

## Research Note

# Evaluation of Trace Elements in Potatoes (*Solanum tuberosum*) from a Suburban Area of Naples, Italy: The “Triangle of Death”

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## ABSTRACT

Human exposure to contaminated food is a general health concern worldwide; it is necessary to evaluate food safety with respect to contaminants present in the edible parts of major food crops. This study evaluated the concentrations of 17 trace elements (As, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Sn, Tl, V, and Zn) from 51 potato plantations in the Campania region, inside the area known as the “Triangle of Death,” with inductively coupled plasma mass spectrometry analysis. Results confirm that the potatoes collected from the suburban area of Naples contained concentrations of trace elements below the safe limits prescribed by the Food and Agriculture Organization of the United Nations and the World Health Organization. The concentrations of elements were similar to those reported for potatoes grown in other countries. Monitoring the content of toxic and potentially toxic elements is one of the most important aspects of food quality assurance. The environmental persistence of metals may result in the accumulation of significant levels of these contaminants in plants. They are absorbed to different extents, depending on their source, soil and climatic factors, plant genotype, and agrotechnical conditions, thereby entering the food chain and representing a risk to human health.

**Key words:** Campania region; Inductively coupled plasma mass spectrometry; Potatoes; Trace elements

In recent years in Italy, increasing attention has focused on metal concentrations in vegetables, with specific regard to those produced in the Campania region, an area that was involved in the illegal dumping and uncontrolled burning of waste along roads bordering cultivated fields. Excessive accumulation in agricultural soils not only contaminates the soil, but also has consequences for food quality and safety. Therefore, it is essential to monitor food quality, given that plant uptake is one of the main pathways through which heavy metals enter the food chain (2).

Metals play positive and negative roles in the human body (19). Lead, mercury, cadmium, and copper are cumulative poisons, which cause environmental hazards and are reported to be exceptionally toxic (6). Iron, copper, zinc, and manganese are essential because they play an important role in biological systems, but they can produce toxic effects when their intake is excessively elevated (16, 17).

Potato, the world’s fourth-largest food crop, is indispensable in many diets around the world. A source of highly digestible carbohydrate and nutritionally complete protein, it is also an excellent source of other essential nutrients and is, therefore, an important component of the human diet (1, 22). Heavy metal concentrations in plants are directly associated

with their concentrations in soils, and potatoes grow in soil. Trace elements from the soil can enter potatoes through their root system and also by diffusion through the peel; this relationship is most evident with cadmium and less so with zinc and lead (12). In view of food safety concerns, this study assessed the contents of some trace elements (As, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Sn, Tl, V, and Zn) in the edible parts of potatoes from the Campania region. Cultivation of potatoes (*Solanum tuberosum*) is one of the main sectors of the region’s agriculture and accounts for 22% of national production (26). Samples were collected in the northern area surrounding Naples, mainly between the towns of Marigliano and Acerra, where there was an intense practice of illegal toxic waste spillage, as already highlighted by a rich literature (14, 15, 24). This area is also known as the “Triangle of Death,” as first defined by Senior and Mazza in 2004 (20) because deaths in the area caused by cancer and other diseases exceed the Italian national average. The rise in cancer-related mortality is thought to be caused mainly by pollution from illegal waste. This area also has the region’s only urban waste incinerator, in Pantano (Acerra), and its emissions have also been at the center of heated controversy.

These data were compared with those obtained for potatoes collected from lands between Avellino and Benevento, an area that was not subjected to extensive illegal toxic waste dumping. Observing the concentration of

