



Manketti nuts (*Schinziophyton rautanenii*) and ushivi beans (*Guibourtia coleosperma*) as a potential source of mineral elements in human diet?– Macro- and microelement composition of exotic seeds

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Abstract

The seeds of *Schinziophyton rautanenii* (manketti) and *Guibourtia coleosperma* (ushivi) could have great potential as food and food ingredient due to their valuable nutritional properties that might make them potential candidates for *Novel Foods*. However, only little has been reported about their mineral nutrient composition. Hence, detailed analysis on the macro- and microelement concentration was performed using inductively coupled plasma sector field mass spectrometry (ICP-SFMS). Method was validated for the analysis of target analytes regarding linearity, instrument precision, limits of detection and quantification, repeatability precision, and accuracy of results (confirmed using certified reference materials). Results obtained showed that manketti nuts offer a valuable source for macroelements Mg, Ca, P and K (571 ± 27 mg/100 g, 225 ± 13 mg/100 g, 1138 ± 63 mg/100 g and 750 ± 47 mg/100, respectively). Regarding essential microelements, Zn and Mn showed highest concentrations (5.82 ± 0.42 mg/100 g and 4.76 ± 0.62 mg/100 g, respectively). Ushivi beans contained high contents of K and Ca (639 ± 72 mg/100 g and 360 ± 99 mg/100 g, respectively). Also of importance were the results of Fe (2.79 ± 0.22 mg/100 g), Se (35.1 ± 17.3 µg/100 g) and Co (3.31 ± 0.57 µg/100 g). In addition, the comparison with the dietary reference values provided by the European Food Safety Authority (EFSA) showed that both seeds could significantly contribute to meeting the required levels of several mineral elements, which emphasizes the high value of manketti nuts and ushivi beans as important food and nutrient source.

Keywords Manketti (*Schinziophyton rautanenii*) · Ushivi (*Guibourtia coleosperma*) · Macro- and microelements · ICP-SFMS · Novel food

Introduction

Numerous organic and inorganic compounds from diet are essential to meet the required amount for metabolic processes in all human beings. Even though only small quantities are

needed regarding e.g., certain vitamins or mineral nutrients, some deficiency symptoms are still widespread nowadays. Mineral elements required by humans can be divided into macro- and microelements. Macroelements (Na, K, Ca, Mg, Cl, P, S) are essential in larger amounts (> 50 mg/kg body weight), while microelements (Fe, J, F, Zn, Se, Cu, Mn, Cr, Mo, Co, Ni) are only required in trace amounts (< 50 mg/kg body weight) and higher concentrations of these metals could even be harmful and toxic. Furthermore, other elements (such as Al, As, Ba, Bi, B, Br, Cd, Cs, Ge, Hg, Li, Pb, Rb, Sb, Si, Sm, Sn, Sr, Tl, Ti, V, W) could also play a vital role in the metabolism, but are required in (ultra-) trace amounts (and many of these elements are toxic even in extremely low concentrations) [1, 2]. The main elements lacking in human diets are Fe, Zn and I, but also Ca, Mg, Cu and Se could be deficient in diets with low intakes of vegetables, fruits, and animal and fish products [2, 3]. The

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chemical species of an element affects its bioavailability. Mineral elements are present in food organically bound and as soluble or insoluble inorganic salts, respectively. Plants offer an important source of essential elements for human beings. Food scientists have been interested in exotic plants and their edible seeds that can offer a valuable source of food or food supplements. The search for nutritionally relevant compounds in uncultivated plants from subtropical Southern Africa has been observed over the past decades. The high added value of certain African trees for the local population and science lies in the potential use of edible seeds in human nutrition and their introduction as *Novel Foods* on the international market [4]. Especially the seeds of *Schinziophyton rautanenii* (Fig. S1) and *Guibourtia coleosperma* (Fig. S2) contain various essential nutrients offering possible positive aspects regarding human health [5, 6].

Schinziophyton rautanenii (locally also called non-gongo, mongongo/mungongo or manketti) is a plant species that grows in Angola, Zambia, Mozambique, Namibia, Botswana and Zimbabwe, and belongs to the botanical family *Euphorbiaceae* [7, 8]. The manketti tree is of great socio-economic importance for rural communities since both the wood and the seeds have been used for centuries. The nutritious manketti fruits (nuts), which can provide an excellent year-round food source for local populations and wildlife, have an estimated annual production of approx. 25 million nuts. The nuts are primarily eaten roasted, but the water-cooked pulp can be eaten as well. Furthermore, both oil and flour can be obtained from the nutritious seeds. Especially the oil of the manketti seeds has great economic value as a food and food ingredient, for medicinal purposes and cosmetic applications due to its unique fatty acid composition and properties [9–11]. Furthermore, manketti nuts offer an excellent source of essential mineral nutrients that are important to maintain good health. Especially macro- and microelements such as P, K, S, Mg, Ca, Fe, Cu, Zn are present in manketti seeds emphasizing the high value of these still under-recognized and under-utilized plant [3, 4, 12].

