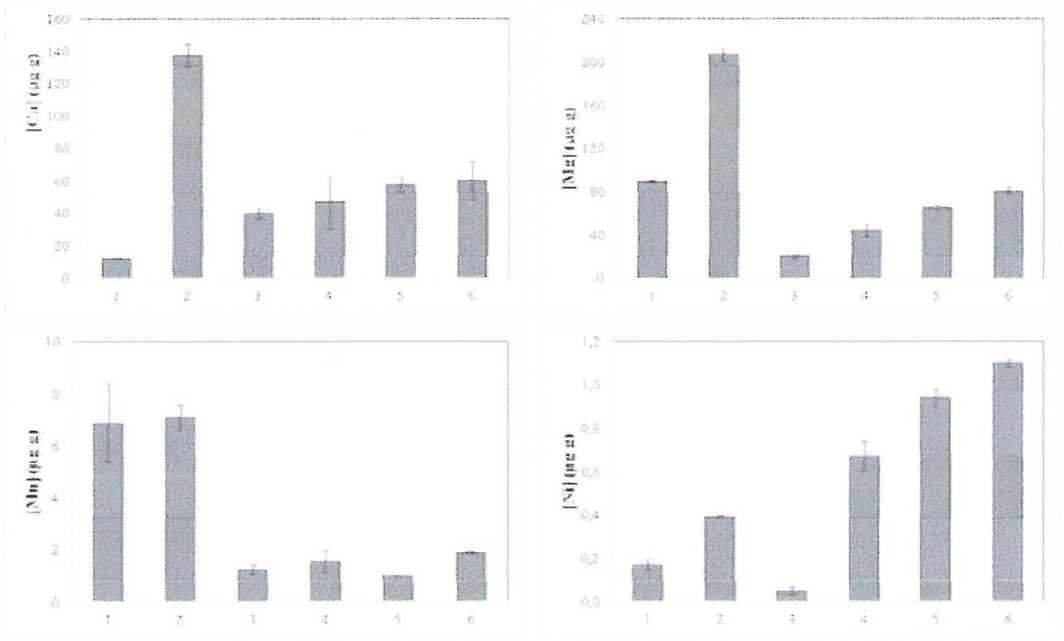


Figura 2 - Ca, Mg, Mn and Ni contents (μg/g) in honeys from the Morais site: 1 – Commercial A; 2-Commercial B; 3- Commercial C; 4 – Morais site A; 5 – Morais site B; 6 – Morais site C.

Honeys collected in the Morais site (4, 5 and 6)showed similar Ca and Mncontents. Calcium is required for bone formation and development, and manganese is important for the good performance of structural and enzymatic functions. The Mg and Ni levels increased from honey 4to honey 6, indicating variability on the metal contents on honeys produced in the same region.Honey collected in the Morais site always showed higher Ni concentrations than commercial honeys. This is probably due to the high Ni concentrations found in soil and vegetationat the Morais site. When present in high concentrations, Ni is toxic; however, it is required in small quantities for the production of red blood cells.

When comparing ourresults with other reported in the literature, we observed that honey collected in Turkey and analyzed by Yilmaz and Yavuz (1999) had Ca and Mn concentrations of51 and 1 μg/g, respectively, of the same order of magnitude ofCommercial Honey no. 3 (Ca = 40 μg/g, Mn = 1.2 μg/g) and all honeys collected inthe Morais site (Ca = 46.6-60.0 μg/g, Mn = 0.99-1.9 μg/g)(Honeys no. 4, 5 and 6).Ca and Ni contents reported by Omode and Ademukola (2008) for Nigerian honeys (Ca = 144-270 μg/g, Ni = 5.0-13.0 μg/g) were higher than thosedetermined in our study (Ca = 12.1-137.5 μg/g, Ni = 0.06-1.1 μg/g). Taking into account theinternational recommendation for Tolerable Upper Intake Level (UL) for Ni of 1 mg Ni/day(National Research Council, 2001), we estimatedthat for the honeywith the highest Ni contentof Moraissite (1.1 μg/g) it would be necessary to consume about 900 g of honey per day to exceed the UL. Thus, these results indicate that the three honeys collectedin the Morais site are not hazardous tohuman health.

4. CONCLUSIONS

Trametes sp. (non-edible) was the mushroom speciesthat showed consistentlythe highest metal concentrations. In relation to the edible species, *Suillus* sp. was the one that presentedthe highest levels of Ca, Mn, Cr and Ni. On the other hand, *Agaricuscampestris* showed the highest Mg concentration. The metal levels found in mushrooms collected in the Morais site were, however, identical to those reported elsewhere.

The honeys collected inthe Morais site showed higher levels of Ni in relation to commercial honeys (control). For the other metals, no differences were detected between these two types of honeys. Even though Morais honeys showed higher Ni levels than the control ones, they are safe for human consumption.

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