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Toxic Elements from Critical Raw Materials Group in Ripe and Unripe Tomatoes in A Contaminated Area: Accumulation and Potential Health Risk Assessment

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Abstract

Accumulation and health risk assessment of cobalt (Co), antimony (Sb), vanadium (V), and lanthanum (La) in tomatoes growing in an area contaminated with municipal wastewater were investigated. For this aim, tomatoe samples were taken and sepertaed into root, stem and leaf parts. Co, Sb, V and La concentrations were detected in plant organs. The arrangement of the elements in the root, stem, and leaf of ripe and unripe tomatoes was V>Co>La>Sb. According to total element values in the ripe and unripe tomatoes; the highest values were 23±1.1 mg/kg and 35±1.7 mg/kg for V, respectively. Co, Sb, V, and La values accumulated by ripe and unripe tomatoes were determined as 24.65 and 25.6 times for Co, 1.8 and 2.7 times for Sb, 46 and 70 times for V and 4.4 and 6.15 times for La, respectively when compared with control. Total Co, Sb, V, and La were male<female<child in ripe and unripe tomatoes. Hazard index (HI) values in ripe and unripe tomatoes were male<female<child. The maximum non-carcinogenic (HQ) values in tomatoes were greater in child. Total hazard indexes (THIs) in ripe and unripe tomatoes were 74.23 and 110.66, respectively. HIs and THIs were greater than 1. As a result, tomatoes were found to accumulate Co, Sb, V, and La well, and hence a non-carcinogenic health risk to tomatoes growing in an area contaminated with municipal wastewater.

Keywords: Accumulation, health risk, non-carcinogenic, tomatoes, wastewater

Kirlenmiş Bir Alanda Olgun ve Olgunlaşmamış Domateslerdeki Kritik Hammadde Grubundan Toksik Elementler: Birikim ve Potansiyel Sağlık Riski Değerlendirmesi

Öz

Kentsel atıksularıyla kirlenmiş bir alanda yetişen domateslerde kobalt (Co), antimon (Sb), vanadyum (V) ve lantan (La) birikimi ve sağlık riski değerlendirmesi araştırıldı. Bu amaçla, domates numuneleri alındı ve kök, gövde ve yaprak kısımlarına ayırt edildi. Bitki organlarında Co, Sb, V ve La konsantrasyonları tespit edildi. Olgun ve olgunlaşmamış domateslerin kök, gövde ve yaprağındaki elementlerin dizilişi V>Co>La>Sb şeklindeydi. Olgun ve olgunlaşmamış domateslerde toplam element değerlerine göre; en yüksek değerler V için sırasıyla 23±1,1 mg/kg ve 35±1,7 mg/kg idi. Olgun ve olgunlaşmamış domateslerin biriktirdiği Co, Sb, V ve La değerleri kontrolle mukayese edildiğinde sırasıyla Co için 24,65 ve 25,6, Sb için 1,8 ve 2,7, V için 46 ve 70 ve La için 4,4 ve 6,15 kat olarak belirlendi. Olgun ve olgunlaşmamış domateslerde toplam Co, Sb, V ve La erkek<kadın<çocuk olmuştur. Olgun ve olgunlaşmamış domateslerde HI değerleri erkek<kadın<çocuk idi. Domateslerde maksimum kanserojen olmayan (HQ) değerler çocuklarda daha fazlaydı. Olgun ve olgunlaşmamış domateslerde toplam tehlike indeksleri (THI'ler) sırasıyla 74,23 ve 110.66 idi. HI'ler ve THI'ler 1'den büyüktü. Sonuç olarak, domateslerin Co, Sb, V ve La' yı iyi şekilde biriktirdiği ve dolayısıyla kentsel atıksu ile kirlenmiş bir alanda büyüyen domatesler için kanserojen olmayan bir sağlık riski oluşturduğu bulundu.