Apart from the manketti tree, the far lesser studied ushivi tree (*Guibourtia coleosperma*) could have great potential for the international market as its edible seeds offer various nutritionally relevant compounds as well [13]. *Guibourtia coleosperma* (Benth.) J.Léonard is a member of the botanical family *Fabaceae*, and is an important leguminous timber species in Southern African regions including Zambia, Zimbabwe, Zaire, Angola and Namibia. The tree is known as false mopane or African rosewood in literature, and locally also called ushivi, musibi or omushii, depending on the geographical region [14, 15]. The ushivi tree has mostly been used as building material by indigenous peoples due to the good properties of the wood. Its bark, roots and leaves have

been important for medicinal purposes for centuries (e.g., to treat symptoms of malaria). Protection of the heart and cardiovascular system due to the high content of proanthocyanidins, antioxidant activity as well as the potential use for plant-based cancer therapy are some of the important health aspects being researched nowadays [5, 16, 17]. Apart from the medicinal use and possible positive health aspects, the ushivi tree offers edible seeds, which are called “non-sivi” in Namibia. These seeds look like beans since they are red-brown in color and oval in shape. The ushivi beans need to be cooked or baked, and might further be mixed with water in order to serve as meal. Moreover, the “juice” of the seeds can be fermented into alcoholic beverages. Ushivi beans have a high energy level being rich in proteins and carbohydrates. Furthermore, a high Ca content was reported as well as the presence of several other essential mineral elements such as K, Mg, Na, P, Fe and Zn. The seeds of *Guibourtia coleosperma* should be considered an important source of nutrients including mineral elements, vitamins and antioxidants not only for local communities but also as potential *Novel Foods* on the international market as they could contribute significantly to the nutritional requirements of humans [15, 18, 19].

Apart from *Schinziophyton rautanenii* and *Guibourtia coleosperma*, several other indigenous fruit species (in Namibia and other African countries) produce pleasant flavored fruits that are used as a food source, for medicinal purposes or that are vital to generate an income e.g., *Sclerocarya birrea* (Marula tree), *Strychnos cocculoides* (corky-bark monkey orange tree), *Phyllogeiton discolor* (syn. *Berchemia discolor*; bird plum) and *Diospyros mespiliformis* (jackalberry or African ebony). Other indigenous plant species with nutritional and economic importance are e.g., *Ximenia caffra* (African sourplum), *Boscia albitrunca* or *Annona stenophylla* [20].

Ushivi beans and manketti nuts provide a vital food source not only in times of food shortage. Both are still under-recognized regarding their nutritional value. Due to the increasing interest in including the edible seeds of exotic plants in human diet, *Schinziophyton rautanenii* and *Guibourtia coleosperma* were investigated regarding their macro- and microelement composition. Very little is known about the exact mineral concentration of these seeds. Hence, the aim of this study was to give a comprehensive insight into the element composition of manketti nuts and ushivi beans. In addition, it should be investigated whether the fruits of both trees could be considered as possible *Novel Foods* in Europe and other parts of the world, particularly as a food ingredient or as a component of dietary supplements, due to their valuable macro- and micronutrients [21]. Both seeds are very important food items, and there is undoubtedly considerable potential for the development of new products,

especially in the snack food markets and health food sector. They could also be processed and consumed as (ingredient of) beverages. Both manketti nuts and ushivi beans could be eaten cooked or roasted. Ushivi beans can be fermented and consumed as a salad. Furthermore, the “juice” of the ushivi seeds can also be fermented to produce alcoholic beverages. In addition, manketti fruits are famous for producing liquor. Manketti nut oil and flour can be obtained to serve as a food ingredient as well [12, 19].

Materials and methods

Samples and sample preparation

Both manketti ($n=11$) and ushivi ($n=10$) samples were provided by Kavango Global Trading cc, and were harvested from Kavango West, Kavango East and the Zambezi Region. After transport, samples were stored at 4 °C until chemical analyses.

Sample preparation for the determination of ash content

Manketti nuts were opened with a hammer, and crushed as finely as possible in a mortar. Ushivi beans were peeled and then crushed with a hammer mill (2 mm sieve followed by a second step using a 0.5 mm sieve) (Polymix® PX-MFC 90 D, Dispersing and Mixing Technology by Kinematica AG, CH-6014 Littau-Luzern, Switzerland). Ground manketti and ushivi samples were then stored at -18 °C.

Sample preparation for elemental analysis

Laboratory water type I (Milli-Q® water, 18.2 MΩ cm⁻¹; SG Water GmbH, Barsbüttel, Germany) was purified using a duoPUR Quartz sub-boiling-system (Milestone-MLS GmbH, Leutkirch, Germany) and is in the following referred to as ultra-pure water. Pro analysis (p.a.) grade HNO₃ (w=65%) and H₂O₂ (w=30%) were obtained from Merck (Darmstadt, Germany). HNO₃ was double sub-boiled in a duoPUR Quartz sub-boiling-system. Certified ICP standards for calibration were purchased from Inorganic Ventures (IV-Stock-6, P 1000 µg/L, In 1000 µg/L). All laboratory consumables used for sample preparation and analysis were made of plastic material and double acid washed (HNO₃, w=10% and w=1%) 24 h each, rinsed three times with Milli-Q®-water and dried in a clean bench before single use. Reference materials TM-23.5, lot 0917 (trace element matrix reference material made from filtered and diluted Lake Ontario water) and Soy Bean NCS ZC73011 (China National Analysis Center for Iron and Steel, Beijing, China)

have been processed to validate trueness of the applied calibration and sample preparation method, respectively.

After delivery to the laboratory, the frozen (-18 °C) manketti nuts and ushivi beans were dried in a laboratory drying oven at 60 °C for 48 h, and subsequently cooled to room temperature and stored in a desiccator pending mineralization. Manketti nuts were obtained shredded by a mortar, and ushivi beans as whole beans. Because of the texture/fat content (of manketti samples) and hardness (of ushivi beans), further crushing by a laboratory mill was not feasible.

