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Original Research Article

Trace elements in vegetables and fruits cultivated in Southern Italy

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ABSTRACT

The levels of trace elements in a variety of fruit and vegetables have been investigated. A total of 161 samples were randomly collected on the field during the proper seasons in Campania region of Southern Italy to be included in this study. The selected agricultural producing area, within the provinces of Naples and Caserta, is well-known for the problem of toxic wastes illegally disposed and buried in its territory, that caused health and food security concerns to the consumers of food cultivated in those lands. Trace element levels were measured by using inductively coupled plasma mass spectrometry (ICP-MS). The results of this study were used to assess the contributions of fruit and vegetables to the intake of heavy metals and the potential health risk for consumers by estimating the daily intake (EDI). The concentrations of Co, Cr, Cu, Mn, Mo, Ni, Sr, Tl, U, V and Zn in selected foodstuffs were detected around the following mean values respectively: 0.010- 0.021- 2.81- 2.99- 0.185- 0.143- 2.64 -0.005- 0.003 -0.018- 4.96 mg/kg fresh weight (f.w.). Results showed that in all groups Cu, Mn, Sr, and Zn were the most abundant elements that are more likely to accumulate in nuts with mean value at 5.69 mg/kg f.w., followed by leaf vegetables with mean value at 1.05 mg/kg f.w. and finally fruit with mean value at 0.43 mg/kg f.w. Although these three groups show the highest contribution to the respective intakes, within all the food categories the EDI was below the threshold values for all the analysed elements, indicating that there is not an obvious health risk for the consumption of vegetables cultivated in the selected area.

1. Introduction

Vegetables are essential ingredients of the human diet that contain important nutrients and trace elements. Consumers are encouraged to eat more vegetables and fruit, which are a good source of vitamins, minerals, fiber and are beneficial for health. However, these foods may also contain both essential and toxic elements, such as heavy metals, in a wide range of concentrations (Bahemuka and Mubofu, 1999; Yang et al., 2017; Song et al., 2009). The addition of fertilizers and metal-based pesticides, industrial emissions, and transportation resulted in a significant increase in the heavy metal content of the agricultural soil. Therefore, plants take up both essential and toxic metals by absorbing them from contaminated soil and water as well as from deposits on parts of the plants exposed to air from polluted environments (Khairiah et al., 2004; Chojnacka et al., 2005). So, the consumption of fruit and vegetables exposed to heavy metals could cause serious health risk (Jarup, 2003).

Metals, such as lead and cadmium are cumulative poisons and environmental hazards reported to be exceptionally toxic (Maleki and Zarasvand, 2008). Notably, for the lead, developmental neurotoxicity in young children, cardiovascular effects and nephrotoxicity in adults have been demonstrated. Therefore, to reduce the dietary exposure to this element in food, maximum levels for lead in essential commodities have been set (Commission Regulation, 2006). Also for cadmium maximum limits were set in various food for human consumption, like vegetables as leafy brassica, and fruit (Commission Regulation, 2006, 2011), due to its potential to induce risk to human health, as adverse effects on kidney function and bones (Godt et al., 2006).

As regards toxic elements, many studies reported the dietary intake of Pb, Cd and As through vegetable consumption (Maleki and Zarasvand, 2008; Szczygłowska et al., 2014; Cherfi et al., 2014; Luo et al., 2016) but very few papers reported studies on other elements (Shaheen et al., 2016; Singha et al., 2016; Roba et al., 2016; Rodriguez et al., 2015; Parveen et al., 2003), especially in vegetables grown in Italy (Agrelli et al., 2017; Ferri et al., 2015; Beccaloni et al., 2013; Salvo et al., 2018). Some metals may be defined essential (cobalt, manganese, zinc, copper), while other elements may be considered as indicators of pollution of various origins (uranium, thallium, strontium, tin,

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chromium, antimony and vanadium). In general, for all trace elements, excessive intake with food may cause toxic effects. Chromium (Cr) is a common metal contaminant in soil and water, and it is of great importance in biological metabolic processes of sugars and lipids into the human body (Duran et al., 2011). However, chronic exposure to chromium can cause damage to liver, kidney, and stomach as well as could cause cancer (Liao et al., 2011). As regarding the estimation of the risk to human health from the presence of chromium in food, particularly in vegetables, the EFSA Panel on Contaminants in the Food Chain (CONTAM Panel) derived a Tolerable Daily Intake (TDI) of 0.3 mg/kg body weight (b.w.) per day for Cr (III) from the lowest NOAEL identified in the National Toxicology Program (NTP) chronic oral toxicity study in rats (EFSA, 2014). Concerning the assessment of human health risks from the presence of nickel (Ni) in food, the CONTAM Panel decided a tolerable daily intake of 2.8 μg Ni/kg b.w. per day (EFSA, 2015). Also, zinc (Zn) was considered an essential element; nevertheless high levels may cause interference with physiological processes (Fosmire, 1990). Only a few information are available regarding the toxicity and levels of the other trace elements in foods. Recent data have been reported by Esposito et al. (2018) on the levels of some trace elements in the two general classes of fruit and vegetables.