Anahtar Kelimeler: Birikim, sağlık riski, kanserojen olmayan, domates, atıksu

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INTRODUCTION

Raw materials are essential for the development of economies and quality of life (Martins and Castro, 2019). Criticality of many raw materials increases with increasing demand because of growing market of consumer goods (Auerbach et al., 2019). Within EU, raw materials initiative ensures that Europe secures and sustains an affordable supply of critical raw materials (CRMs) which are identified as being of high economic importance and having a risk to their supply (Cusack et al., 2019). European Commission has given the list of CRMs for the EU (Topal et al., 2020). EU published last list on CRMs in 2020. Some of these CRMs have toxic characteristics. Depending on the development of technology, as a result of the widespread use of critical raw materials in many areas recently, their concentrations in the environment have gradually increased. Therefore, they are likely to begin to pose as many or even more threats to human health as many other pollutants. In order to detect potential threats to human health, it is important to investigate the health risk of vegetables grown in areas exposed to wastewater. Wastewater may contain various pollutants such as toxic pollutants that are nonbiodegradable in the ecosystem and can accumulate in the food chain (Ahmad et al., 2015; Topal and Arslan Topal, 2017; Arslan Topal and Elitok, 2018). In the present study, antimony (Sb), cobalt (Co), lanthanum (La), and vanadium (V) that are given in the list of CRMs are investigated because of their toxicity.

Sb occurs in the environment as a result of natural processes and human activity (mining, smelting, and use as a fire retardant) (Guo et al., 2009; Pierart et al., 2015). It is similar to as in toxicity. It is a pollutant of priority interest to the EU and the USEPA. Furthermore, it is a toxic environmental pollutant and has implications for cancer development (Guo et al., 2009). Cobalt, which is considered a CRM, is used in many various industries (Cobalt Institute, 2019; van den Brinck et al., 2020). Global demand for Co is expected to quadruple over the next two decades, particularly because of the demand for lithium-ion batteries and electric vehicles (van den Brinck et al., 2020). Co is toxic in large doses, and Co ions and Co metal are cytotoxic. Furthermore, cobalt metals and salts are genotoxic. Co is accumulated in kidney, heart, pancreas, and liver (Simonsen et al., 2012). La, a member of the element group called rare earth elements or lanthanides, is relatively common in the earth's crust (D'Haese et al., 2019). La is used in industrial applications (agricultural, iron, ceramics, catalysts, etc.) (Hong et al., 2014; Chevinli et al., 2019; D'Haese et al., 2019). Presence of lanthanum in water brings danger to humans and other species due to the toxicity of it (Chevinli et al., 2019). Vanadium is used in many industries (paint, photographic, glass, electrochemical, chemical, and refining industries) (Ścibiora et al., 2020). It is toxic in excess amounts. Its excessive concentrations may lead to a range of pathologies and cause irreversible damage to different organs and tissues (Ścibior et al., 2020).

Global production of tomatoes exceeds 100 million tons/year. In terms of health of humans, tomatoes are source of nutrients and secondary metabolites, minerals, etc. (Dyshlyuk et al., 2020). Consumption of vegetables and fruits, especially tomatoes, reduces risk of cardiovascular diseases and cancer and hence, has become important component in a healthy diet (Lu et al., 2020). Therefore, both ripe and unripe tomatoes are widely preferred and used by humans as food. Unripe tomatoes are mainly consumed as pickles while pipe ones consumed in dishes as tomato paste, sauce as well as consumed as raw vegetable.

There is no study dealing with accumulations and health risk assessment of cobalt, antimony, vanadium, and lanthanum in the tomatoes growing in an area contaminated with municipal wastewater. The main purpose of this study is; (i) accumulation and health risk assessment of cobalt, antimony, vanadium and lanthanum in the tomatoes growing in an area contaminated with municipal wastewater were investigated. Because tomatoes are consumed by humans and it is not known whether they pose a health risk (ii) The concentrations of cobalt, antimony, vanadium, and lanthanum in municipal wastewater determined (iii) It was determined whether or not these elements accumulate in the tomatoes (root, stem, leaf). Therefore, our study contains fairly new information that will contribute to the literature.