All nuts and beans were processed in triplicates. Approximately 0.2 g of shredded manketti nuts and one whole ushivi bean (weights of the individual beans ranged from 0.391 to 0.628 g), were accurately weighted and mineralized by microwave assisted acid digestion (Anton Paar, Graz, Austria, Multiwave 3000, rotor HF 100) using 4 mL of concentrated double sub-boiled HNO₃ and 1 mL of H₂O₂ at 1200 W for 10 min. After cooling down the vessels to room temperature, the obtained digests were quantitatively transferred into 10 mL polypropylene vials and gravimetrically diluted to 10 g with ultra-pure water. For analysis, the samples were further volumetrically diluted by a factor of 200 and 20 with ultra-pure water and diluted HNO₃, respectively, resulting in an acid concentration of 2% (v/v) HNO₃, and spiked with indium (In) as an internal standard (final concentration of 1 µg/L In in the sample). Quantification was performed by an 8-point matrix-matched external calibration with multi-element standard solutions and internal standardization. All preparatory laboratory work for elemental analysis and measurements were performed in an ISO class 8, and an ISO class 7 clean room with laminar flow hoods ISO class 5 according to ISO 14644-1, respectively.

Chemical analyses

All chemical analyses were performed in triplicate.

Ash content

Determination of ash content was performed gravimetrically by incineration of samples in a muffle furnace (at 550 °C) according to AOAC [22].

ICP-SFMS measurements

Quantification of the total elemental concentrations was performed on the ICP-SFMS Element2 High Resolution ICP-SFMS (ThermoFisher, Bremen, Germany), which is specified for three fixed resolution settings ($R=m/\Delta m$ at 5% peak height): low resolution (LR, $m/\Delta m$ 300), medium resolution (MR, $m/\Delta m > 4500$) and high resolution (HR, $m/\Delta m > 10000$). Measurements were performed by continuous

acquisition (sample intake via PFA-ST nebulizer and a 0.25 mm i.d. uptake capillary (Elemental Scientific Inc., ESI, Omaha) in self-aspiration mode (sample uptake: 100 $\mu\text{L}/\text{min}$). Tuning parameters were optimized to obtain best possible sensitivity (min 1×10^6 cps/ $1 \mu\text{g}/\text{L}$ In in LR), signal stability and an oxide rate ($^{238}\text{U}^{16}\text{O}^+ / ^{238}\text{U}^+ < 5\%$). Instrumental parameters and masses monitored are shown in Table 1.

Data evaluation

Further data processing and evaluation as well as related artworks were conducted using Microsoft Excel 2016 (version 16.0). Mean values, standard deviations (SD) as well as minimum (Min) and maximum (Max) contents of the respective compounds were presented as tables. In addition, box-whisker plots were created showing the median ($\tilde{x}$), quartiles, and mean ($\bar{x}$) of selected macro- and microelements of manketti and ushivi seeds.

Results and discussion

The following macro- and microelements were determined applying ICP-SFMS in manketti and ushivi samples: Na, Mg, P, K, Ca, B, Mn, Fe, Ni, Cu, Zn, Co, Se, Mo, Cr, Li, Be, Ga, As, Ag, Cd, Tl, Pb, Bi, U. The average macro- and microelement concentrations $\pm$ SD as well as the concentration range of manketti nuts ($n=11$) and ushivi beans ($n=10$) are presented in Table 3. Element concentrations of the individual samples analyzed are shown in Tables S1a, S1b, S2a and S2b in the supplementary material.

Box-whisker plots showing the median ($\tilde{x}$), quartiles and mean ($\bar{x}$) of selected essential elements are presented in Fig. 1. The results obtained were compared with published

values, nutritional reference values and, in the case of *Schinziophyton rautanenii* seeds, with other nuts, and since *Guibourtia coleosperma* is a legume species, the results obtained were compared with other legumes. Furthermore, the mineral element concentrations of both manketti nuts and ushivi beans were also compared to other important indigenous fruit species in Namibia.

Performance of ICP-SFMS method

Blank control and control of memory effects were performed by analyzing instrumental blanks (2% (v/v) HNO_3) after every unknown sample. In addition, method blanks (three per digestion cycle) were determined for the assessment of the contamination risk during sample processing. No significant difference (± 1 SD) in the obtained blank levels could be observed for instrumental and method blanks except for Na and P, however, the mean of the method blanks ($n=20$) was used for blank correction of the unknown samples. Method limit of detections (LOD) and limit of quantifications (LOQ) were calculated according to DIN 32,645 [23] (3s and 10s criterion) from 6 independently prepared method blanks. Quantification of the elemental concentrations was performed by external calibration and internal standardization using In applying a calibration range of 0.01–10 $\mu\text{g}/\text{L}$, 0.1–100 $\mu\text{g}/\text{L}$ and 1–1000 $\mu\text{g}/\text{L}$, depending on the certified concentrations of the ICP standards used. The linearity of the obtained calibration curves, expressed as R^2 , was >0.999 for all target analytes. Validation of the trueness of the external calibration and internal standardization *via* In was performed based on the reference material TM-23.5. Furthermore, aliquots of the certified reference material Soy Bean NCS ZC73011 were repeatedly processed (one per digestion cycle, 8 in total).

Table 2 shows a comparison of mean measured and assigned values and certified values, respectively, for the reference materials TM-23.5 and Soy Bean NCS ZC73011. The uncertainty of the measured values represents ± 2 standard deviations, uncertainties for TM-23.5 and Soy Bean NCS ZC73011 were taken from the product information sheet and certificate. A statistical comparison of measured values and reference values was performed according to Linsinger [24]. Method performance was evaluated accordingly: if the absolute difference between the mean concentration of the measured value and the reference value $\Delta_m \leq$ the expanded uncertainty ($k=2$) U_Δ , then there is no significant difference. As can be seen, there is a significant difference in the measured and assigned value for As in the reference material TM-23.5 (indicated by an asterisk). Hence, recovery corrections have been applied for As according to IUPAC [25].

Please note that only elements are depicted with measured values $>$ LOD and certified values $\pm$ uncertainty given.

