Research Article

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Cultivation of *Solanum tuberosum* in a former mining district for a safe human consumption integrating simulated digestion

María José Sierra,[a*] Rubén López-Nicolás,[b] Carlos A González-Bermúdez,[b] Carmen Frontela-Saseta[b] and Rocio Millán[a]

Abstract

BACKGROUND: Potato (*Solanum tuberosum*) is a global crop and by far the most important non-cereal crop in the world. Therefore, it is necessary to assure its safe consumption. This is especially relevant in the case of its cultivation in abandoned mining areas, where the population tends to return to agriculture. In the present work, the objective is to evaluate the contribution to the diet of nutrients and contaminants of potato grown in soils from the Almadén area (mining district) by studying the intestinal absorption (*in vitro*) of the tuber, taking into account the preparation methods for its consumption.

RESULTS: The results of contaminant and nutrient contents show that the potato peel retains significantly more elements (mainly in the case of toxic elements) than the flesh. Furthermore, potato (peel and flesh) is a good source of iron.

CONCLUSION: It is recommended to boil potatoes with the peel in order to minimize nutrient loss and, before consumption, peeling them to eliminate possible risks due to contaminants. In addition, to minimize the risk due of mercury and to improve the levels of calcium, magnesium, potassium and sodium, it is recommended to add salt during the boiling process.

Keywords: contaminants; mercury; nutrients; *Solanum tuberosum*; simulated digestion; bioaccessibility

INTRODUCTION

Potato (*Solanum tuberosum*) is a tuber crop that ranks fourth in production as a world food crop. There are over 1000 different types of potatoes, which adapt to very different conditions; thus its production is continuously increasing worldwide.[1] Furthermore, 2008 was declared the International Year of the Potato by the United Nations, highlighting the role of the potato as a staple food in fighting global hunger. As part of a balanced and healthy diet, potato represents a main food source and thus its nutritional value must be worth considering. Therefore, potato has several uses and is a good source of macro- and micronutrients.[2–4] Due to the large production and the economical and nutritional importance of potato, it has become necessary to assure that it can be consumed under safe conditions. This is especially relevant in the case of its cultivation in abandoned mining areas, where the population tends to return to traditional land uses including agriculture. In this case, it is important to evaluate the contribution to the diet of nutrients and contaminants from agricultural products obtained from those soils. In the present work, the old Almadén mining district has been chosen as a study area. This mining district is considered to be the largest mercury (Hg) reservoir in the world, which was exploited for over 2000 years. In addition of this main mining activity, other metals such as lead (Pb), zinc (Zn) and copper (Cu) were also mined within the same area.[5] Over centuries, the economy of the Almadén area depended on mining activities until halting in 2004, when this area went into an economic depression. In order to mitigate this situation, interest was focused on developing strategies that integrate new economic possibilities for the local population, including the implementation of alternative land use such as agriculture. Nowadays, agricultural farming products and, in particular, the cultivation of potato is widespread in this area as it is a common ingredient used in the local cuisine. Given that Hg and other contaminants can be mobilized and absorbed by plants,[6,7] their impact in agricultural products from Almadén soils is a concern. The consumption of the edible part of crops[8–12] could be a pathway by which contaminants might enter the food chain.

Millán *et al.*[8] gathered data of Hg concentrations in different common crops (grain and fruit) from this area in order to provide a series of safe consumption recommendations applicable to other areas with the same problem. The results obtained in the present work could be transferred to Hg-contaminated areas due to traditional gold mining activities in South America, Africa or Asia where potato cultivation is of great importance, as well as to areas affected by chlor-alkali plants. Moreover, although there are studies on the accumulation of other heavy metals (mainly

* Correspondence to: MJ Sierra, CIEMAT, Department of Environment, Unidad de Conservación y recuperación de suelos, Avenida Complutense 40, E-28040 Madrid, Spain. E-mail: mj.sierra@ciemat.es

a CIEMAT, Department of Environment, Unidad de Conservación y recuperación de suelos, Madrid, Spain

b Department of Food Science and Nutrition, Faculty of Veterinary Sciences, Murcia, Spain

Cd and Pb) by leafy or tuber crops from other sites,[13–16] there is little information focused on Hg accumulation. Studies have traditionally focused on the aquatic food chain and organic Hg compounds.

Regarding human consumption, potato is an essential crop in Europe where per capita consumption is still the highest in the world (82 kg per year), being 60 kg per year in Spain.[17] It is a versatile food that can be prepared and consumed in a variety of ways. It can be boiled (with or without peel), baked or fried, and can be consumed as a main or as a side dish. From a nutritional point of view, each preparation method affects the potato composition in a different way.[1,18] In the literature there are studies on the effect of different preparation methods on Hg in fish and its bioaccesibility.[19] This type of food, which accounts on average for 4% of the total food consumption in Spain,[20] is the main contributor to Hg intake in the diet according to Commission Regulation (EC) No. 1881/2006.[21] However, those studies on vegetal food are scarce and, up to now, in the particular case of potato, the authors have found no studies on this subject that also include both aspects (Hg accumulation and bioaccessibility).