MATERIAL AND METHODS

Study Area and Analysis

Discharge area of a treatment plant collecting and treating the domestic and industrial wastewater of Elazig province (Turkey) was selected as the study

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area. This area was chosen because tomatoes are exposed to municipal wastewater. The tomatoes samples (TSs) growing in an area contaminated with municipal wastewater (MW) and MWs were taken from 4 points (n=12). Tomatoes were cleaned with pure water in the laboratory. Then, the organs (root, leaf, and stem) of tomatoes were dried and powdered. The samples are cold-leached with HNO_3 before digested in a hot water bath. Aqua Regia solution of equal parts concentrated HCl (hydrochloric acid), HNO_3,(nitric acid) and DI H_2O (deionized water) are added. Sample is made up to volume with dilute HCl before filtration. Samples were analyzed by ICP/MS (ICP/MS-Perkin-Elmer ELAN 9000) in a laboratory with ISO 9001:2008 accreditation. pH value was measured by pH Orion SA 720 while EC value was measured by EC Delta OHM. Tomatoes are consumed as food by humans and non-carcinogenic (HQ) effects should be determined since contaminants in tomato pose a risk to human health. Therefore, HQ risks were evaluated by determination of Co, Sb, V, and La in tomatoes. Non-carcinogenic risk (HQ) values were determined as given (Lian et al., 2019):

$$HQ = \frac{CDI}{RFD} \tag{1}$$

$$HQ = \sum_{k=1}^{n} \frac{CDIk}{RFDk} \tag{2}$$

RFD = reference dose (mg/kg.day). Daily exposure dose (CDI) can be determined as given (USEPA, 2001, 2011).

$$CDI_{dietary} = C_{ripe} x \frac{I_{intake} xEFxED}{BWxAT}\ x\ 10^{-3} \tag{3}$$

$$CDI_{dietary} = C_{unripe} x \frac{I_{intake} xEFxED}{BWxAT}\ x\ 10^{-3} \tag{4}$$

where $CDI_{dietary}$: expression for dietary. C_{ripe}: value in ripe tomatoes (mg/kg), C_{unripe}: value in unripe tomatoes (mg/kg), EF: exposure frequency (day/year), I_{intake}: intake of tomato (g/day), ED: exposure duration (year), AT: averaged time (day), BW: body weight (kg)

Hazard index (HI) and total hazard index (THI) is calculated as given in equation 5 and 6, respectively (USEPA, 1989):

$$HI = \sum HQ \tag{5}$$

$$THI = \sum HI \tag{6}$$

BCF is ratio of value in tomato and Co, Sb, V, and La values in municipal wastewater. The BCF was follow as:

$$BCF = \frac{C_T}{C_{MW}} \tag{7}$$

where C_T is Co, Sb, V, and La value in tomatoes and C_{MW} is Co, Sb, V, and La value in municipal wastewater. BCFs were follow as (Arnot and Gobas, 2006; Pinto et al., 2019):

$$\text{BCF1} = C_{Troot}/C_{soil} \tag{8}$$

$$\text{BCF2} = C_{Tstem}/C_{soil} \tag{9}$$

$$\text{BCF3} = C_{Tstem}/C_{MW} \tag{10}$$

$$\text{BCF4} = C_{Troot}/C_{MW} \tag{11}$$

$$\text{BCF5} = C_{Tfruit}/C_{soil} \tag{12}$$

where C_{Troot}, C_{soil}, C_{Tstem}, C_{Tfruit}, C_{MW} are Co, Sb, V, and La values in root, soil, stem, fruit, and municipal wastewater, respectively.

TF (translocation factor): It is the ratio between Co, Sb, V, and La detected in organs (Bonanno et al., 2018).

$$\text{TF1} = C_{Tleaf}/C_{Troot} \tag{13}$$

$$\text{TF2} = C_{Tstem}/C_{Troot} \tag{14}$$

$$\text{TF3} = C_{Tleaf}/C_{Tstem} \tag{15}$$

where C_{Tstem}, C_{Tleaf}, C_{Troot} and are Co, Sb, V, and La value in tomato stems, leaves, and roots, respectively.

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RESULTS AND DISCUSSION

Determination of Co, Sb, V, and La in wastewaters

In this study, pH, electrical conductivity (EC), Co, Sb, V, and La values were determined in municipal wastewaters. pH was 7.1-8.2, EC was 1.13-1.19 mS/cm. Co, Sb, La, and V concentrations in municipal wastewater were 0.26±0.02, 0.38±0.02, 0.02±0.01, and 7.2±0.4 µg/L, respectively. The pharmacologic amounts of V are 10 to 100 times greater than normal intake in human beings (Ścibior et al., 2020). V in urine is estimated to be around 12 % of intake (Sitprija and Eiam-Ong, 1998; Ścibior et al., 2020).