In this paper, we determined human exposure through consumption of fruit and vegetables cultivated in an area of Campania region mainly involved in the illegal phenomena of waste's dumping and uncontrolled burning along the roads bordering cultivated fields (Triassi et al., 2015; De Roma et al., 2017). Fruit and vegetables collected in this same area have already been analysed in a previous study in order to evaluate only the presence of lead and cadmium (Esposito et al., 2015) and levels of these metals resulted much lower than the maximum limits. Therefore, the aim of this study was to analyze different potentially toxic trace elements on these matrices and to quantify the exposure through the diet. The main objective was to detail the trace element's concentration and the relative intake for the different plant species, in order to identify those with the potentially greatest risk of contamination. Moreover, comparing our data with those from other countries, this study may be considered useful support to the consumer's requests to be informed about the composition and the analysis of food, mainly for products from this high impact sampling area.

2. Material and methods

2.1. Selection of vegetables and sampling area

Based on the typical plantation of the Campania region lands, 161 samples of most common fruit and vegetables were collected between 2014 and 2016 in the proper seasonal period and analyzed for the presence of eleven trace elements by using inductively coupled plasma mass spectrometry (ICP-MS). Among below-ground growing vegetables, 14 tubers were sampled. The fruiting vegetable group contains peppers, tomatoes, aubergines (47 samples), while the salad plant group consist of leafy vegetables at ground level (lettuce, chicory, endive), and legume vegetables include peas, cabbage was considered among the Brassica vegetables.

As regards the fruit, they were gathered in a single group "Stone fruit" that includes various drupaceous (47 samples including apricot, peach, plum, olive, and grape). Walnut and hazelnut were reported in the nuts group (21 samples).

All vegetable samples were collected in their specific growing period from orchards or vegetable plantations located in different lands of Campania Region (Latitudine, 40° 54' 38 N; Longitudine, 14° 55' 13 E), mainly in the so-called "Land of fires" area, where some potential sources of contamination have been identified, such as an incinerator or waste burning. In particular, this area is located between the Domizio-Phlegrean coast, the Agro Aversano-Atellano lands, the districts of Acerra and Nola, the lands around the volcano Vesuvius and the city of Naples, including a total of 95 municipalities (Fig. 1). Fruit and vegetables from these lands have already been involved in previous work to verify the presence of dioxins and polychlorobiphenyl (Esposito et al., 2017).

To make the sampling entirely representative, approximately 2 kg of each vegetable or fruit were collected from cultivated lands by technicians wearing vinyl gloves and immediately sent to the laboratory. Before analysis, adherent matter such as soil, foul parts, non-edible leaves or stems were removed manually. For each type of fruit or vegetable, individual samples were combined to make a pooled sample. The remaining of the individual samples were stored at −20 °C and available for further investigations.

2.2. Materials

Standard solution of cobalt (Co), chromium (Cr), copper (Cu), manganese (Mn), molybdenum (Mo), nickel (Ni), strontium (Sr), thallium (Tl), uranium (U), vanadium (V) and zinc (Zn) at 1000 mg/L were obtained from CPA Ltd (Stara-Zagora, Bulgaria).

Super pure grade nitric acid 68% (v/v), hydrogen peroxide 30% (v/v) and ultrapure water (R > 18.0 MΩ) were obtained from Romil Ltd (Cambridge, UK). Argon gas (99.9999%) was supplied from SAPIO S.r.l. (Monza, Italy) and anhydrous ammonia from AIR Liquide S.p.a. (Milano, Italy). All glassware was soaked in a solution of nitric acid (10% w/v), then rinsed with high-purity water and dried before use.

2.3. Sample analysis

For trace element analysis, 2.0 g of each sample were weighed in Teflon vessels and 6.0 mL of nitric acid 68% (v/v), and 2.0 mL of hydrogen peroxide 30% (v/v) were added. After tight closure, the vessels were placed into a microwave Milestone Ethos-One apparatus (FKV S.r.l., Italy). After acid digestion, the vessels were cooled at room temperature, and the samples were quantitatively recovered by filtration in 50.0 mL class A volumetric flasks, then brought to 50.0 mL with Milli-Q water.

2.4. Instrumental analysis and quality assurance

The analysis was performed using the Elan DRC II (PerkinElmer, Waltham, USA) inductively coupled plasma mass spectrometer (ICP-MS) equipped with a concentric nebulizer (Meinhard Associates, Golden, USA), a cyclonic spray chamber (Glass Expansion, Inc., West Melbourne, Australia) and a quartz torch with a quartz injector tube (2 mm internal diameter). The instrumental conditions/parameters of ICP-MS are reported in Table S1 of supplementary material. To eliminate isobaric interferences, the Dynamic Cell Reaction (DRC) system was used with ammonia gas (100%, high purity) at 0.5 mL/min for the determination of Co, Cr, V, Ni, Zn, Mn, and Cu. A solution of bismuth (Bi) and rhodium (Rh) (approximately 200 ng/mL) added on-line was used as internal standard.