The effect of potato processing on their nutrient content has been also evaluated.[3] However, it is very important not only to evaluate the content of micronutrients in foods or the quantity of micronutrient that is ingested but also their bioaccessibility. In this case, the amount of micronutrients from foods that is actually absorbed and utilized for body functions compared with intake has a key role on the knowledge of what constitutes a balanced diet.[22] As mineral deficiency is a major problem for health,[23,24] the wide consumption of potato must be considered from this perspective. This study has assessed the availability of key minerals in human nutrition after an *in vitro* gastrointestinal digestion process and has then measured the mineral solubility and dialyzability through a semipermeable membrane that is highly correlated with the amount of minerals in the gastrointestinal tract that can be absorbed.[25] Regarding Hg and other contaminants, they can share and compete for some of the same cellular transport and absorption receptors as iron. Therefore, diets with reduced non-heme iron bioavailability could enhance the retention of mercury.[26]

In order to evaluate the availability of Hg and other contaminants from potato foods and the risk for human consumption, the objective of this study was to determine the uptake of nutrients and total Hg and other contaminants by the potato tuber (edible part of plant) grown in soils from the Almadén area, and to study the *in vitro* intestinal absorption (solubility: potential absorption; and dialysis: true absorption) of these elements. Furthermore, the effect of different methods of preparation, processing and consumption of potato (boiling, peeled or not, salt or not) were assessed to determine the content and absorption of elements for human consumption. Finally, considering the World Health Organization (WHO) recommendations for maximum intake, the suitability of the produce and the consumption of this crop was evaluated.

EXPERIMENTAL

Plant culture

The experimental work was performed under close-to-real conditions in lysimeter experiments located at the installations of the Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT). Each lysimeter experiment used in the present work consisted of a cubic meter of an unaltered soil monolith within a metallic structure.[27–29] They were extracted in the surroundings of Almadenejos village, in an agricultural area within the Almadén mining district. This area lies in a fluvial valley and its main land use is grassland[7] pasture. The seed potatoes (var. Kennebec) used throughout the experiments were provided by a local farmer from Almadén. The crop density was the same as implemented in Almadén and the irrigations were carried out taking into account the necessities of the potato culture.[30] No phytosanitary treatments were applied. Five potato plants were grown in each lysimeter during two harvest seasons.

Sampling and analysis

Thirty-six potato tubers were sampled for the experimental work, as well as the aerial parts and the roots of the plants. The bulk soil fraction around each potato plant was sampled. Furthermore, potato tubers were shaken to sample the soil directly adhered to potato peel. In both soil samples, total Hg and that easily available to plants were extracted and measured. Easily available Hg was obtained from the two first steps of the seven-step sequential extraction procedure (soluble + exchangeable soil fraction).[31] Moreover, different edaphic parameters were measured in the bulk soil. These parameters included: pH (H_2O, 1:2.5) and electrical conductivity (EC), which were determined according to Burt and Soil Survey Staff;[32] cation exchange capacity (CEC), which was determined using the EPA 9081 method (NaOAc 1N, pH 8.2); organic matter (OM), which was measured following the Walkey–Black method; and soil texture, using the Bouyoucos method according to standard procedures.[33]

Aerial parts and roots were cleaned in distilled water using an ultrasonic bath (Ultrasons-H, Selecta) in cycles of 10 min (up to nine) in order to remove external contamination. All samples were then placed in a beaker to dry them at room temperature until a constant weight was reached. After that, each fraction was ground to obtain a homogeneous sample to determined Hg concentration using an atomic absorption spectrophotometer specifically designed for mercury determination (Advance Mercury Analyzer, AMA-254, LECO Instruments). This equipment analyzes solid and liquid samples without the need for a chemical pre-treatment and with a detection limit of 0.01 ng Hg. Certified reference materials (CRM) were used to determine the accuracy and precision of the Hg measurements.

Treatments

Different treatments were applied to the potato samples. One part of the samples was washed using an ultrasonic bath (Ultrasons-H, Selecta) as mentioned above, and the other part was washed carefully under tap water as a person at home would do it. These samples were then dried in a furnace at 30 °C until a constant weight was reached.

The remaining potatoes were also washed under tap water but, in addition, they were boiled in different ways: peeled potatoes with salt and without salt; and potatoes with peel with salt and without salt (Fig. 1). The cooking water was sampled after each treatment.

In all cases, potato samples were divided in two fractions (peel and flesh) to measure Hg concentration after treatment.