Table 1 ICP-SFMS operating parameters

Plasma [W]	1200
Plasma gas flow [L/min]	16
Auxiliary gas flow [L/min]	0.9
Nebulizer gas flow [L/min]	1.050–1.1
LR mode ^a	^7Li , ^9Be , ^{11}B , ^{82}Se (with Kr-correction monitoring ^{83}Kr), ^{107}Ag , ^{111}Cd , ^{121}Sb , ^{205}Tl , ^{208}Pb , ^{209}Bi , ^{238}U ; ^{115}In (internal standard)
MR mode ^b	^{23}Na , ^{24}Mg , ^{31}P , ^{44}Ca , ^{52}Cr , ^{55}Mn , ^{56}Fe , ^{59}Co , ^{60}Ni , ^{65}Cu , ^{66}Zn , ^{95}Mo ; ^{115}In (internal standard)
HR mode ^c	^{39}K , ^{69}Ga , ^{75}As ; ^{115}In (internal standard)
Data acquisition	E-scan mode, 3 runs*3 passes, 30 samples/peak, 100 ms

^aLR mode: low resolution ($m/\Delta m$ 300)

^bMR mode: medium resolution ($m/\Delta m > 4500$)

^cHR mode: high resolution ($m/\Delta m > 10000$)

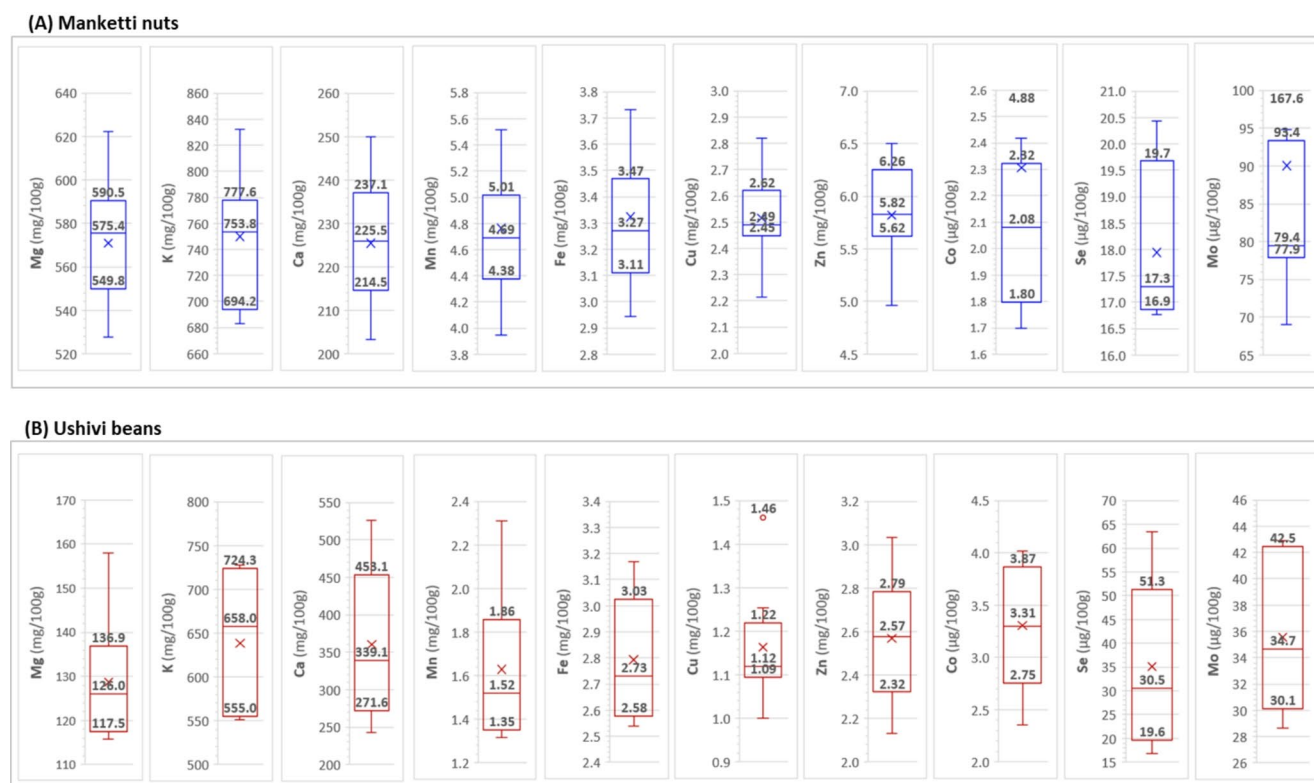


Fig. 1 Box-whisker plots of selected essential macro- and microelements of **A** manketti ($n=11$) and **B** ushivi ($n=10$) seeds with median ($\tilde{x}$), quartiles, and means (x). Given values represent the median, the lower and upper quartiles as well as outliers

Repeatability precision was assessed by the determination of 8 independently prepared replicates of Soy Bean NCS ZC73011. Relative standard deviations ranged between 2% and 10% for all investigated elements. Higher standard deviations of replicate analysis of the investigated manketti nuts and ushivi beans may result from a sample inhomogeneity.

Mineral element composition of manketti nuts

The average ash content was $4.08 (\pm 0.12)$ g/100 g (results of individual samples are given in Table S3). Manketti nuts showed high amounts of certain macro- and microelements. The most abundant macroelement analyzed was P with an average concentration of $1138 (\pm 63)$ mg/100 g, followed by K with $750 (\pm 47)$ mg/100 g. Regarding essential microelements, especially Zn and Mn showed high concentrations with average values of $5.82 (\pm 0.42)$ mg/100 g and $4.76 (\pm 0.62)$ mg/100 g, respectively. The average Fe concentration was more than 3 mg/100 g. Non-essential and heavy-/toxic microelements analyzed were below the limit of quantification ($<LOQ$) for all elements, except for Pb (determined in two samples) and As (determined in one sample) (Table S1a and b).