Quantitative determination was carried out by means of the method of standard additions in the mineralized solution through the use of calibration curves at four levels of spiking: for U and Tl at 0.001 – 0.005 – 0.020 – 0.10 ng/ml; for Co, Cr, Mo, Ni and V at 0.1 – 0.5 – 2.0 – 10 ng/mL; for Cu and Mn at 0.5 – 2.5 – 10 – 50 ng/mL, for Zn and Sr at 4 – 20 – 80 – 400 ng/mL. The correlation coefficients (R^2) of standard calibration curves for all the trace elements were always higher than 0.99, showing an excellent linear relationship throughout the selected ranges of concentrations.

The accuracy of the method was verified by using NIST 1570a Spinach leaves certified reference material. For those elements not included in the list of certified parameters, spiking tests were carried out by addition of standard mono-element solution. The recovery factors ranged from 96.0% (Mn) to 110% (V). The results were not corrected for recovery factors because they were statistically comparable to 100%. Two replicates of each sample were analysed, and the trace

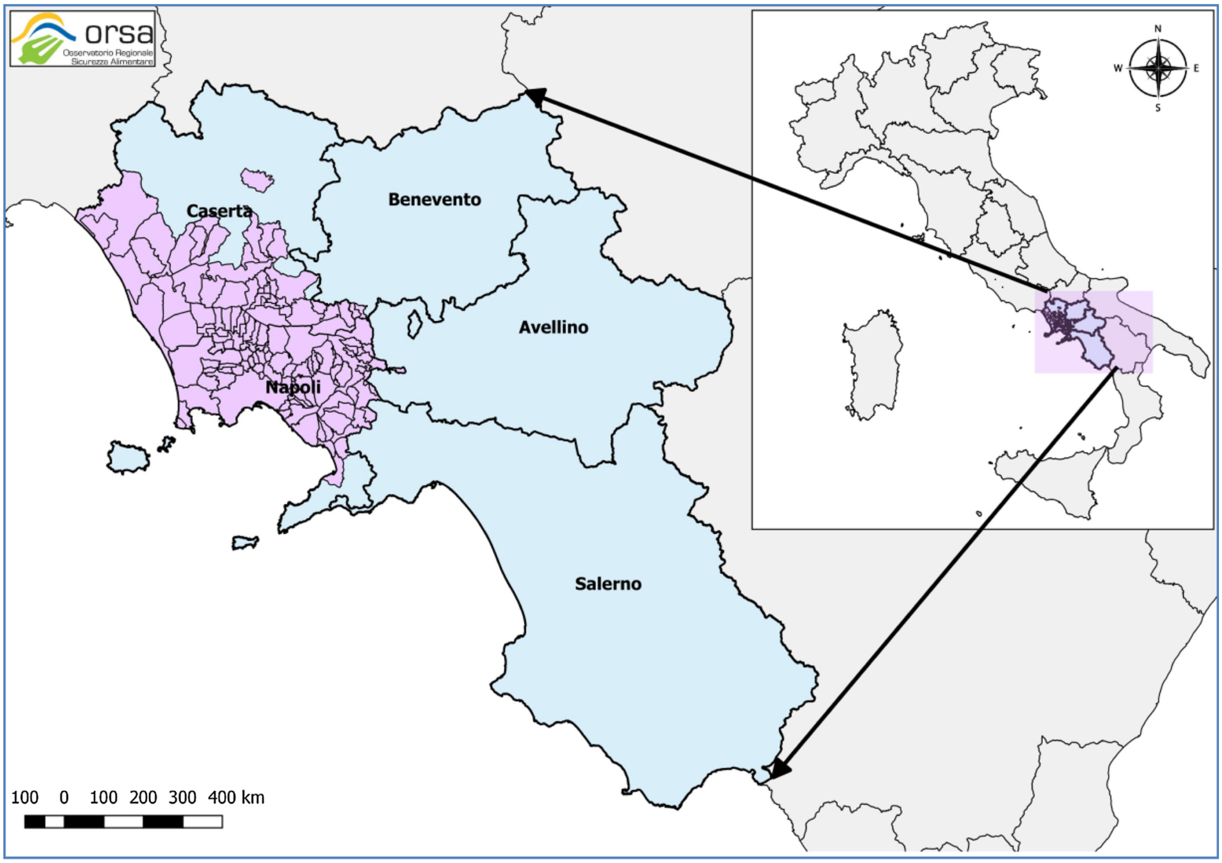

Fig. 1. Sampling sites of fruit and vegetables in the "Land of fires" (Campania, Southern Italy).

Table 1
Validation parameters and reference material analysis.