In vitro gastrointestinal digestion and mineral content determination

Materials and reagents

Deionized water (MilliQ; Millipore, Bedford, MA, USA) was used throughout the study. Pepsin (P-7000, from porcine stomach

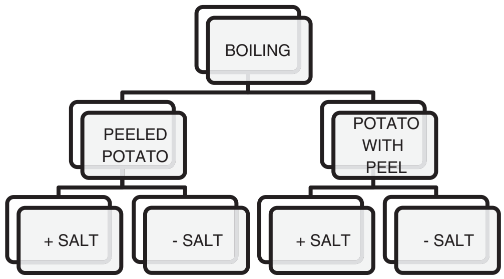

Figure 1. Diagram of different methods of boiling *Solanum tuberosum*.

mucosa), bile salts (B-8756) and pancreatin (P-1750, from porcine pancreas) were purchased from Sigma (St Louis, MO, USA). For mineral dialysis assays, dialysis membranes with molecular mass cut-offs (MMCO) of 12 000 Da were purchased from Medicell International Ltd (London, UK). Mineral content in the raw material, as well as in soluble and dialyzable fractions, was determined by inductively coupled plasma–optical emission spectrometry (ICP-OES; ICAP 6500 Duo Thermo-One Fast).

Experimental assay

To measure the solubility and dialyzability of minerals, each sample was reconstituted with deionized water. After reconstitution, samples were digested using the widespread *in vitro* method described by Boato *et al.*[34] The *in vitro* digestion process consisted of two phases (gastric and intestinal). At the end of the intestinal stage, aliquots of 20 g sample were centrifuged (Eppendorf 5804-R centrifuge, Hamburg, Germany) at $3500 \times g$ for 1 h at 4 °C. The supernatant (soluble fraction) was used to determine the mineral content. Dialysis comprised the gastric stage, followed by an intestinal step in which a dialysis bag containing 50 mL deionized distilled water and an amount of $NaHCO_3$ equivalent to the titratable acidity (previously measured) was placed in flasks containing 20 g aliquots of the pepsin digest. Minerals dialyzed through the semipermeable membrane represented the available fraction (expressed as a percentage) of the total minerals present in the sample.[25,35]

Data analysis

The software package used to perform the statistical analysis was SPSS for Windows (version 11.5, IBM, Armonk, NY, USA). Shapiro–Wilk's test was performed to determine the normal distribution of the dataset, and the Levene test was carried out to check the homoscedasticity of values. These assumptions (normality and homoscedasticity) were not met, therefore the non-parametric Mann–Whitney test was used in order to compare conditions when different participants take part in each condition. In the Mann–Whitney test, the significance level was calculated as follows: $0.001/k$, where k is the number of pair combinations to compare. Results with probability values equal to or below 0.001 were considered significant. Values in figures and tables are expressed as means ± standard errors (SE).

RESULTS AND DISCUSSION

Soil and potato plants

The lysimeter soils have been classified as Mollic Haploxeralf according to USDA's *Keys to Soil Taxonomy*.[36] Table 1 shows their main physical and chemical characteristics, which indicated that this soil was suitable for potato cultivation.[37–40] Soil texture was excellent for plant growth, since it had the advantages of both sands and clays (good water and nutrient holding capacity, moderate permeability). Neutral pH indicated that most of the nutrients could be absorbed by plants.[41] Finally, the values of OM and CEC were optimal for agricultural soils under the influence of the Mediterranean climate and with a semi-arid to arid moisture regime.[41,42]

Table 1. Physical and chemical parameters of soil (n = 6)

	pH	EC ($dS\ cm^{-1}$)	OM (%)	CEC ($cmol\ kg^{-1}$)	Texture
Lysimeter soil	6.7–7.2	0.37 ± 0.10	4.2 ± 0.2	27.7 ± 0.3	Sandy clay loam

Table 2. Mercury concentration in soil ($n = 6$)

	Soil adhering to potato peel	Bulk soil
Total Hg ($mg\ kg^{-1}$)	20.2 ± 1.0	18.1 ± 0.9
Easily available Hg ($mg\ kg^{-1}$)	0.016 ± 0.002	0.033 ± 0.002

Mercury was measured in the bulk soil and in soil adhering to the potato peel including total Hg and that easily available to plants (Table 2). There were no significant differences between total Hg concentration in bulk soil and soil adhering to potato peel. However, the Hg easily available to plants in bulk soil was significantly higher than in soil adhering to potato peel ($U = 0.00$, $z = -3.24$, $P \leq 0.001$, $r = -0.84$). As mentioned above, Hg easily available to plants is the sum of soluble and exchangeable Hg. Of these, the soluble Hg in bulk soil ($0.027 \pm 0.001\ mg\ kg^{-1}$) was significantly higher than in soil adhering to the potato peel ($0.008 \pm 0.002\ mg\ kg^{-1}$) ($U = 0.00$, $z = -4.00$, $P \leq 0.001$, $r = -0.79$), whereas there were no significant differences between exchangeable fractions of both soils.

Despite the high total Hg concentrations in the studied soils, they can be considered normal in Hg mining areas and in agreement with the range measured in the Almadén area by Lindberg *et al.*,[43] Higueras *et al.*,[44] Millán *et al.*,[7] and Sierra *et al.*[10] Agricultural use is conditioned by the concentration of Hg in bioavailable form and the Hg concentration in the edible part of the plant. Thus those parameters are necessary in order to evaluate the possible consumption of this crop without any health risk.

