RESIDUES AND TRACE ELEMENTS

Trace Element Profile of a Wild Edible Mushroom (*Suillus granulatus)*

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Seventeen elements, Al, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, V, and Zn (macroelements and trace elements) were investigated by Atomic Spectrometries on a particular wild edible mushroom collected in the central region of Argentina during 2 different years in the same season. The metal content profile in *Suillus granulatus* samples is given. The found quantities of Na, K, Ca, Mg, Fe, P, V, and Al were 0.40, 10.84, 0.48, 0.30, 0.57, 4.24, 0.18, and 1.23 g/kg dry weight, respectively. The levels of Li, Cu, Zn, Cd, Co, Ni, Cr, and Mn were 0.98, 23.02, 22.30, 0.26, 0.16, 1.17, 0.90, and 28.75 mg/kg dry weight, respectively. Pb was not detected at the investigated levels. The results indicate that the levels of metals in the analyzed samples are not considered to be a health risk. In order to demonstrate the validity of our method, a recovery study was performed with acceptable results.

Mushrooms are a very popular and appreciated delicacy in different parts of the world, not only for their texture and flavor but also for their chemical and nutritional properties. Mushrooms have also been reported as therapeutic foods, useful in preventing diseases such as hypertension, hypercholesterolemia, and cancer (1–3). These functional characteristics are mainly due to their chemical composition. In addition, some species contain dangerous toxins, many of which are not yet fully understood (4).

Several species of mushrooms exist in nature but only about 22 species are intensively cultivated for commercial purposes (5). Although cultivated mushrooms are widely accepted for consuming, wild edible mushrooms have been traditionally eaten only by specific groups of people. Nevertheless, their consumption is becoming increasingly important in human diet because of their nutritional and pharmacological characteristics (5, 6).

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It has been reported that heavy metal concentrations in mushrooms are considerably higher than those in plants, vegetables, and fruits. This suggests that mushrooms possess a very effective mechanism that enables them readily to take up heavy metals from the ecosystem and accumulate them in their structures (7). Metals like Fe, Cu, Zn, and Mn are essential metals which play an important role in biological systems, whereas Pb and Cd are nonessential metals that are toxic even in traces (8). However, the essential metals can also produce toxic effects when the metal intake is excessively elevated. Therefore, it is necessary to investigate the levels of essential and toxic elements particularly in wild mushrooms.

Although the literature contains data about other similar mushrooms (9–11), there is not much available information about *Suillus granulatus* (L: Fries) Kuntze (12, 13). There are several reported data of the metal content of mushrooms measured in different countries (14); however, qualified studies about wild-grown edible mushrooms in Argentina have not been reported.

The present study describes metal levels in mushrooms collected from Argentina's central region (San Luis) and concerns 17 elements found in specimens of *S. granulatus*. The Al, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, V, and Zn concentrations were determined by using flame atomic emission spectrometry (FAES), flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS), and ultrasonic nebulization system coupled to inductively coupled plasma-optical emission spectrometry (USN-ICP-OES).

Experimental

Reagents and Chemicals

The water used in all studies was ultrapure (18 MΩ cm) obtained from a Barnstead EASYpure® Reservoir Feed (RF; Dubuque, IA) compact ultrapure water system. HNO_3, $HClO_4$, and hydrofluoric acid (HF) were of ultrapure quality (Merck, Buenos Aires, Argentina). Metal standard solutions were prepared by appropriate dilutions of 1000 mg/L stock standard solutions immediately before use. Matrix modifier [$(NH_4)H_2PO_4$] used was supplied by Merck. During Co determination, the use of the matrix modifier was not necessary, in agreement

Table 1. ICP-OES instrumental parameters used to determine Al, Cr, Fe, Ni, Mn, P, V, and Zn

RF generator	1.0 kW
Forward power	40.68 MHz
Nebulizer	Pneumatic and ultrasonic
Plasma gas flow rate	8.5 L/min
Auxiliary gas flow rate	1.0 L/min
Sample gas flow rate	0.5 L/min
Solution uptake rate	1.5 mL/min
Observation height	15 mm
Ultrasonic nebulizer conditions	
Healer temperature	140°C
Condenser temperature	4°C
Carrier gas flow rate	1.0 L/min
Analytical wavelengths, nm	
Al[a]	308.215
Cr[a]	283.653
Fe[a]	240.488
Mn[a]	257.610
P[a]	213.618
V[a]	309.311
Ni[b]	221.647
Zn[b]	213.856

[a] Pneumatic nebulizer system.
[b] Ultrasonic nebulizer system.

with a previously reported approach (15). For Cd and Pb determination (NH_4) H_2PO_4 was the matrix modifier used at a concentration level of 0.05 mg/mL (5 μL, 1%, w/v).