Element	*Unit of measure*	*LOQ*	*Correlation Coefficient (R^2)*	NIST SRM 1570a Spinach Leaves		*Mean Recovery (%) (n = 10)*	*RSD (%) (n = 10)*
				Certified Value ± U	Measured Value ± U		
Co	mg/kg (f.w.)	0.0011	0.9981	0.390 ± 0.050	0.383 ± 0.059	98.2	6.4
Cr		0.0024	0.9980	N. A.	1.63 ± 0.20	105.2	7.2
Cu		0.020	0.9987	12.20 ± 0.60	13.0 ± 1.6	106.6	4.1
Mn		0.083	0.9953	75.9 ± 1.9	72.9 ± 10.1	96.0	3.7
Mo		0.0031	0.9992	N. A.	0.394 ± 0.059	96.3	4.1
Ni		0.040	0.9875	2.140 ± 0.100	2.23 ± 0.31	104.2	5.9
Sr		0.018	0.9995	55.60 ± 0.80	53.8 ± 8.2	96.8	2.1
Zn		1.70	0.9986	82.0 ± 3.0	79 ± 12	96.3	2.9
Tl	µg/kg (f.w.)	0.3	0.9996	N. A.	28.0 ± 3.2	98.7	3.1
U		1.0	0.9984	155	159 ± 17	102.5	4.2
V		0.50	0.9891	570 ± 30	630 ± 90	110	7.8

element concentrations were evaluated as the mean of both measurements. A good repeatability (less than 10%) was obtained for all the determinations. A certified material (NIST 1570a Spinach leaves) was analysed at each working session for quality assurance purpose. Validation parameters which characterize the analytical procedure are reported in Table 1. The Limits of Quantifications (LOQs) of the method have been calculated as 10 fold the standard deviations of the signals of twenty blanks after mineralization (Menichini and Viviano, 2004). Results were expressed in mg/kg fresh weight (f.w.) or in µg/kg (f.w.).

2.5. Estimation of daily dietary intake

The estimation of trace element daily intakes through the consumption of vegetables cultivated in Campania Region is aimed to evaluate possible health risks to consumers. The estimated daily intakes (EDI) (as ng/kg b.w. day) of trace elements were calculated using their respective average contents in vegetable (f.w.) samples and the amount of food consumed by the following equation,

$$EDI = (C \times DI) / b.w.,$$

where C is the mean metal concentrations in analyzed samples expressed as ng/kg, DI is the human daily intake calculated using the INRAN data (INRAN, 2012) expressed as g/day and b.w. is the average body weight in kg (70 kg for adults).