In the present case, easily available Hg for plants, considering both soils, ranged between 0.08% and 0.18% of the total Hg. Regarding the Hg concentrations in different fractions of the edible part samples washed by ultrasonic bath, Hg concentration in potato peel ($42 \pm 3\ \mu g\ kg^{-1}$) was significantly (five times) higher than Hg concentration in the potato flesh ($9 \pm 2\ \mu g\ kg^{-1}$) ($U = 0.00$, $z = -3.78$, $P < 0.001$, $r = -0.85$). These concentrations were within the global range stated by Adriano[6] for edible parts of common crops (from <1–300 $\mu g\ kg^{-1}$ dry weight). Regarding the whole plant, the relation between Hg concentrations is as follows: Hg concentration in the tuber was significantly lower (39 times) than in the aerial part, which, in turn, was significantly lower (2.5 times) than the Hg concentration in the root (Fig. 2). This could indicate a physiological mechanism that prevents tuber, mainly potato flesh, from excessive Hg accumulation. It has been proposed that xylem connections between basal roots and tubers are non-functional.

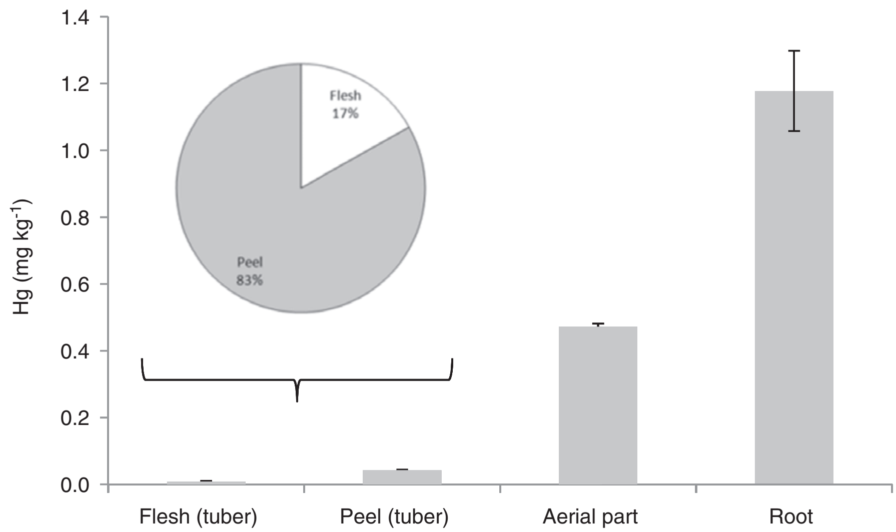

Figure 2. Mercury distribution in *Solanum tuberosum* plants.

Xylem is driven by transpiration, and tubers have a very low transpiration rate due to the combination of a protective periderm, a low surface area to volume and a moist soil environment.[15,45] Furthermore, there is anatomical evidence for the existence of a suberized hypodermis in the outer layers of the tuber[46] that would serve to inhibit entry of solutes into the cortex, and loss of water. Thus phloem, in the absence of a functional xylem connection, must be the pathway for uptake into the tuber for most other nutrients and non-nutrient contaminants. However, for those elements with low phloem mobility, alternative pathways must exist such as transfer from basal roots or direct uptake across the periderm or via stolon and tuber roots.[47,48] Mercury transfer to tuber, mainly to flesh, is extremely low considering the significantly higher Hg concentration in the rest of the plant and Hg concentrations in soil.

At present, little is known about Hg accumulation in potato tubers, but there are several studies about the accumulation of other heavy metals in them. Thus the fact that the Hg concentration in potato peel was significantly higher than in the potato flesh is in agreement with that happens with other contaminants. Renu and Kalpana,[49] Dudka *et al.*,[50] Dunbar *et al.*,[16] Zhifan *et al.*[51] and Reid *et al.*[15] reported that there were differences in Pb, Cd, Fe, Zn and Cu concentrations between the peel and the flesh. The peel retained more content of elements (mainly in the case of toxic elements) than flesh, although the differences did not seem to be significant in those cases. In the present potato study, there could be a slight Hg diffusion process from the soil adhering to the peel[52] or remains of fine soil particles enriched in Hg strongly adhering to the tuber surface even after careful washing. It seems that the peel worked as a barrier to block toxic elements (i.e. physical barrier, less available Hg for diffusion process) from entering into the potato flesh in a significant way.