These results are comparable to the reviewed values published by Maroyi [12] stating that the seed tissues of manketti are excellent sources of essential mineral nutrients such as P (845 mg/100 g), Mg (527 mg/100 g), K (673 mg/100 g), Ca, Fe, Cu and Zn. Results obtained are also comparable to the findings obtained after Soxhlet oil extraction of manketti cakes [4]. Concentrations of K (624 mg/100 g), Mg (449 mg/100 g), Ca (336 mg/100 g), Zn (4.1 mg/100 g), Mn (3.8 mg/100 g) and Cu (3.2 mg/100 g) were reported. Elements such as P, Ni or Cr showed higher values in this study, while Na had a far lower average content. Furthermore, Kamati et al. [26] reported comparable concentrations for Ca and P in manketti oil cake. The high P concentration in manketti samples analyzed is likely due to a high proportion of plant-available phosphates in the soil. Since P is also an important component of phospholipids, P content could possibly be related to the high fat content of these seeds (54.09 ± 2.80 g/100 g) [27].

Since there are very few studies about the element content and composition of manketti nuts, results obtained were compared to different nuts and seeds (all given in mg/100 g). The Ca and Fe content of manketti nuts analyzed can be compared to hazelnut (Ca: 226, Mg: 156, K: 636, Fe: 3.8, Zn: 1.9, Co: 0.01) and almond (Ca: 252, Mg: 170, K: 835, Fe: 4.1, Zn: 2.2), while other nuts showed (far) lower

Table 2 Comparison of mean measured and assigned values/certified values for TM-23.5, lot 0917 ($n=3$) and soy bean NCS ZC73011 ($n=8$)

	Measured value	2 SD	Value/certified value	Uncertainty ^a	Absolute difference Δ_m	Expanded uncertainty U_A
TM-23.5, lot 0917						
As* [$\mu\text{g/L}$]	10.4	0.4	8.00	0.77	2.4	2.1
B [$\mu\text{g/L}$]	17.7	0.6	17.2	3.3	0.5	6.8
Be [$\mu\text{g/L}$]	2.30	0.04	2.12	0.21	0.18	0.81
Bi [$\mu\text{g/L}$]	3.26	0.06	2.99	0.70	0.27	1.60
Cd [$\mu\text{g/L}$]	3.06	0.12	3.00	0.26	0.06	1.11
Co [$\mu\text{g/L}$]	7.85	0.13	7.39	0.54	0.46	1.48
Cu [$\mu\text{g/L}$]	7.98	0.13	7.61	0.67	0.37	1.69
Cr [$\mu\text{g/L}$]	7.44	0.18	7.10	0.51	0.34	1.52
Fe [$\mu\text{g/L}$]	18.2	0.9	16.0	2.2	2.2	4.8
Li [$\mu\text{g/L}$]	10.6	0.4	9.95	0.90	0.6	2.3
Mn [$\mu\text{g/L}$]	8.59	0.10	8.44	0.54	0.15	1.41
Mo [$\mu\text{g/L}$]	4.26	0.09	4.11	0.30	0.15	1.07
Ni [$\mu\text{g/L}$]	5.34	0.15	5.00	0.52	0.34	1.49
Pb [$\mu\text{g/L}$]	2.80	0.06	2.92	0.28	− 0.12	0.97
Se [$\mu\text{g/L}$]	4.59	0.33	5.00	0.91	− 0.41	2.28
Tl [$\mu\text{g/L}$]	3.79	0.19	4.06	0.33	− 0.27	1.32
U [$\mu\text{g/L}$]	4.77	0.08	5.00	0.42	− 0.23	1.20
Zn [$\mu\text{g/L}$]	4.78	0.29	3.65	0.98	1.13	2.37
Soy Bean NCS ZC73011						
B [$\mu\text{g/kg}$]	18.5	2.0	15.8	1.5	− 2.7	4.6
Ca [%]	0.163	0.015	0.153	0.008	− 0.010	1.184
Co [$\mu\text{g/kg}$]	0.129	0.008	0.125	0.012	0.004	1.085
Cu [$\mu\text{g/kg}$]	11.0	0.9	10.2	0.5	− 0.8	2.6
Fe [$\mu\text{g/kg}$]	130	12	139	4	9	25
K [%]	1.97	0.34	1.86	0.09	− 0.11	1.88
Mg [%]	0.230	0.019	0.230	0.014	0.000	1.219
Mn [$\mu\text{g/kg}$]	32	2	28	1	− 4	5
Mo [$\mu\text{g/kg}$]	0.82	0.07	0.71	0.04	− 0.11	1.44
Ni [$\mu\text{g/kg}$]	4.2	0.4	4.0	0.3	− 0.2	2.0
P [%]	0.82	0.03	0.66	0.03	− 0.16	1.31
S [%]	0.400	0.030	0.364	0.027	− 0.036	1.293
Zn [$\mu\text{g/kg}$]	34	2	38	2	4	5

The absolute difference Δ_m was calculated according to: $\Delta_m = c_{\text{measured}} - c_{\text{certified}}$. Method performance was evaluated according to: no significant difference if $\Delta_m \leq U_A$ (expanded uncertainty) [24].

*Significant difference from the (certified) value

^aUncertainty given as stated on the product information sheet (TM-23.5, lot 0917) and certificate (Soy bean NCS ZC73011)

Ca concentrations such as pistachio (Ca: 136, Mg: 158, K: 1020, Fe: 7.3, Zn: 1.4), Brazil nut (Ca: 132, Mg: 160, K: 644, Fe: 3.4, Zn: 4.0), walnut (Ca: 87, Mg: 129, K: 544, Fe: 2.5, Zn: 2.7, Co: 0.009), pecan nut (Ca: 73, Mg: 142, K: 604, Fe: 2.4), macadamia nut (Ca: 51, K: 265, Fe: 0.2) or cashew nut (Ca: 31, Mg: 267, K: 552, Fe: 2.8, Zn: 2.1, Co: 0.01) [28]. Manketti nuts could be considered a valuable source for Ca, K, P, Mg, Fe, Zn and Co. Furthermore, a very low Na content might enhance the nutritional relevance.