2.6. Statistical analysis

All results were statistically analysed through determination of

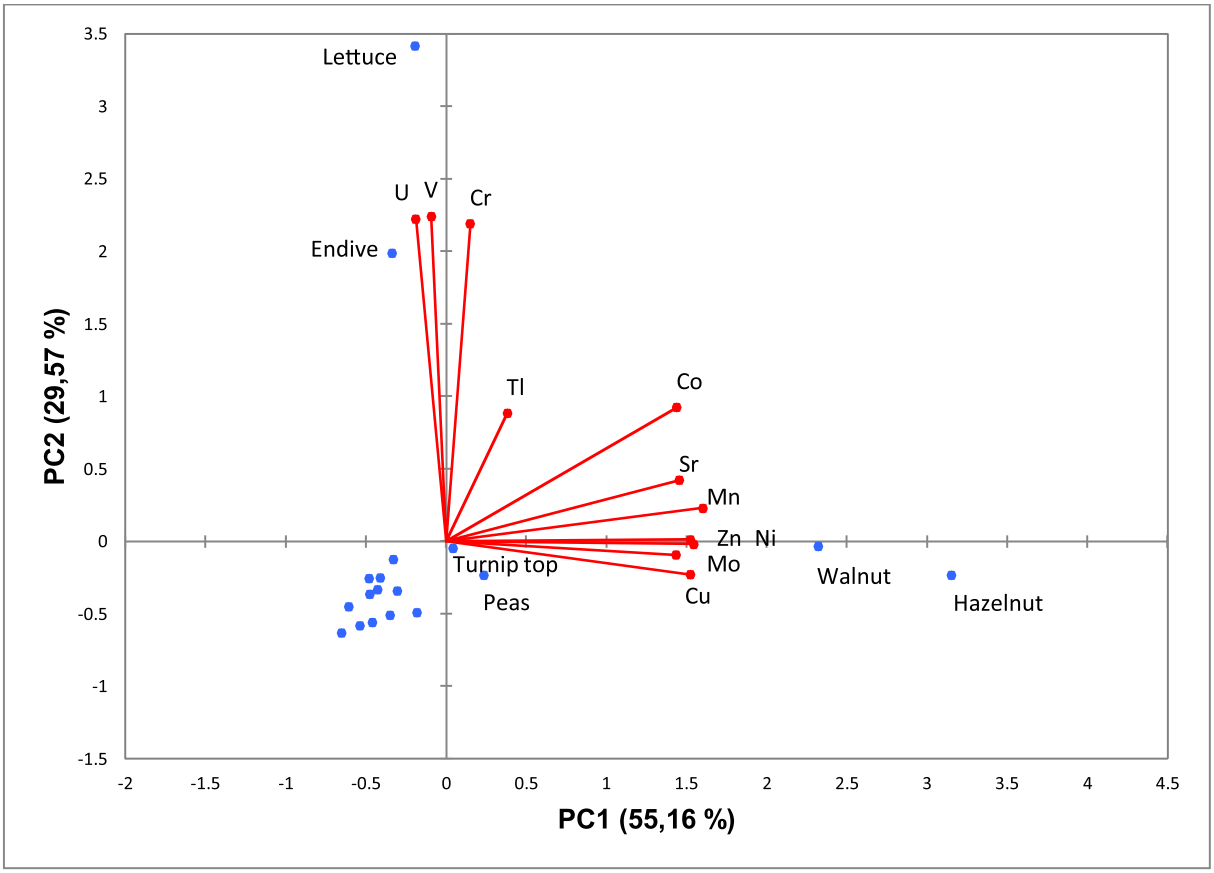

Fig. 2. Biplot after Varimax rotation of the first two components PC1 and PC2.

Pearson correlation coefficients and the Principal Component Analysis (PCA) using the XL-STAT 2016 software (Microsoft Corporation, Redmond, CA) (Fig. 2).

The assumptions of normality and homogeneity of the residuals were checked. Multivariate principal component analysis (PCA) was employed for all the elements in order to understand the complex nature of associations of these metals within the selected matrices. The significant principal components (PCs), linear combinations of the observed variables, with VARIMAX normalized rotation, were selected accounting to the Kaiser criterion (Kaiser, 1960).

3. Results

The trace element mean concentrations found out in fruit and vegetables are summarized in Table 2.

Within all the analysed elements Cu, Mn, Sr, and Zn are most abundant in all groups of vegetables. The results show the highest levels of Co, Mn, Sr, Zn in nuts but also in leafy vegetables such as lettuce, endive turnip top, and cabbage.

Copper is an oligo-element widely present in all vegetables analyzed; the highest concentrations were measured in grapes (mean value 5.50 mg/kg f.w.). This result could be influenced by the use of copper sulfate in viticulture. The average content of Mn in the fruit samples ranged between 0.621 and 13.8 mg/kg; the lowest value was determined in apricot and the highest in hazelnut. In vegetables, the concentration range was between 0.998–3.92 mg/kg, in pepper and turnip top, respectively. Manganese content also prevails in peas (3.06 mg/kg f.w.). These legumes, grapes, and zucchini also show a high value of strontium (2.06 mg/kg, 2.56 mg/kg and 2.08 mg/kg respectively).

Zinc levels found out in this study varied from 1.60 mg/kg (tomatoes) to 7.60 mg/kg (peas) in vegetables,and ranged between 0.590 mg/kg (prune) and 27.4 mg/kg (walnut) in fruit.

Thallium was present especially in peas (13.4 μg/kg), nuts (12.9 μg/kg) and leafy vegetables as lettuce (10.6 μg/kg) but in amounts lower than those already reported for the same matrices in other countries, such as South China (Liu et al., 2017). In the vegetable samples, the maximum concentration of cobalt was found out in lettuce (0.032 mg/kg), whereas the minimum level in fennel (0.003 mg/kg); in fruit, Co content was shallow except for nuts (0.056 mg/kg in hazelnut).

Nuts showed the highest levels of all elements except for the uranium and vanadium. The content of nickel in vegetables is very interesting in order to monitor consumer's intake as required by the Recommendation EU/1111/2016 of the European Commission (Commission Recommendation, 2016). In our study, nickel concentrations are in the range from 0.018 mg/kg (tomatoes) up to 0.058 mg/kg in nuts.

4. Discussion

Metals released into the environment can enter the food chain, delivering their toxic effects to humans through different intake pathways (Wuana and Okieimen, 2011). Therefore it is fundamental to understand the incidence of trace elements in plants, above all those intended for eating, and to realize if there are differences in patterns of accumulation by different plant varieties in order to give useful suggestions to consumers.

The overall median levels observed are in general relatively lower than those reported in similar background contamination studies from other countries (Cherfi et al., 2016) except for zinc and copper. Zinc from products cultivated in our lands is more abundant in three vegetables: 2.0 mg/kg in aubergine compared to 1.54 mg/kg from France (Cherfi et al., 2016) and 1.70 mg/kg from China (Song et al., 2009), 4.25 mg/kg in zucchini compared to 3.55 mg/kg from France and

Table 2
Average trace metal content (fresh weight) of trace elements in fruit and vegetables.