Potato preparation procedure and Hg

The potato washing process is the first step in preparing potatoes for consumption. It is essential for removing soil particles adhering to the peel. In this way, the studied potatoes were washed thoroughly under tap water. However, it was observed that this thorough washing did not remove all adhered soil and some Hg content may remain on the peel surface. As Fig. 3 shows, Hg concentration in the peel after washing under the tap was significantly

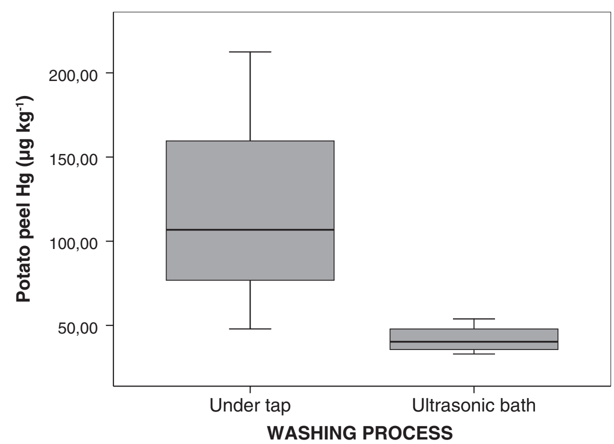

Figure 3. Mercury concentration in *Solanum tuberosum* peel depending on the washing process.

higher than in peel after washing in an ultrasonic bath ($U = 8.00$, $z = -4.44$, $P < 0.001$, $r = -0.70$). Therefore, it would be advisable to peel a potato grown in soil before it is consumed in order to remove possible contaminants adhering to the peel.

Once potatoes are washed thoroughly, there are several methods of preparation for their consumption. Since the starch in raw potato cannot be digested by humans, they are boiled (with or without the peel), baked or fried. Boiling the potatoes is the most common option and this can be done in many ways.[1] The present work studies how the potato composition was affected depending on the method of boiling, shown in Fig. 4.

The studied potatoes were boiled with peel and without peel. With the former, the peel had significantly higher Hg concentration when no salt was added compared to when salt was added ($U = 8.00$, $z = -3.63$, $P < 0.001$, $r = -0.74$). Mercury in the presence of Cl^- forms stable complexes: $HgCl_2$, $HgCl_3^-$, $HgCl_4^{2-}$. These easily seize the metal, rendering it unavailable for absorption by the plants or other organisms. These complexes contribute to the mobilization of the metal from the potato peel. This is in agreement with the effects of chloride on adsorption of Hg reported by Yin *et al.*[53] and with results obtained in several studies showing that salt could also considerably promote Hg removal

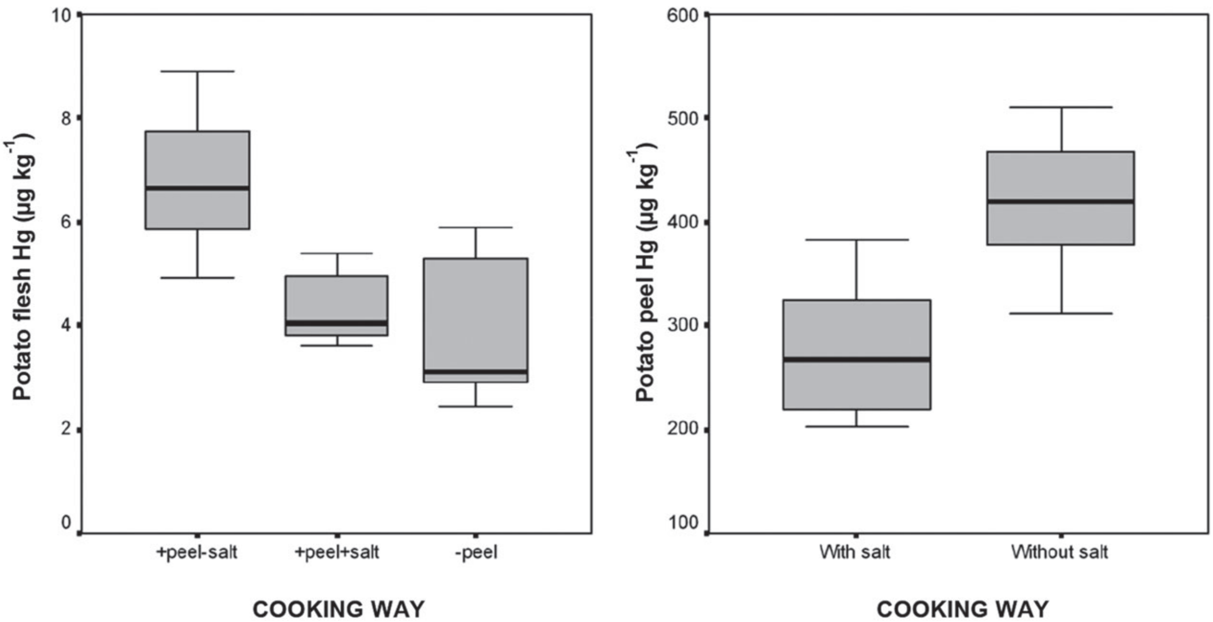

Figure 4. Mercury concentration in *Solanum tuberosum* flesh and peel depending on method of boiling.

from fish tissue.[54,55] Moreover, the flesh of the potatoes boiled with peel but without salt had significantly higher Hg concentration than the flesh of potatoes boiled with peel and salt ($U = 3.00$, $z = -3.29$, $P < 0.001$, $r = -0.78$). There was probably an Hg diffusion process from the peel directly through the periderm into the flesh of the potato. Hg values of the potato flesh boiled with peel and salt were similar to potatoes boiled without peel both with and without salt. Considering only Hg and the above premises, it is advisable to boil potatoes without peel. However, given that the FAO recommendation is to boil potato with peel in order to avoid a significant loss of vitamin C,[1] the best option would be to boil potatoes with the peel and with salt (Fig. 4).