Assessment of ripe tomatoes

Co, Sb, V, and La values determined in ripe tomatoes growing in an area contaminated with municipal wastewater are shown in Figure 1.

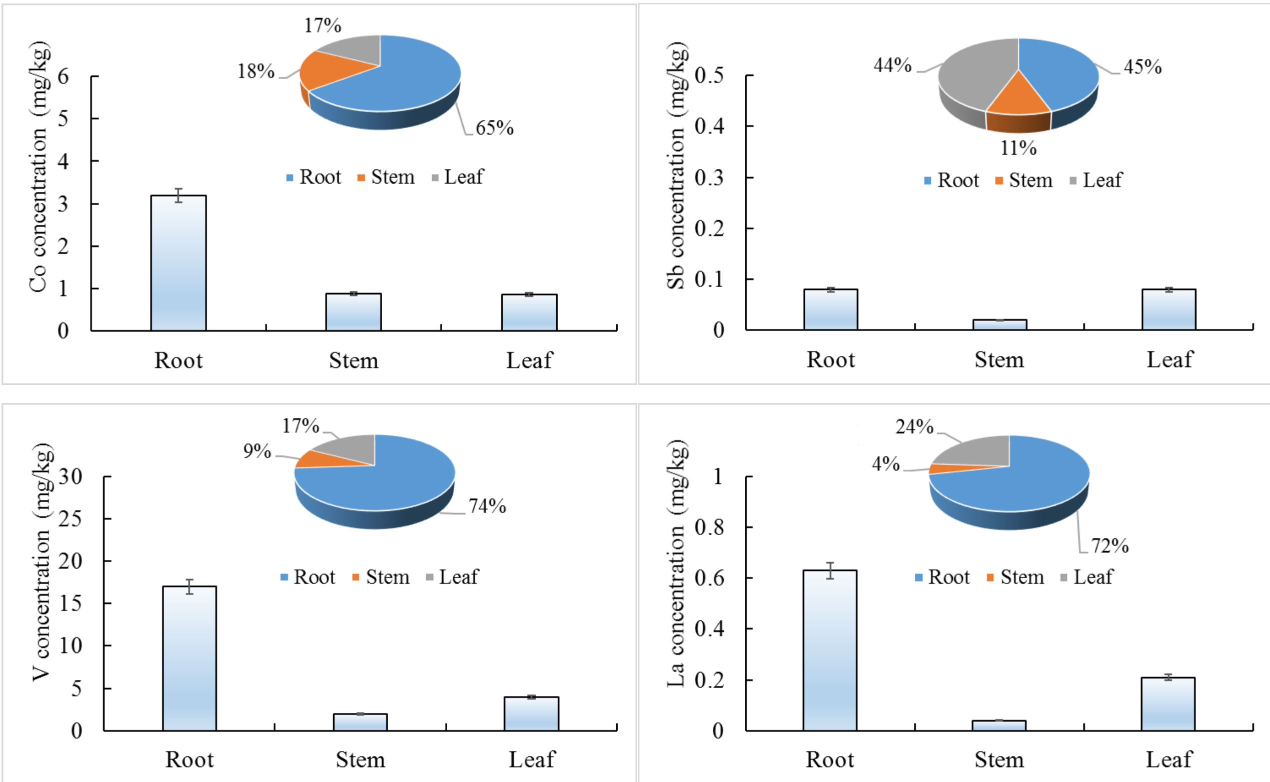

Figure 1. Co, Sb, V, and La values in ripe tomatoes

When Co values were examined, highest Co value was 3.19±0.16 mg/kg in root and minimum Co value was 0.86±0.04 mg/kg in leaf. Co value in stem was 0.88±0.04 mg/kg. Co values for ripe tomatoes were leaf<stem<root. Co ratios for root, stem, and leaf in ripe tomatoes were 65%, 18%, and 17%, respectively. The highest Sb was 0.08±0.004 mg/kg in leaf and root, lowest Sb was 0.02±0.001 mg/kg in stem. Sb values for ripe tomatoes were stem<root=leaf. Sb ratios for root, stem, and leaf in ripe tomatoes were 45%, 10%, and 45%, respectively. The highest V value was 17±0.8 mg/kg in root, lowest V value was 2.0±0.1 mg/kg in stem. V value in leaf was 4.0±0.2 mg/kg. V values for ripe tomatoes were stem<leaf<root. V ratios for root, stem, and leaf in ripe tomatoes were 74%, 17%, and 9%, respectively. The highest La was 0.63±0.03 mg/kg in root, lowest La value was 0.04±0.002 mg/kg in stem. La value in leaf was 0.21±0.001 mg/kg. La values for ripe tomatoes were stem<leaf<root. Similarly, Topal et al.

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(2022) reported that values for La were stem<leaf<root in grapevines contaminated with mining effluents. La ratios for root, stem, and leaf in ripe tomatoes were 72%, 4%, and 24%, respectively. The arrangement of the elements in the root, stem, and leaf of ripe tomatoes was V>Co>La>Sb. Different arrangement of the elements was reported by Topal et al. (2022) for grapevines. CRMs values in grapevine roots were Co > V > La > Sb while V > Co > Sb > La in grapevine stems and leaves. According to total element values in the ripe tomatoes; the highest value was 23±1.1 mg/kg for V, the lowest was 0.18±0.01 