Mineral element composition of ushivi beans

The average ash content was 2.08 (± 0.07) g/100 g (results of individual samples are given in Table S4). Regarding ushivi beans analyzed, high concentrations of certain

macro- and microelements were observed. The most abundant mineral nutrient was K with an average content of 639 (± 72) mg/100 g, while the lowest macroelement content was found for Mg 129 (± 13) mg/100 g. Certain essential microelements such as Se and Mo showed high concentrations of 35.1 (± 17.3) $\mu\text{g}/100$ g and 35.6 (± 5.3) $\mu\text{g}/100$ g, respectively.

With respect to non-essential microelements, Cd concentrations could be quantified in all 10 samples (see also Table S2a and b for the individual samples analyzed). Cd is classified as very toxic. The most dangerous form of occupational exposure to cadmium is inhalation of fine dust and fumes, or ingestion of highly soluble cadmium compounds [29]. Hence, heavy metal pollution should be considered a severe problem.

Table 3 Concentration of macro- and microelements in Manketti ($n=11$) and Ushivi ($n=10$) samples (LODs/LOQs^a of elements analyzed are given below)

	Manketti nuts				Ushivi beans			
	Mean	± SD	Min	Max	Mean	± SD	Min	Max
Macroelements [mg/100 g]								
Na	0.38	0.15	0.25	0.67	< LOQ			
Mg	571	27	528	622	129	13	116	158
P	1138	63	995	1223	261	21	231	303
K	750	47	683	832	639	72	551	728
Ca	225	13	203	250	360	99	243	526
Essential microelements								
B [mg/100 g]	1.28	0.07	1.15	1.43	1.66	0.35	0.90	2.13
Mn [mg/100 g]	4.76	0.62	3.95	6.21	1.63	0.31	1.32	2.31
Fe [mg/100 g]	3.32	0.23	2.94	3.73	2.79	0.22	2.54	3.17
Ni [mg/100 g]	1.47	0.09	1.31	1.65	0.58	0.21	0.34	0.88
Cu [mg/100 g]	2.52	0.21	2.17	2.89	1.16	0.12	1.00	1.46
Zn [mg/100 g]	5.82	0.42	4.97	6.50	2.57	0.27	2.13	3.03
Co [μg/100 g]	2.31	0.85	1.70	4.88	3.31	0.57	2.35	4.01
Se [μg/100 g]	17.9	1.5	16.8	20.4	35.1	17.3	16.8	63.4
Mo [μg/100 g]	90.0	25.6	69.0	168	35.6	5.3	28.7	42.9
Cr ^b [μg/100 g]	13.4	5.3	9.0	24.5	< LOQ			
Non-essential microelements [μg/100 g]								
Li	< LOQ				< LOQ			
Be	< LOQ				< LOQ			
Ga	< LOQ				< LOQ			
As ^c	8.48	–	< LOQ	8.48	< LOQ			
Ag	< LOQ				< LOQ			
Cd	< LOQ				2.94	2.93	0.36	8.06
Tl	< LOQ				< LOQ			
Pb	7.50	6.40	1.10	13.9	< LOQ			
Bi	< LOQ				< LOQ			
U	< LOQ				< LOQ			

^aLOD (limit of detection)/LOQ (limit of quantification) given in the respective mass unit: Na (0.06/0.19), Mg (0.3/1.0), P (0.1/0.4), K (3.4/11.2), Ca (1.4/4.6), B (0.03/0.10), Mn (0.01/0.02), Fe (0.20/0.65), Ni (0.03/0.09), Cu (0.004/0.012), Zn (0.04/0.15), Co (0.25/0.84), Se (4.2/14.1), Mo (1.0/3.3), Cr (1.92/6.40), Li (1.30/4.33), Be (0.31/1.04), Ga (0.54/1.79), As (1.62/5.41), Ag (0.02/0.05), Cd (0.03/0.09), Tl (0.004/0.015), Pb (0.04/0.13), Bi (0.12/0.40), U (0.01/0.03)

^bCr: In 2014, the European Food Safety Authority excluded chromium as essential element

^cAs: individual result (all other samples < LOQ)

Results obtained are perfectly comparable to the mineral content of ushivi beans originating from two different regions of Botswana as reported by Matlhodi et al. [13]. Ushivi beans analyzed from Namibia showed similar results for Ca, Mg, Fe and Zn, while higher concentrations for K and P could be obtained in the present study.

Results obtained were also compared to other legumes and oilseeds (all given in mg/100 g). The Ca content of ushivi beans analyzed was higher compared to soybean (Ca: 200, Mg: 220, K: 1800, Fe: 6.6, Zn: 4.2, Co: 0.01), linseed (Ca: 198, Mg: 2.6, K: 725, Fe: 8.2, Zn: 5.5, Co: 0.06), bean (Ca: 113, Mg: 140, K: 1337, Fe: 6.5, Zn: 2.5, Co: 0.005), sunflower (Ca: 98, Mg: 420, K: 725, Fe: 6.3, Zn: 5.7), lentil (Ca: 65, Mg: 129, K: 837, Fe: 8.0, Zn: 3.4, Co: 0.02) or peanut (Ca: 41, Mg: 160, K: 660, Fe: 1.8, Zn: 2.8, Co: 0.03), but lower in comparison to oriental sesame (Ca: 783, Mg:

347, K: 458, Fe: 10) or poppy seed (Ca: 1460, Mg: 333, K: 705, Fe: 9.5, Zn: 8.1, Co: 0.02). The Mg content can be compared to lentils or beans, while a similar K content was found in peanut or poppy seed. Furthermore, ushivi beans could offer a good source for Se showing a higher average concentration (approx. 35 μg/100 g) compared to other leguminous species such as soybean (19 μg/100 g), bean (14 μg/100 g), lentil (9.8 μg/100 g), peanut (5.7 μg/100 g) or pea (0.9 μg/100 g). Ushivi beans analyzed had a lower Fe content compared to other legumes/oilseeds, while Zn or Co concentrations are comparable [28]. Overall, ushivi beans could be considered a valuable source for Ca, K, Fe, Se, Zn and Co (Table 3).