Groups	Samples	N°	Co	Cr	Cu	Mn	Mo	Ni	Sr	Zn	Tl	U	V
			mg/kg								µg/kg		
Fruit	Apricots	7	0.003 ± 0.001	0.008 ± 0.003	1.18 ± 0.49	0.621 ± 0.147	0.022 ± 0.030	0.145 ± 0.133	1.08 ± 1.04	1.54 ± 0.27	1.10 ± 0.70	0.80 ± 0.60	3.90 ± 2.00
	Peach	14	0.001 ± 0.0008	0.016 ± 0.042	1.25 ± 0.87	0.681 ± 0.240	0.018 ± 0.013	0.036 ± 0.033	0.327 ± 0.154	1.40 ± 0.79	2.50 ± 2.10	0.30 ± 0.30	0.70 ± 1.00
	Prune	18	0.001 ± 0.0003	0.005 ± 0.003	1.02 ± 0.87	0.693 ± 0.163	0.013 ± 0.008	0.013 ± 0.007	0.483 ± 0.165	0.590 ± 0.238	2.10 ± 1.80	0.20 ± 0. 10	0.60 ± 0.40
	Olive	5	0.004 ± 0.001	0.034 ± 0.033	3.05 ± 2.30	1.55 ± 0.218	0.054 ± 0.019	0.114 ± 0.049	1.23 ± 0.37	3.29 ± 0.46	0.70 ± 0.90	1.30 ± 0. 60	8.5 ±12.9
	Grapes	4	0.001 ± 0.001	0.010 ± 0.002	5.50 ± 1.00	0.906 ± 0.400	0.031 ± 0.009	0.018 ± 0.006	2.56 ± 0.70	0.760 ± 0.400	3.10 ± 3.00	0.70 ± 0.40	3.40 ± 1.50
Fruiting vegetables	Tomatoes	29	0.003 ± 0.001	0.007 ± 0.007	1.45 ± 0.96	1.16 ± 0.43	0.086 ± 0.087	0.028 ± 0.025	0.522 ± 0.206	1.60 ± 0.45	0.30 ± 0.30	1.20 ± 1.00	2.50 ± 2.00
	Pepper	6	0.005 ± 0.002	0.015 ± 0.017	1.08 ± 0.83	0.998 ± 0.234	0.042 ± 0.029	0.052 ± 0.039	0.586 ± 0.371	1.90 ± 0.61	7.50 ± 8.00	0.90 ± 0.70	1.60 ± 1.20
	Aubergine	12	0.002 ± 0.001	0.008 ± 0.004	0.885 ± 0.287	1.36 ± 0.34	0.088 ± 0.046	0.037 ± 0.050	0.391 ± 0.157	2.00 ± 0.49	9.50 ± 5.00	0.50 ± 0.30	1.60 ± 2.00
Legume	Peas	5	0.005 ± 0.001	0.013 ± 0.012	1.50 ± 0.17	3.06 ± 0.65	0.464 ± 0.441	0.200 ± 0.186	2.06 ± 1.31	7.60 ± 1.57	13.4 ± 9.0	0.50 ± 0.20	1.50 ± 0.80
Leafy vegetables	Lettuce	4	0.032 ± 0.027	0.085 ± 0.056	0.898 ± 0.263	3.67 ± 2.51	0.056 ± 0.030	0.125 ± 0.048	3.52 ± 1.99	3.17 ± 0.85	10.6 ± 9.0	20.1 ± 29.0	149 ± 106
	Endive	3	0.015 ± 0.001	0.059 ± 0.038	0.653 ± 0.022	2.20 ± 0.57	0.131 ± 0.039	0.084 ± 0.063	3.82 ± 3.50	2.37 ± 0.31	6.40 ± 3.00	13.1 ± 10.0	102 ± 14
	Turnip top	5	0.005 ± 0.001	0.022 ± 0.0053	0.488 ± 0.144	3.92 ± 1.32	0.480 ± 0.227	0.073 ± 0.039	5.34 ± 1.46	3.10 ± 0.70	0.90 ± 0.20	3.80 ± 1.00	15.3 ± 6.6
	Cabbage	4	0.003 ± 0.002	0.007 ± 0.004	0.271 ± 0.045	1.78 ± 0.001	0.076 ± 0.160	0.257 ± 0.226	3.07 ± 3.47	2.82 ± 0.70	1.40 ± 2.12	2.00 ± 1.40	1.20 ± 0.55
Stem vegetables	Fennel	3	0.003 ± 0.001	0.015 ± 0.005	0.873 ± 0.136	1.52 ± 1.13	0.038 ± 0.027	0.113 ± 0.003	1.36 ± 0.10	1.82 ± 0.74	4.10 ± 1.22	1.30 ± 1.25	2.40 ± 1.66
Tubers	Potatoes	14	0.006 ± 0.004	0.010 ± 0.015	1.10 ± 0.26	1.20 ± 0.40	0.087 ± 0.050	0.080 ± 0.052	0.583 ± 0.364	2.64 ± 0.56	6.90 ± 13.40	1.60 ± 1.50	9.30 ± 1.82
Cucurbits	Zucchini	7	0.005 ± 0.002	0.011 ± 0.005	0.980 ± 0.400	1.49 ± 0.50	0.080 ± 0.033	0.088 ± 0.064	2.08 ± 1.80	4.25 ± 1.70	5.10 ± 7.00	1.30 ± 1.46	4.30 ± 3.02
Nuts	Hazelnut	16	0.056 ± 0.015	0.021 ± 0.008	16.4 ± 3.20	13.8 ± 5.2	1.16 ± 0.56	0.539 ± 0.248	12.6 ± 8.8	21.0 ± 3.4	2.50 ± 1.00	0.50 ± 0.20	10.1 ± 6.3
	Walnut	5	0.036 ± 0.024	0.026 ± 0.030	12.0 ± 2.80	13.2 ± 3.8	0.414 ± 0.251	0.584 ± 0.178	5.91 ± 3.60	27.4 ± 3.7	12.9 ± 4.0	0.20 ± 0.08	2.30 ± 0.95

Table 3
Estimated daily intake (EDI) (ng/kg b.w. day) of trace elements evaluated in the analysed samples.