Recommendation for potato consumption considering Hg concentrations

Potato and leafy vegetables have the highest contribution to metal intake by humans,[56] although, as mentioned previously, there is a lack of studies about Hg accumulation in these types of cultivations. In order to evaluate the risk of consumption of potatoes grown in the Almadén soils, this crop is considered as the only product to contribute to the Hg intake pathway. Therefore, the maximum quantity of potato processed by the different methods applied in the present study that a person could consume per day without risk of intoxication was calculated according to the recommendations of the World Health Organization.[57] The tolerable daily intake of total Hg for adults is 0.57 μg kg^{-1} body weight per day. Considering an average body weight of 60 kg, an adult would be able to consume 34.2 μg Hg per day. The maximum rations of potato that can be eaten with no risk, depending on food processing and percentage of total Hg retained in the body, are shown in Table 3.

The results show that between 1.2 and 12.4 kg dry weight of the studied potatoes per day could be consumed, considering that the 100% of total Hg is retained in the body in order to provide greater protection; and between 12.2 and 69.9 kg considering the values of dialyzability percentage. The studied potatoes contained, on average, between 19.5% and 26.9% dry matter depending on food processing. Therefore, the calculated maximum rations could even increase. In Spain, the average daily intake of potatoes is 73 g per capita and per day. Although potato consumption in Spain represents approximately 4% of the total Spanish food consumption, the amounts calculated as maximum rations are high for potato.[20]

It is important to note that the European Commission Regulation (EC) No. 1881/2006[21] establishes maximum concentrations for Hg only in fish and seafood (0.5–1.0 mg kg^{-1} fresh weight). This is because they are in the food category considered as the main source of Hg mostly in the form of methylmercury, which is considered the most toxic.[58] All cases in the present study are also far below that established limit.

Intestinal absorption of nutrients and contaminants (non-nutrient)

The values of the mineral content in potato after the different treatments, related to those elements of nutritional interest and those non-nutrients, as well as its solubility (%) and dialyzability (%), were obtained as a result of an *in vitro* digestion process. As can be seen in Tables 4 and 5, within the same treatment (boiled potato), the content of most minerals in peeled potatoes was lower than in the whole potato. The content of Fe and Zn should be highlighted, since a reduction of nearly 10 mg kg^{-1} was observed after the peel was removed. This is in agreement with other studies reporting that most minerals in potato are found in the peel.[59] According to results obtained in the present study, the distribution of minerals varies greatly within the potato tuber.

Regarding raw potato (Table 5), no great variations were observed compared with boiled potato (Table 4), the only exception being iron content in the peel of raw potato, where a very high content was detected (202.4 mg kg^{-1}). However, as described previously, the nutritional importance of mineral content in foods is highly related to its intestinal absorption.[60] Related to this, results of mineral solubility and dialyzability were determined after a simulated gastrointestinal digestion process. Boiled potato showed an important amount of minerals with high solubility

Table 3. Maximum ration of *Solanum tuberosum* recommended by the World Health Organization[58] for adults (body weight = 60 kg), considering it as the only mercury contribution to the diet

Processing method	$[Hg]_{total}$ (μg kg^{-1})	Maximum ration (kg potato DW d^{-1})	Hg dialyzability (%)	Maximum ration (considering % of dialyzability) (kg potato DW d^{-1})
Flesh of raw *S. tuberosum*	3.7 ± 0.3	9.4	17.8 ± 4.1	52.4
S. tuberosum 's flesh boiled without peel	3.8 ± 0.0	9.2	75.0 ± 37.2	12.2
S. tuberosum 's flesh boiled with peel (+salt)	4.5 ± 0.5	7.7	49.8 ± 14.4	12.3
S. tuberosum 's flesh boiled with peel (−salt)	6.7 ± 0.7	5.1		
Whole *S. tuberosum* boiled (+salt)	10.0 ± 5.2	3.5	ND	ND
Whole *S. tuberosum* boiled (−salt)	29.0 ± 8.4	1.2	ND	ND

DW, dry weight; ND, not determined.