mg/kg for Sb. Co, Sb, V, and La in ripe tomatoes were compared with reference values (cobalt:0.2, antimony:0.1, vanadium:0.5 and lanthanum:0.2 mg/kg) given by Markert (1992). Co, Sb, V, and La value accumulated by ripe tomatoes was determined as 24.65 times for Co, 1.8 times for antimony, 46 times for vanadium and 4.4 times for La, respectively. BCF and TF values of Co, Sb, V, and La for ripe tomatoes are given in Table 1.

Table 1. *BCF and TF values of in ripe tomatoes*

	BCF1 (root/soil)	BCF2 (stem/soil)	BCF3 (stem/water)	BCF4 (root/water)	BCF5 (fruit/soil)	TF1 (leaf/root)	TF2 (stem/root)	TF3 (leaf/stem)
Co	0.20	0.06	3.38	12.27	0.02	0.27	0.28	0.98
Sb	0.32	0.08	0.05	0.21	0.08	1.00	0.25	4.00
V	0.14	0.02	0.28	2.36	0.02	0.24	0.12	2.00
La	0.14	0.01	2.00	31.50	0.00	0.33	0.06	5.25

BCFs and TFs are used for determination of hyperaccumulator property of tomato for Co, Sb, V, and La. BCF>1: accumulator and BCF=1: translocation effective (Ma et al., 2001; Gonzaga et al., 2006; Hegazy et al., 2011). BCF1, BCF2, and BCF5 of ripe tomatoes were < 1. This indicates that Co, Sb, V, and La do not accumulate well from the soil to the roots, stems and fruits. BCF3 was >1 for Co and La. This indicates that Co and La accumulate well from wastewater to the stems. BCF4 was >1 for Co, V, and La. This indicates that Co, V, and La accumulate well from wastewater to the roots. The highest TF value was 5.25 for La, while lowest TF value was 0.06 for La. TF1 values were between 0.24 and 0.21. TF2s were between 0.06 and 0.28. TF3s were between 0.98 and 5.25. Co, V, and La values were <1 for TF1 and Co, Sb, V, and La values were <1 for TF2. Co value was<1 for TF3. Sb, V, and La values were>1 for TF3. TF values greater than 1 indicate a good translocation of Sb, V, and La in ripe tomato organs (stem, leaf, and root). Estimated daily exposure doses (ED) of Co, Sb, V, and La in ripe tomatoes are shown in Table 2.