Fruits	DI*	Co	Cr	Cu	Mn	Mo	Ni	Sr	Tl	U	V	Zn
Apricot (7)	4.3	0.21	0.53	82.5	43.5	1.5	10.1	75.5	0.07	0.055	0.27	108
Peach (14)	18.3	0.36	5.09	388	211	5.6	11.3	101	0.79	0.079	0.22	435
Prune (18)	4.3	0.05	0.33	71.7	48.5	0.9	0.9	33.8	0.14	0.017	0.04	41.4
Olive (5)	1.1	0.09	0.68	61.0	31.1	1.1	2.3	24.7	0.01	0.026	0.17	65.8
Grape (4)	4.5	0.10	0.68	385	63.4	2.1	1.3	179	0.22	0.050	0.24	53.5
Hazelnut (16)	0.3	0.56	0.21	164	138	11.6	5.4	126	0.03	0.005	0.10	210
Walnut (5)	0.4	0.36	0.26	120	132	4.1	5.8	59.1	0.13	0.002	0.02	274

*Tabulated INRAN values.

1.33 mg/kg from Algeria (Cherfi et al., 2014), 2.93 mg/kg in leafy vegetables against 1.56 mg/kg from France, 1.75 mg/kg from Algeria and 1.60 from USA (Pennington and Young, 1990).

Mean value found out for copper is higher in potatoes (1.10 mg/kg) if compared to the data reported by Cherfi et al. (2016) for Algeria (0.8 mg/kg), USA (0.51 mg/kg), Sweden (0.77 mg/kg), Pakistan (0.1 mg/kg), India (0.17 mg/kg) and China (1.03 mg/kg). These two oligo-elements (Zn and Cu) play key role in many enzyme processes of plants, animals, and humans; therefore their amounts are not alarming due to their essential absorption. Uranium and vanadium are more abundant in lettuce, endive and turnip top. The higher levels of these trace elements found out in leafy vegetables could be closely related to the presence of these pollutants in irrigation water, farm soil, but also to the pollution from traffic on the highways.

The average intakes of the trace elements studied were also estimated taking into consideration the mean consumption of the various vegetables per capita (grams of vegetables on average consumed by adults per day) and the trace element concentrations found out in these vegetables.

The resulting EDI of eleven trace elements analyzed, expressed as ng/kg b.w./day are shown in Tables 3 and 4.

It appears that tomatoes and potatoes account for the highest total intake of Cu, Mn, Mo, and Zn. Zinc intake ranges from 0.14 (from cabbage) to 1090 ng/kg b.w./day (from tomato). Lettuce seems to be the main source of Mn, V and Strontium. This element also has the highest EDI for zucchini, potatoes, and tomatoes. Within fruit, all the trace elements, except for Co and Mo, showed the highest levels in peach. On the other hand, Co and Mo are more abundant in nuts, Sr in grapes and V in apricots. The total mean dietary intake of Cu and Zn (229.0 and .441.0 ng/kg b.w./day, respectively) are mainly below the Provisional Tolerable Daily Intake values (PTDI) set by FAO/WHO (500–1000 μg/kg b.w./day for Cu and Zn, respectively). It can also be concluded that the higher contribution to the total intake of the trace element we studied was due by the consumption of vegetables such as potatoes, tomatoes and lettuce and fruit such as peaches, and hazelnut.

The consumption of products cultivated in areas with high environmental pollution is one of the most important exposure route to toxic elements, particularly arsenic (Salvo et al., 2018). Anyway, our results support the general consideration from other authors (Esposito et al., 2018), that environmental pollution of the selected area, caused by the illegal disposal of urban and industrial wastes, should not affect food safety of fruit and vegetable production.

The determination of Pearson matrix (Table 5) shows the correlation coefficients between the analysed elements: the closer the value gets to zero, the higher the variation the data points are around the line of best fit. The correlation coefficient was higher than 0.99 only between two elements (U and V), indicating a strong linear association at the 0.01 significance level and a common origin of these metals,

Table 4
Estimated daily intake (EDI) (ng/kg b.w. day) of trace elements evaluated in the analysed samples.