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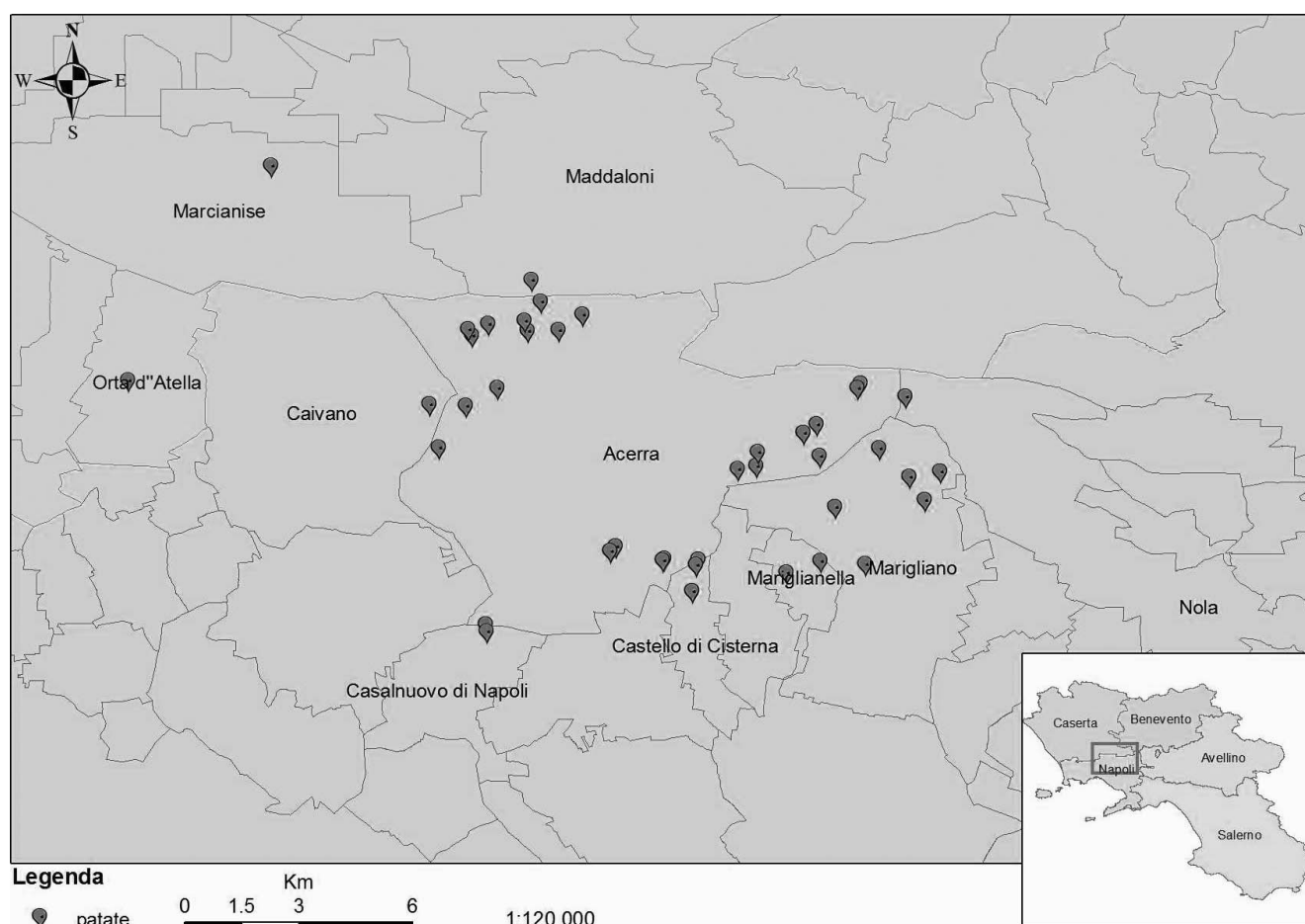


FIGURE 1. Geographical distribution of the potato collection points in the selected area of the Campania region.

these elements in potatoes could be useful to assess the level of their consumption and, therefore, the risk to which consumers are exposed.

## MATERIALS AND METHODS

**Sample collection.** Samples (51) of potatoes (*Solanum tuberosum*) were collected from three areas of the Campania region, around the towns of Acerra and Marigliano, just outside of Naples, Italy. In particular, 13 samples came from the area around Marigliano (Marigliano, Mariglianella, Castello di Cisterna, Nola), 33 from the area around Acerra (Acerra, Casalnuovo, Orta di Atella, Marcianise), and five from the area between Benevento and Avellino (Cervinara, Montesarchio, Rotondi). The detailed map in Figure 1 shows the Campania region between the towns of Acerra (40°57'00"N, 14°22'00"E) and Marigliano (40°55'29"N, 14°27'22"E).

**Chemicals and reagents.** All aqueous solutions and dilutions were prepared using ultrapure water (18.2 MOhm-cm), from an Arim611VF system (Sartorius Stedim Italy S.p.A., Firenze, Italy). Nitric acid (HNO<sub>3</sub>, 70%, v/v) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30%, v/v) were of the highest quality grade (Suprapure, Merck, Darmstadt, Germany). A 10-mg/L multielement stock solution (Accustandard Inc., New Haven, CT) was used to prepare calibration curves, whereas 10 mg/L rhodium (Fluka, Milano, Italy) and 1,000 mg/L germanium (Accustandard Inc.) stock standard solutions were used to prepare an internal standards working solution.