Table 4. Mineral composition (content, solubility and dialyzability) of *Solanum tuberosum* flesh boiled previously, washed as in a domestic setting

	Solanum tuberosum flesh boiled with peel			*Solanum tuberosum* flesh boiled without peel		
Mineral	Raw material (mg kg^{-1})	Solubility (%)	Dialyzability (%)	Raw material (mg kg^{-1})	Solubility (%)	Dialyzability (%)
B	6.45	99.9 ± 13.3	99.6 ± 28.1	5.02	100.5 ± 15.6	99.7 ± 13.3
Ca	0.04	42.3 ± 1.5	50.3 ± 9.4	0.02	52.0 ± 28.7	70.9 ± 37.9
Cu	4.15	1.1 ± 0.8	1.4 ± 1.2	2.96	1.8 ± 1.2	2.4 ± 1.6
Fe	36.85	26.8 ± 1.9	31.9 ± 7.2	23.44	4.3 ± 0.83	42.1 ± 1.7
K	2.11	63.7 ± 12.2	76.6 ± 26.0	1.43	30.7 ± 1.8	94.2 ± 34.2
Li	ND	ND	ND	ND	ND	ND
Mg	0.10	63.0 ± 1.6	74.5 ± 9.5	0.09	69.1 ± 20.1	94.5 ± 25.6
Mn	13.74	47.0 ± 5.8	55.2 ± 1.6	12.82	37.4 ± 12.4	51.2 ± 15.9
Mo	1.03	31.5 ± 10.2	38.3 ± 17.8	0.45	54.4 ± 11.0	74.8 ± 16.7
Na	0.02	98.3 ± 9.6	98.9 ± 56.1	0.16	111.5 ± 19.2	100.1 ± 17.3
P	0.22	39.0 ± 14.0	47.4 ± 23.6	0.16	41.1 ± 6.3	56.3 ± 7.4
Sb	ND	ND	ND	ND	ND	ND
Se	ND	ND	ND	ND	ND	ND
S	0.13	45.3 ± 8.1	54.4 ± 17.8	0.09	63.1 ± 19.5	86.3 ± 24.9
Sr	1.49	57.8 ± 9.8	67.6 ± 1.2	1.28	52.9 ± 30.8	72.1 ± 40.8
Zn	22.75	100.3 ± 16.1	96.1 ± 0.1	14.97	99.6 ± 49.3	102.5 ± 48.5

ND, not determined.

and dialyzability, especially after the peel was removed, indicating that some components in the potato peel reduce mineral absorption. In this case, values were similar to those found by Repo-Carrasco-Valencia *et al.*[61] studying other food crops. The percentages of dialyzability of iron and zinc are around 40% and 100%, respectively, showing an important net intake of these minerals, so we can consider potato as a good source of these micronutrients. In the case of iron, a wide consumption of boiled potato flesh, and attending to the daily iron requirements (8–15 mg),[62] the consumption of 100 g of this food will provide 10% of the total daily requirements of iron. Also for zinc, the same product provides 1.5% of the daily requirement in adults. However, potato showed calcium values lower than 0.1 mg kg^{-1} in all cases. This has been previously reported,[63] indicating that the potato provides a low amount of calcium in the diet.

Magnesium, phosphorus and potassium are other nutritionally important minerals, which showed very low levels in every analyzed sample. This reinforces previous studies that the potato is not an important source of these minerals, depending on the varieties studied.[64] Sodium, a mineral positively related to blood pressure, showed high percentages of solubility and dialyzability; however, its level in the raw material is almost absent, so the absorbed mineral is quite negligible.

Regarding contaminants, solubility and dialyzability of Hg in all analyzed samples were quite similar, showing a good mineral availability. However, it should be noted that Hg in the flesh of raw potato showed quite a low dialyzability, indicating a very low absorption (Table 3) compared to boiled potato. These results are opposite to those obtained by Maulvault *et al.*[65] and Ouédraogo and Amyot,[66] who showed that cooking (frying and boiling) could reduce the bioaccessibility of Hg in fish. Furthermore, the solubility and dialyzability of the raw potato peel is lower than 1%, which is around 72 times lower than in potato flesh. In summary, available Hg is very low in all samples, highlighting potato peel. Despite a high Hg concentration in this fraction, raw or boiled, its availability was negligible. As expected, fiber could chelate some micronutrients in this part of the tuber.

Other important mineral contaminants (Pb, Cd and As) remain in low amounts, or undetectable, in every potato sample. The concentrations in studied potatoes (fresh weight) were below the maximum levels of 0.10, 0.10 and 0.2 mg kg^{-1} established by Commission Regulation (EU) No. 1881/2006,[21] Commission Regulation

Table 5. Mineral composition (content, solubility and dialyzability) of raw *Solanum tuberosum* flesh and peel previously washed as in a domestic setting