Vegetables	DI	Co	Cr	Cu	Mn	Mo	Ni	Sr	Tl	U	V	Zn
Tomato (29)	41.9	2.17	4.47	985	788	58.5	18.8	355	0.23	0.82	1.73	1090
Aubergine (12)	9.30	0.32	1.16	133	204	13.2	5.58	58.6	1.42	0.071	0.24	301
Pepper (6)	4.30	0.38	1.06	75.6	69.9	2.97	3.64	41.0	0.53	0.066	0.11	133
Potato (14)	49.3	4.93	8.63	915	0.54	72.7	66.2	484	5.72	1.32	7.68	2187
Zucchini (7)	14.3	1.20	2.50	225	344	8.51	20.2	478	1.18	0.29	0.98	978
Pea (5)	5.2	0.45	1.16	135	276	41.8	18.0	186	1.21	0.049	0.13	684
Fennels (3)	0.10	0.26	1.53	87.3	152	3.81	11.3	136	0.41	0.13	0.24	182
Cabbage (4)	0.04	0.14	0.28	10.8	71.2	3.03	10.3	123	0.06	0.081	0.05	0.14
Lettuce (4)	17.5	8.56	22.9	243	990	15.1	33.8	949	2.86	5.44	40.15	856
Turnip top (5)	3.80	0.00031	1.33	29.3	235	28.8	4.36	320	0.05	0.23	0.92	186
Endive (3)	1.1	0.00029	1.17	13.1	44.1	2.61	1.68	76.3	0.13	0.26	2.03	47.3

*Tabulated INRAN values.

Table 5
Pearson's correlation matrix of the selected trace elements in vegetables and fruit from Campania Region.

Variables	Co	Cr	Cu	Mn	Mo	Ni	Sr	Tl	U	V	Zn
Co	**1**	0.470	0.821	**0.905**	0.753	0.812	0.870	0.294	0.303	0.366	0.812
Cr		**1**	0.013	0.195	0.025	0.094	0.259	0.325	**0.926**	**0.942**	0.089
Cu			**1**	**0.904**	0.774	0.835	0.812	0.107	−0.217	−0.141	0.878
Mn				**1**	0.834	**0.929**	0.875	0.293	−0.017	0.036	**0.963**
Mo					**1**	0.731	**0.900**	0.103	−0.119	−0.074	0.737
Ni						**1**	0.779	0.287	−0.106	−0.062	**0.947**
Sr							**1**	0.028	0.126	0.166	0.742
Tl								**1**	0.262	0.291	0.391
U									**1**	**0.992**	−0.145
V										**1**	−0.089
Zn											**1**

Bold values show the significant values.

probably occurring through sources like crustal contamination. Within the three more abundant elements (Zn, Mn, and Cu), positive correlation at the 0.05 significance level is exhibited only between Zn-Mn, and Zn-Ni, explaining that they naturally occur at sufficient levels, suggesting that they were not affected by human activities. Correlation coefficients between 0.95 and 0.90 were for V and Cr, U-Cr, Mn-Ni, Mn-Co, Mn-Cu, and Sr-Mo. Similar results were obtained for the correlation analysis reported by Basha et al. (2014) for these trace metals in vegetables and fruit cultivated in Andhra Pradesh, India.

Multivariate principal component analysis (PCA) explained, through the two PCs (PC1 And PC2), about 85% of the total variance of the dataset. PC 1, which accounted for 55.16% of the total variance, had high loadings (> 0.80) for Co, Cu, Mn, Mo, Ni, Zn and Sr, and a negative loading for the others (Table S2 of supplementary material). PC 2, which accounted for 29.57% of the total variance, exhibited high loadings only for Cr, U and V and negative loading for the other elements. The Biplot represents the observations and variables simultaneously and visually illustrates the associations among these elements in the analysed matrices. In this plot, only turnip top, peas, hazelnut and walnut samples were mainly located in the positive direction of the first principal component (PC1), whereas the majority of the other samples were restricted in the axis centre, in the negative direction of the two PCs, revealing their reduced influence on the reference sample group (De Roma et al., 2017). Thus, results of the PCA indicated that the metal profile of hazelnut and walnut were richer in Mn, Cu, Zn and than the other samples. Samples of leafy vegetable (lettuce and endive) show the highest concentrations of U and V (positive side of PC2, a similar distance between the two matrices and the elements) if compared with those obtained for all the other matrices (greater distance between matrices and elements). Samples grouped in the negative side of the two PCs have the lowest content of all the elements, revealing their reduced influence on the reference sample groups.

5. Conclusions

In the present study, different vegetables from cultivated areas in Campania region (Southern Italy) were analysed to monitor the levels of eleven trace elements. The study generated additional useful data about metal contents in fruit and vegetables and the possible health risks to consumers, based on the estimated daily intakes (EDIs).

The concentrations of some oligo-elements were found out to be in the ranges between 0.001 mg/kg (Co in peaches) and 16.4 mg/kg (Cu in hazelnuts). The levels of the analysed trace elements in vegetables are lower than those already described and this suggests there is no concern about their consumption. As a matter of fact, the daily intakes of trace elements through fruit and vegetables from farmlands located in Campania are below the recommended DI of these metals. A control about the trace element concentrations in the soil has not been performed as was not considered necessary by the Regional Health Authority. Our aim as a public official control Organization for assessing food safety was to focus the analyses on the food reaching the consumers; this is compliant with the concept of controls "from farm to fork" that are the basis of the precaution principle and the food safety politics of the European Union.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jfca.2019.103302.

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