Before analysis, potatoes were washed several times with tap water, followed by ultrapure water; once dry, they were peeled, chopped to small pieces, and homogenized using a knife mill (Grindomix GM 200, Retsch, Haan, Germany).

**Procedure.** Samples were weighed in duplicate (ca. 0.65 g) in separate Teflon reaction vessels, and HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> were added immediately before wet digestion in an EHOS 1 microwave system (Milestone S.r.l., Sorisole, Italy). The following program was applied: heating to 130°C in 8 min, holding at 130°C for 2 min, heating from 130 to 200°C in 8 min, and holding at 200°C for 5 min. Digested samples were then diluted with ultrapure water to ca. 50 g by weighing. Prior to analysis using inductively coupled plasma mass spectrometry, internal standards working solution was added to all samples to achieve a final concentration of 10 pg/L. Calibration curves with internal standards working solution at 10 pg/L and elemental concentrations ranging from 0.5 to 100 µg/L were prepared. Instrumental determination was performed using an Xseries II inductively coupled plasma mass spectrometry instrument (Thermo Scientific, Bremen, Germany) equipped with a CETAC ASX 500 model 520 (CETAC Technologies, Omaha, NE) autosampler and a peristaltic pump nebulizer.

Instrumental settings were optimized daily with a tuning solution. Collision cell technique, performed with a helium-hydrogen mixture (95/5), was used to remove interferences (4).

All results were subjected to statistical analyses through determination of Pearson correlation coefficients and principal component analysis (PCA) using XL-STAT 2016 software (Microsoft Corporation, Redmond, CA).

TABLE 1. Mean elemental contents in potato tuber samples collected from three different areas of the Campania region<sup>a</sup>

Element	Marigliano	Acerra	Avellino-Benevento
As	0.009 ± 0.006	0.008 ± 0.006	0.007 ± 0.003
Be	0.010 ± 0.000	0.010 ± 0.000	0.010 ± 0.000
Cd	0.011 ± 0.003	0.011 ± 0.002	0.011 ± 0.005
Co	0.008 ± 0.003	0.008 ± 0.003	0.007 ± 0.003
Cr	0.021 ± 0.009	0.020 ± 0.009	0.017 ± 0.007
Cu	1.898 ± 0.528	1.868 ± 0.526	1.306 ± 0.236
Fe	5.735 ± 1.88	5.651 ± 1.825	5.898 ± 0.530
Mn	1.686 ± 1.067	1.663 ± 1.010	1.268 ± 0.096
Mo	0.143 ± 0.184	0.139 ± 0.176	0.084 ± 0.022
Ni	0.029 ± 0.018	0.029 ± 0.018	0.017 ± 0.015
Pb	0.015 ± 0.013	0.015 ± 0.014	0.015 ± 0.015
Sb	0.010 ± 0.001	0.010 ± 0.000	0.010 ± 0.000
Se	0.099 ± 0.067	0.098 ± 0.065	0.084 ± 0.053
Sn	0.010 ± 0.000	0.010 ± 0.000	0.010 ± 0.000
Tl	0.005 ± 0.000	0.005 ± 0.000	0.005 ± 0.000
V	0.005 ± 0.002	0.005 ± 0.002	0.005 ± 0.000
Zn	1.783 ± 0.499	1.760 ± 0.492	1.850 ± 0.635

<sup>a</sup> Values are expressed in milligrams per kilogram ± standard deviations.

## RESULTS AND DISCUSSION

The results of the elemental analysis of the 51 samples of potatoes are shown in Table 1. All the analyzed potato samples were found to contain values under the limit of quantification for Be, Cd, Sb, Sn, Tl, and V. Amounts greater than or close to the limit of quantification were obtained for As, Co, Cr, Mo, Ni, and Se. Higher amounts were found for Fe (10.84 mg/kg), followed by Cu (3.36 mg/kg), Zn (3.02 mg/kg), and Mn (7.92 mg/kg). The higher concentrations of the nutrients Fe and Zn in the samples from all areas could be attributed to their availability in the soil of the farmland.