Instrumentation

The atomic absorption measurements were performed with a Shimadzu Model AA-6800 atomic absorption spectrometer (Tokyo, Japan) equipped with a deuterium background corrector, and the measurements were based on peak height. FAES wavelengths used were 589.0, 766.5, 670.8, and 422.7 nm for Na, K, Li, and Ca, respectively. The graphite furnaces used were pyrolytic and platform. Metals hollow-cathode lamps (Hamamatsu Photonics K.K., Shizuoka, Japan) were used as radiation source; wavelengths were 228.8, 240.7, and 283.3 nm for Cd, Co, and Pb, respectively. The temperature program was the following: drying 120 and 150°C, pyrolysis 500°C, atomization 2500°C for Cd; drying 120 and 250°C, pyrolysis 400°C, atomization 2500°C for Co. The temperature program for Pb was drying 120 and 150°C, pyrolysis 800°C, and atomization 2400°C.

The ICP-OES measurements were performed with a sequential ICP spectrometer (ICP 2070; Baird, Bedford, MA). The 1 m focal length Czery-Turner monochromator was based on a holographic grating with 1800 grooves/mm. Tygon-type pump tubing (Ismatec; Cole-Parmer, Vernon Hills, IL) was used to carry the sample. The ICP-OES instrumental parameters used for Al, Cr, Fe, Ni, Mn, P, V, and Zn determinations are shown in Table 1. Nebulization was performed with an ultrasonic nebulizer with a desolvation system (U-5000 AT; CETAC Technologies, Omaha, NE).

Preparation of Samples

S. granulatus fruiting bodies in different growth stages were collected during autumn in 2004, 2005, and 2006 from 2 different pine wood highland areas in the province of San Luis, Argentina. The samples were correctly identified in the UNSL Herbarium. After removal of plant and substrate debris with a plastic knife, fresh mushrooms were dried in an oven at 40°C for 72 h and crushed with mortar and pestle. Dried samples were stored in cleaned hermetic vases at 4°C until analysis.

A digestion method with an acid mixture (including HNO_3, $HClO_4$, and HF) was used to destroy the organic material. A 2.0 g solid sample was digested in a Teflon vessel by treatment with 10 mL concentrated HNO_3. The solution was evaporated to dryness. The solid samples (dried powered mushrooms) were then treated by strong oxidation with 10 mL concentrated $HClO_4$. Subsequently, the silica salts which could occlude the analytes were digested with HF until white

Table 2. Literature data previously reported for *Suillus* genus

	Elements (mg/kg, dry wt)						
Suillus species	Hg	Pb	Cd	Cu	Mn	Zn	Fe
S. granulatus[a]	WD[b]	WD	1.5	35.8	77.5	59.8	658
S. variegatus[c]	<0.5	0.5–1	0.5–1	WD	WD	WD	WD
S. grevillei[c]	<0.5	1–2	1–2	WD	WD	WD	WD
S. luteus[c]	ND[d]	1–2	0.5–1	WD	WD	WD	WD

[a] Ref. 12.
[b] WD = Without data.
[c] Ref. 13.
[d] ND = Not detected.

Table 3. Element concentrations of the *S. granulatus* samples analyzed (g/kg and mg/kg, dry wt), mean ± standard deviation, *n* = 12

	Element concentration, g/kg								Element concentration, mg/kg								
	Na[a]	K[a]	Ca[a]	Mg[b]	V[c]	Al[c]	Fe[c]	P[c]	Li[a]	Cu[b]	Zn[d]	Cd[e]	Co[e]	Ni[d]	Pb[e]	Cr[c]	Mn[c]
S. granulatus	0.40 ± 0.02	10.84 ± 0.26	0.48 ± 0.03	0.30 ± 0.02	0.18 ± 0.01	1.23 ± 0.04	0.57 ± 0.02	4.24 ± 0.21	0.98 ± 0.04	23.02 ± 0.71	22.30 ± 1.05	0.26 ± 0.02	0.16 ± 0.01	1.17 ± 0.05	ND[f]	0.90 ± 0.03	28.75 ± 0.97

[a] FAES (flame atomic emission spectrometry).
[b] FAAS (flame atomic absorption spectrometry).
[c] ICP-OES (inductively coupled plasma-optical emission spectrometry).
[d] USN-ICP-OES (ultrasonic nebulizer-inductively coupled plasma-optical emission spectrometry).
[e] ETAAS (electrothermal atomic absorption spectrometry).
[f] ND = Not detected.

fumes were observed. The residue was diluted to 50 mL with ultrapure water in a plastic volumetric flask, and filtered.