	Raw *Solanum tuberosum* flesh			Raw *Solanum tuberosum* peel		
Mineral	Raw material (mg kg^{-1})	Solubility (%)	Dialyzability (%)	Raw material (mg kg^{-1})	Solubility (%)	Dialyzability (%)
B	5.94	43.1 ± 0.1	53.7 ± 0.6	12.47	37.7 ± 0.3	47.9 ± 1.4
Ca	0.02	36.1 ± 1.6	44.9 ± 2.3	0.10	10.4 ± 0.1	13.2 ± 0.3
Cu	3.12	1.7 ± 0.2	2.2 ± 0.2	7.08	3.0 ± 0.1	3.8 ± 0.1
Fe	30.00	43.0 ± 0.6	53.5 ± 1.1	202.40	4.9 ± 0.2	6.2 ± 0.0
K	1.98	77.2 ± 2.6	96.2 ± 4.0	3.06	69.4 ± 2.2	88.1 ± 0.6
Li	0.11	ND	ND	0.66	ND	ND
Mg	0.11	79.1 ± 0.3	98.5 ± 1.1	0.14	69.0 ± 0.2	87.7 ± 3.6
Mn	14.31	77.6 ± 3.0	96.6 ± 3.0	20.69	51.5 ± 0.5	65.4 ± 1.9
Mo	0.63	38.3 ± 1.9	47.7 ± 2.7	0.99	1.1 ± 0.2	1.4 ± 0.3
Na	0.01	100.0 ± 16.9	98.7 ± 16.5	0.02	99.9 ± 3.0	99.8 ± 6.9
P	0.18	72.8 ± 0.2	90.7 ± 0.8	0.24	62.7 ± 1.1	79.6 ± 1.7
Sb	ND	ND	ND	ND	ND	ND
Se	ND	ND	ND	ND	ND	ND
S	0.12	73.3 ± 0.4	91.2 ± 1.1	0.16	58.6 ± 1.3	74.3 ± 1.3
Sr	0.90	10.0 ± 0.2	12.4 ± 0.4	5.56	4.5 ± 0.2	5.7 ± 0.5
Zn	17.06	71.6 ± 0.2	89.1 ± 0.9	26.53	53.4 ± 1.2	67.8 ± 1.1

Table 6. Maximum ration of *Solanum tuberosum* recommended by the World Health Organization[58] for adults (body weight = 60 kg), considering it as the only aluminum contribution to the diet

Processing method	$[Al]_{total}$ (mg kg^{-1})	Maximum ration (kg potato DW d^{-1})	Al dialyzability (%)	Maximum ration (considering % of dialyzability) (kg potato DW d^{-1})
Flesh of raw *S. tuberosum*	10.6	1.62	2.13	75.9
S. tuberosum 's flesh boiled without peel	12.0	1.43	2.88	49.7
S. tuberosum 's flesh boiled with peel	11.4	1.50	3.38	44.4
Peel of raw *S. tuberosum*	264.8	0.06	4.07	1.6

DW, dry weight.

(EU) No. 420/2011[67] and Codex Alimentarius Commission[68] for Pb, Cd and As, respectively. Furthermore, the percentages of solubility and dialyzability were undetectable in all cases.

The amount of aluminum in the potato peel is higher than in flesh samples, showing similar solubility and dialyzability percentages, indicating that potato peel is an important source of this contaminant (Table 6). Following the recommendation of the World Health Organization[69] for maximum aluminum daily consumption (0.29 mg kg^{-1} body weight per day), an adult of 60 kg could have an intake of 17.2 mg of this mineral per day. The maximum rations of potato depending on food processing that can be eaten with no risk are shown in Table 6. The high concentration of aluminum in potato peel was around 20-fold higher than in potato flesh. This could be the result of soil contamination since this mineral is one of the most abundant elements in soils. Even so, the dialyzability of this element was very low in all cases (Table 6), indicating that the mineral absorption and storage in different tissues is almost residual.

Considering that potato as the only product to contribute to the Hg and Al intake pathway and according to the recommendations given by the World Health Organization, the maximum ration of boiled potato grown in Almadén soil that a person could consume without risk would be 1.2 or 12.2 kg per day, if considering total concentration or dialyzability percentage, respectively.

CONCLUSIONS

In summary, there is a physiological mechanism that prevents the tuber, mainly the potato flesh, from excessive accumulation of Hg and other contaminants. Potato peel retains significantly more content of elements (mainly in the case of toxic elements) than the flesh. In the case of Hg, although its concentration in the peel is higher than in the flesh, its solubility and dialyzability are lower than 1%, which is much lower than Hg in the flesh. The percentages of solubility and dialyzability for Pb, Cd and As are undetectable and for Al is around 4%, in all cases. Considering the results obtained for all contaminants and essential minerals, it is recommended to boil the potato with the peel in order to avoid losing essential minerals and, before consumption, to remove the potato peel to eliminate the possible risks of contaminants (i.e. Al and Hg). In addition, for minimizing even more the risk due to Hg, it is recommended to add salt in the boiling process. Regarding mineral content and its availability, with importance from a nutritional point of view, the high level of iron, even after the peel is removed, should be noted. However, calcium, magnesium, phosphorus, potassium and sodium levels are almost negligible. This reinforces the idea of adding salt to the boiling water as a healthier way of cooking potatoes grown in soil from the Almadén district.

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