The levels of Cu and Mg in the potatoes are higher in the Marigliano and Acerra areas than in the area between Benevento and Avellino, probably because elements such as N, P, K, S, Cu, and Mg are more abundant in the soil and are highly soluble and able to move into the plant tissue (3). Furthermore, farmers usually use manure and organic

residues as fertilizer to enhance production, and an adequate supply of Cu for growing plants should be ensured through artificial or organic fertilizers (11). Cu concentrations significantly differed among the potato cultivars: Marigliano and Acerra areas had the highest Cu levels (1.90 and 1.87 mg/kg, respectively), followed by samples from the Benevento-Avellino area (1.31 mg/kg).

In plants as well as in humans, manganese can cause both toxicity and deficiency symptoms. The maximum Mn concentrations (7.92 mg/kg) were found in northwestern Acerra. Concentrations of elements found in potato (peeled and unpeeled) samples obtained in other regions of the world are shown in Table 2.

Cu concentrations in our samples were lower than those reported for potatoes from the high Tiber Valley (Tuscany, Italy) (23) but were higher than those found in all four potato varieties from Tenerife (5). The latter were unpeeled samples, unlike the Italian ones, so this could be considered a characteristic of our local product. Also Mn, Fe, and Zn concentrations found in potato samples analyzed in this survey were lower than those reported in the literature (Table 2). Different results were obtained for Cd and Pb, which were found at higher levels than in peeled potatoes from the United Kingdom (18) but at lower, or in some cases similar, levels compared with the unpeeled samples from Brazil (9). Cd and Pb results are also in line with those reported by Esposito et al. (7) from the zone known as the “Land of Fires” (mean value of Pb, 0.020 mg/kg; mean value of Cd, 0.008 mg/kg). In any case, the average concentrations of Cd and Pb were below the permissible limit (0.05 and 0.1 mg/kg in peeled potato, respectively) according to European Commission, and World Health Organization and Food and Agriculture Organization guidelines for heavy metals in foodstuffs (8, 25). Our results are also lower than all selected data for Ni, Co, and Cr found in unpeeled potatoes from Brazil and Bangladesh (9, 21).

Trace element analysis in potatoes in the three areas showed higher concentrations in Acerra and Marigliano. The only exceptions were Fe and Zn, which were more abundant in the Benevento-Avellino area.

Statistical analysis among the trace elements, assessed through the determination of Pearson correlation coefficients

TABLE 2. Trace elements concentrations for potatoes obtained in different areas of the world<sup>a</sup>

	Mn	Fe	Cu	Zn	Cd	Pb	Ni	Co	Cr	Reference
Tiber Valley, Italy (P) <sup>b</sup>	3.6–5.3	7.0–11.0	4.2–8.1	10.7–25.4						Tamasi et al. 2015 (23)
United Kingdom (P)					0.0072	0.005				Norton et al. 2015 (18)
Tenerife Spain Palmera (U)	1.74	10.4	1.71	4.34						Casañas Rivero et al. 2003 (5)
Tenerife Spain Peluca (U)	1.77	9.37	1.72	4.58						
Tenerife Spain Cara (U)	1.43	7.19	0.54	2.18						
Tenerife Spain Rosada (U)	1.68	7.78	0.88	3.52						
São Paulo State, Brazil-Agata (U)					0.09	0.99	0.22	0.13	0.27	Guerra et al. 2012 (9)
São Paulo State, Brazil-Asterix (U)					0.09	1.02	0.37	0.28	0.13	
São Paulo State, Brazil-Caesar (U)					0.11	0.48	0.27	0.16		
São Paulo State, Brazil-Monalisa (U)					0.12	0.77	0.22	0.21	0.03	
Bangladesh (U)	6.928		4.3	3.019	0.013	0.007	0.643		0.528	Shaheen et al. 2016 (21)

<sup>a</sup> Concentrations are expressed in milligrams per kilogram. P, peeled; U, unpeeled.

<sup>b</sup> Mean range.

TABLE 3. Pearson's correlation matrix of selected trace elements in potatoes from the Campania region<sup>a</sup>

	Cu	Fe	Mn	Ni	Se	Zn
Cu	1					
Fe	-0.926	1				
Mn	1.000	-0.925	1			
Ni	1.000	-0.925	1.000	1		
Se	0.999	-0.907	0.999	0.999	1	
Zn	-0.955	0.996	-0.954	-0.954	-0.940	1

<sup>a</sup> Values >0.7 are significant at  $P < 0.01$ .