Comparison of manketti nuts and ushivi beans

Both manketti nuts and ushivi beans showed high concentrations for certain macro- and microelements (compared to other nuts and legumes, respectively). Furthermore, results obtained were compared to the dietary reference values provided by EFSA [30] (for male adults) as well as several other indigenous fruit species.

Regarding macroelements analyzed, differences were observed especially for Mg with a more than four times higher content in manketti nuts (571 mg/100 g) compared to ushivi beans (129 mg/100 g). EFSA suggested an adequate intake (AI) of 350 mg Mg per day. Hence, manketti nuts could be a good source to support Mg intake. Manketti nuts also showed a four times higher concentration of P (1.1 g/100 g) compared to ushivi beans, and being above the suggested AI of 550 mg P per day. However, the actual quantity consumed must be taken into account. Both manketti nuts and ushivi beans showed high concentrations for K (750 mg/100 g and 639 mg/100 g, respectively), and could therefore support K intake as the AI is 3.5 g per day. Regarding Ca, ushivi beans had a more than 1.5-times higher content compared to manketti samples analyzed (360 mg/100 g and 225 mg/100 g, respectively). Both might be considered important to support sufficient Ca intake as the average requirement (AR) for adults is suggested to be 750 mg per day. Nutritional relevance might be enhanced due to the very low Na concentrations present in both seeds.

With respect to essential microelements, manketti nuts showed twice the Cu concentrations of ushivi beans, but both could significantly contribute to the suggested Cu AI of 1.6 mg per day according to EFSA. Regarding Fe, an AR of 6 mg per day is recommended for men. Concentrations were comparable in both types of seeds and an intake of 100 g of them could cover up to 50% of the daily Fe requirement. Furthermore, the concentration of Mn was found to be high especially in manketti nuts (4.76 mg/100 g) being almost 3-times higher compared to ushivi beans (1.63 mg/100 g). Hence, the AI of 3 mg Mn per day could be supported by these seeds. Regarding Zn, manketti nuts had more than twice of the Zn content compared to ushivi beans (5.82 mg/100 g and 2.57 mg/100 g, respectively). According to EFSA, an AR between 7.5 and 11 mg Zn per day (depending on the level of phytate intake) is essential for adults. Manketti nuts had also a more than 2.5-times higher content of Mo (90.0 µg/100 g in manketti samples and 35.6 µg/100 g in ushivi samples). Mo has an AI of 65 µg per day making especially manketti nuts a valuable source to support meeting the required daily amount. But also ushivi beans might be seen as a good source to supply Mo. Regarding Se, ushivi beans had almost twice the concentration compared to manketti nuts (35.1 µg/100 g and 17.9 µg/100 g, respectively).

However, individual ushivi samples ranged between 16.8 and 63.4 µg/100 g. The AI of Se is 70 µg per day according to EFSA making ushivi beans a valuable source for the element. Other essential mineral elements such as Co showed relevant concentrations as well. Moreover, manketti nuts showed a Cr content of 13.4 µg/100 g, which could not be detected in ushivi beans analyzed. In the United States, trivalent chromium ions are recognized to be an essential element for humans (needed for insulin, sugar and lipid metabolism). However, it has been reported that there was insufficient evidence for Cr to be an essential nutrient by EFSA in Europe [31].

A comparison of manketti nuts and ushivi beans with other common and important Namibian fruit species showed that both have significantly higher concentrations of macroelements such as Ca, Mg, P and K compared to *Sclerocarya birrea* (Marula tree) with only 35 mg/100 g, 19 mg/100 g, 31 mg/100 g, and 325 mg/100 g, respectively. Microelements such as Zn and Cu showed also higher contents in both manketti nuts and ushivi beans compared to Marula tree (0.31 mg/100 g and 0.16 mg/100 g), respectively. Regarding Fe, manketti nuts analyzed showed almost the same average concentration as found in *Sclerocarya birrea* (3.4 mg/100 g) [32]. Mineral element concentrations published by Malebana et al. [33] showed a Ca content of 143 mg/100 g in *Sclerocarya birrea*, which is also below the values analyzed for manketti nuts and ushivi in the present study. The P concentration (1 g/100 mg) can be compared to manketti nuts analyzed, while Mg and K contents were higher in manketti nuts compared to Marula tree (487 mg/100 g and 633 mg/100 g, respectively). Moreover, Zn and Cu concentrations in *Sclerocarya birrea* (5 mg/100 g and 2 mg/100 g, respectively) were similar to manketti nuts. Another study on the mineral element content of kernels of *Sclerocarya birrea* (from Mozambique) showed that the concentration of K can be compared to ushivi beans analyzed, while both manketti nuts and ushivi beans had higher average values of Ca [34].

The comparison of manketti nuts and ushivi beans with *Strychnos cocculoides* (monkey orange; from Tanzania) showed higher concentrations of Ca, P, K and Zn in the present study compared to the findings of Mapunda & Mlilo [35] (58.96 mg/100 g, 61.70 mg/100 g, 476.66 mg/100 g, and 0.01 mg/100 g, respectively). Regarding Fe, manketti nuts and ushivi beans had lower contents compared to monkey orange (5.65 mg/100 g).