Results and Discussion

Determination of Metal Content

The metal content in mushrooms depends on the ability of the species to extract elements from the substrate and on the selective uptake and deposition of elements in tissues (16, 17). Concentrations have usually been expressed as mg/kg dry matter. There exists a consensus that dry matter content of mushrooms is 10%. Some countries have established statutory limits for the metals in edible mushrooms (14).

According to the results reported by other authors for different edible mushrooms species (9–13, 18) and those obtained in the present study, it is possible that the metal profile obtained for *S. granulatus* is much lower, especially for heavy metals levels, which have been detected at concentration levels not considered to be a health risk (19). The usual concentrations of some metals in fruiting bodies of *Suillus* genus are shown in Table 2 (12, 13).

The quantification of the 17 elements was performed for *S. granulatus* samples collected in the same season in 3 different years from 2 different rural locations in highland areas. Samples were divided into 6 batches, considering year and location, and determinations were done in duplicate (n = 12). Comparison of results showed no significant difference among the batches. An average quantity of each element is shown in Table 3.

As in other mushroom species, potassium was the most abundant element in our sample. Sodium, which is generally the most variable element in mushrooms, was present in a significantly lower concentration (Table 3; 18). Another abundant element in mushrooms is Mg. In the sample under study, the concentration of Mg found was lower than those values previously reported. It is well known that the content of Ca is not too high in mushrooms; nevertheless the Ca concentration for *S. granulatus* was slightly higher than those given for other species (18). There is little information in the literature concerning phosphorus content in mushrooms; however, it was detected in high concentration in the sample under study.

The Cd and Pb values in *S. granulatus* (Table 3) are not considered to be a health risk (14). Previous studies have reported concentrations of Hg, Cd, and Pb in *Suillus* genus (mg/kg dry matter; Table 2).

Method Validation and Recovery Test

After a digestion procedure, different methods (FAAS, FAES, ETAAS, and USN-ICP-OES) were applied for the quantification of macroelements and trace amounts of metals in *S. granulatus* samples collected in the Argentinean central region.

The method of standard addition is considered to be a validation method (20, 21). In order to demonstrate the validity of our method, a recovery study was performed. A synthetic solution containing Al, Ca, Cd, Co, Cr, Cu, Fe, K, Li,

Table 4. Validation and recovery test

Element	Base value, mg/kg	Concentration added, mg/kg	Concentration found[a], mg/kg	Recovery, %[b]
Na	400	500	897 ± 10	99.40
K	10840	5000	15829 ± 325	99.78
Ca	480	500	979 ± 11	99.80
Mg	300	100	398 ± 3	98.00
V	180	100	279 ± 2	99.00
Al	1230	1000	2228 ± 16	99.80
Fe	570	500	1067 ± 11	99.40
Li	0.98	1.0	1.97 ± 0.1	99.00
Cu	23.02	20	42.99 ± 1	99.85
Zn	22.30	20	42.11 ± 1	99.05
Cd	0.26	0.2	0.45 ± 0.03	95.00
Co	0.16	0.2	0.35 ± 0.02	99.50
Ni	1.17	2.0	3.15 ± 0.1	99.00
P	4240	5000	9230 ± 185	99.80
Pb	ND[c]	1.0	1.01 ± 0.02	101.0
Cr	0.90	1.0	1.89 ± 0.07	99.00
Mn	28.75	10	38.73 ± 2	99.85

[a] Mean value (n = 6) ± standard deviation.

[b] 100 × [(Found – base)/added].

[c] ND = Not detected.

Mg, Mn, Na, Ni, P, Pb, V, and Zn was prepared for the performance of the recovery test (Table 4). Then 20 g of dried powdered mushroom sample was weighed and divided into 10 portions of 2 g each. The proposed method was applied to 6 portions, and the average quantity of the metals obtained was taken as a base value. The other aliquots of sample were then spiked with the synthetic solution, and the elements were determined following the recommended procedure, after dilution of the samples to 50 mL. The recovery values obtained were all within the range of 95.00–101.00%.

Conclusions

The present study comprises an element profile in Argentinean *S. granulatus* samples of the central region. Until now, there have been no qualified studies available from Argentine edible mushrooms. The levels of 17 elements in wild edible mushroom were determined. The techniques used for element profile determination, FAES, FAAS, ETAAS, and USN-ICP OES, were demonstrated to be suitable for this type of sample.

The profile obtained in this work may be of interest for comparative studies of other cultivate and wild species from different parts of the world and a helpful tool for monitoring the environmental quality.

The levels of the studied analytes were found to be in agreement with those reported in other regions. From the nutritional point of view, the studied sample can be considered a source of minerals such as K, Fe, and Zn. It also provides a moderate quantity of Ca, P, Na, Cu, Mg, and Mn for the diet. Considering that the heavy metal levels detected are not a health risk, *S. granulatus* could be regarded as a feasible source of minerals.

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