(Table 3), shows the correlation matrix of the selected elements (Cu, Fe, Mn, Ni, Se, and Zn). A linear relationship is shown between two sets of data. The closer the value gets to zero, the greater the variation of the data points around the line of best fit. The correlation coefficient between most elements was higher than 0.99; this indicates that there is a strong linear correlation at the 0.01 significance level and that these metals have a common origin. Among the three more abundant elements (Zn, Mn, and Cu) a positive correlation is exhibited only between Zn and Mn; these occur naturally at abundant levels, which suggests that they were not affected by human activities.

Multivariate PCA was used for selected results (Zn, Fe, Cu, Mn, Ni, and Se) to understand the complex nature of associations of these metals among the three sites. The significant principal components (PCs), linear combinations of the observed variables, with VARIMAX normalized rotation, were selected accounting to the Kaiser criterion (13). Table 4 shows the factor loadings of the trace elements from the PCA.

Two PCs explained approximately 100% of the total variance of the data set. PC1, which accounted for 56.21% of the total variance, had elevated loadings (>0.80) for Cu, Mn, Ni, and Se and had a negative loading for Fe and Zn. PC2, which accounted for 43.79% of the total variance, exhibited medium loadings for Cu, Mn, Ni, and Se and negative loading for the other two elements (10). The PCA loadings for the first two rotated components are plotted in Figure 2.

The biplot (Fig. 2) represents the observations and variables simultaneously in space and visually illustrates the associations among these elements in the three Campania region sites. Samples from the Acerra and Marigliano areas present higher concentrations of Mn, Cu, Ni, and Se (positive side of PC2, similar distance between the two sites and the elements) than those obtained from the area

TABLE 4. The component matrix of elements in potatoes from the Campania region after Varimax rotation<sup>a</sup>

	PC1	PC2
Cu	<b>0.816</b>	0.578
Fe	-0.537	-0.843
Mn	<b>0.818</b>	0.576
Ni	<b>0.818</b>	0.575
Se	<b>0.843</b>	0.538
Zn	-0.608	-0.794

<sup>a</sup> PCA factor loadings greater than 0.70 are shown in bold.

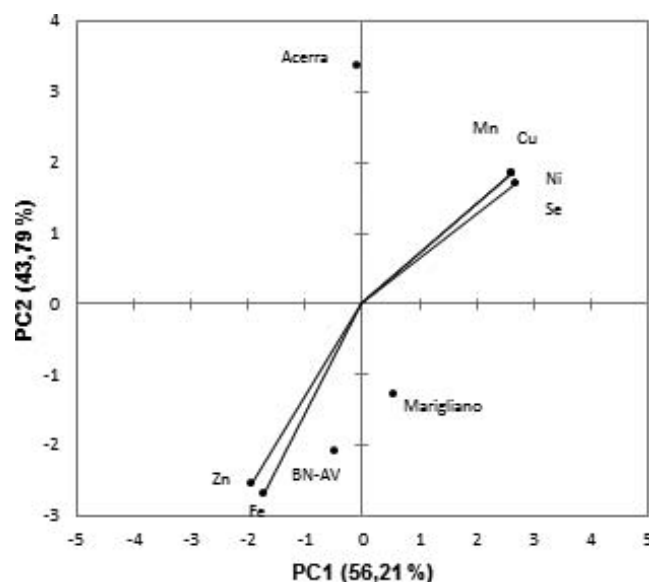


FIGURE 2. Biplot of PC1 and PC2 for trace element data after Varimax rotation.

between Benevento and Avellino (greater distance between site and elements), which are more abundant in Fe and Zn, as shown from their lesser distance in respect to the two variables. Samples grouped on the negative side of the two PCs, from Benevento and Avellino, have the lowest content of all the elements, revealing their reduced influence on the reference sample group.

This study clearly shows that trace element concentrations in potatoes from the suburban area of Naples are below the safe limits prescribed by the World Health Organization and Food and Agriculture Organization and, in most cases, are also below the concentrations that have been reported from other countries. Our results are relevant for food security, but also for commercial and economic considerations. Our results clarify that not all vegetables produced in the critical lands of the Campania region are responsible for introducing these contaminants into the food chain. Further analysis of different kinds of vegetables could be useful in understanding whether those products are, in fact, contaminated, as has been indicated by conspicuous news items about the Campania region farms.

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