The comparison of manketti nuts and ushivi beans with *Berchemia discolor* (bird plum; from South Africa) showed a higher concentration of Fe (approx. 6 mg/100 g) compared to manketti nuts and ushivi beans, while the Ca content is similar to manketti [36].

The comparison of manketti nuts and ushivi beans with fruits of *Ximenia caffra* (African sourplum; from Tanzania) showed higher average concentrations of mineral elements such as Ca, P and Zn in the present study compared to African sourplum (23.18 mg/100 g, 128.29 mg/100 g, and 0.02 mg/100 g, respectively). The K content in African sourplum (671.73 mg/100 g) is comparable to ushivi beans analyzed [34]. Another study on the mineral element content in fruit juice produced from *Ximenia caffra* showed that the concentrations of Ca, K, Mg, P, Fe, Zn, Mn, Mo, Se Cu, Cr and Pb are higher in manketti nuts and ushivi beans analyzed, whereas Ni content is lower in the present study. The values of Co are comparable to the fruit juice from African sourplum [37].

It has to be mentioned again that As was found in one out of 11 manketti sample. The high arsenic concentration in this sample was likely due to contamination caused by the mining of mineral resources such as arsenic concentrates in some mines in northern Namibia (e.g., Tsumeb Mine, Rubicon Mine), which leads to environmental pollution (soil, water, air, and as a consequence also plants) [38, 39]. In addition, Pb could be detected in two manketti samples, while Cd was found in all ushivi beans analyzed. Environmental heavy metal pollution should be considered an important and severe issue in production areas of both manketti and ushivi trees. Such elemental data have not been reported yet making further research necessary. Nevertheless, both manketti nuts and ushivi beans provide a valuable source for several macro- and microelements. Despite the potential benefits, existing literature indicates that consumers in Europe are generally hesitant to accept and consume *Novel Foods* because of various reasons (primarily unfamiliarity and food neophobia, e.g., in the case of insects). However, especially manketti nuts have been an important staple food in the Kalahari Desert (South Africa, Namibia, Botswana) for at least 7000 years. Both seeds offer a wide variety of possible food applications such as snack food or valuable food ingredient or even dietary supplement due to various nutritionally relevant compounds (ranging from fatty acids and amino acids to B-vitamins or mineral elements) [27, 40, 41]. Therefore, manketti and ushivi seeds might gain acceptance as *Novel Food* or food ingredient similar to Baobab dried fruit pulp [42] or the seeds and seed flour of Bambara (*Vigna subterranea*) [43] in the near future.

Conclusions

In order to find out whether manketti nuts and ushivi beans contain essential macro- and microelements in considerable amounts, ICP-SFMS was applied to give comprehensive insight into the mineral nutrient composition (Na, Mg, P, K,

Ca, B, Mn, Fe, Ni, Cu, Zn, Co, Se, Mo, Cr, Li, Be, Ga, As, Ag, Cd, Tl, Pb, Bi, U).

Results obtained showed that manketti nuts offer a valuable source for Mg, P, K, Ca, Fe, Zn, Mn, Cu, Mo, Se and Co. Compared to other nuts, especially the high Ca content should be noted. Ushivi beans contained essential mineral elements such as K, Ca, Fe, Mn, Cu, Se and Co in considerable amounts. Regarding the comparison to several other legumes/oilseeds, ushivi samples showed a higher Ca content, and the concentration of Se was superior to other legumes.

Comparison of manketti nuts and ushivi beans showed that they are similar regarding the concentration of macro- and microelements such as Ca, K, Fe, Co or B, while they differ regarding their content of P, Mg, Mn, Se, Mo, Cu or Zn. The comparison of manketti nuts and ushivi beans with the dietary reference values provided by EFSA showed that both seeds are a valuable source for mineral nutrients such as Ca, K, Fe or Cu. Manketti nuts offer further an important source for Mg, P, Zn, Mn or Mo, while ushivi beans can contribute to meet the required amounts of Se. However, the actual amount consumed must be taken into account. Furthermore, the comparison of manketti nuts and ushivi beans with several other nutritionally and economically relevant indigenous fruit species showed that in almost all cases both had higher concentrations regarding macroelements. Regarding microelements, many results are similar or slightly higher.

To the best of our knowledge, this study is the first to provide extensive insight into the macro- and microelement composition of manketti nuts and ushivi beans by analyzing so many different mineral elements. The high value of the seeds of *Schinziophyton rautanenii* and *Guibourtia coleosperma* needs to be considered, and further research on the chemical composition as well as the growing conditions in Namibia and other parts of Africa is required. Results presented could provide a basis for further research, and limitations of the present study need to be investigated and improved (e.g., higher number of samples, samples from more different regions and/or countries in Africa, and samples collected over several years/seasons). Furthermore, it is well-known that the total concentration of an element in a sample does not provide information about the different forms of an element in the environment, in which it is active. Thus, speciation of an element, i.e., determination of various forms of the elements (e.g., concentration of bound fractions, or chemical forms [inorganic, organic, co-ordination, or complexes], or different oxidation states) would be of utmost importance to assess the nutritional availability of most elements for human consumption. Future studies about bioavailability or toxicity of mineral elements will certainly benefit from the research data provided.

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Data availability No datasets were generated or analysed during the current study.

Declarations

Conflict of interest Sabrina P. Van den Oever, Lisa Fischer, Stephan Hann and Helmut K. Mayer declare that they have no competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. Cecilia K. Maruta is the owner of Kavango Global Trading cc, which may be considered as potential competing interest.

Human or animal participants Research presented in this article did not involve any human or animal subjects.

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