Table 2. *Estimated daily exposure doses in ripe tomatoes (mg/kg.day)*

	Ripe tomatoes			
	Co	Sb	V	La
Male	2.88E-03	4.80E-04	3.60E-02	2.40E-04
Female	3.26E-03	5.44E-04	4.08E-02	2.72E-04
Children	7.27E-03	1.21E-03	9.09E-02	6.06E-04
Total	1.34E-02	2.23E-03	1.68E-01	1.12E-03

The max. total ED (TED) for humans in ripe tomatoes were calculated as 1.68E-01 mg/kg.day for V, minimum TED were 1.12E-03 mg/kg.day for La. TED values for humans in ripe tomatoes were

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La<Sb<Co<V, respectively. Max. ED for male (M), female (F) and child (C) in ripe tomatoes were 3.60E-02, 4.08E-02 and 9.09E-02 mg/kg.day for V, minimum EDs were 2.40E-04, 2.72E-04 and 6.06E-04 mg/kg.day for La, respectively. Total Co, Sb, V, and La values for M, F, and C were as calculated as 3.96E-02, 4.49E-02 and 1.00E-01 mg/kg.day, respectively. Total Co, Sb, V, and La in ripe tomatoes were M<F<C. Non-carcinogenic (HQ) risks for ripe tomatoes are shown in Figure 2.

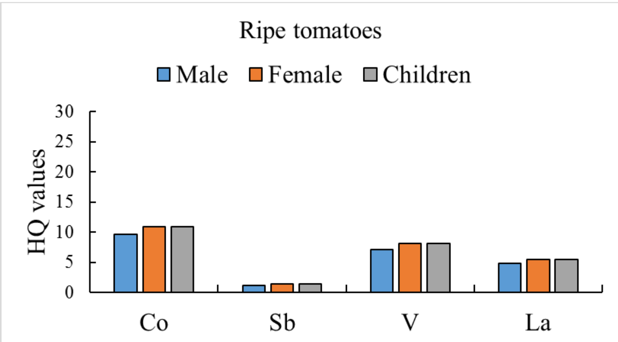
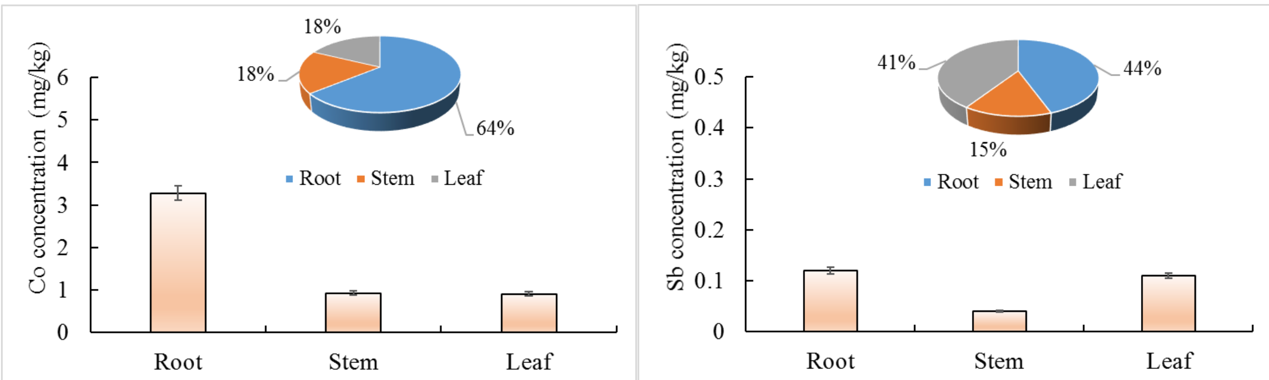


Figure 2. HQ values in ripe tomatoes

The maximum HQ_{die} for male in ripe tomatoes was observed as 9.59 for Co, while minimum HQ_{die} was 1.20 for Sb. When the HQ_{die} for female in ripe tomatoes were examined, maximum HQ_{die} was 10.87 for Co, while minimum HQ_{die} was 1.36 for Sb. When the HQ_{die} for children in ripe tomatoes were examined, maximum HQ_{die} was 10.88 for Co and minimum HQ_{die} was 1.37 for Sb. HQ_{die} values for C, F, and M for ripe tomatoes were Sb<La<V<Co. HQ_{die} values for M, F, and C in ripe tomatoes were>10.0 for Co, V and La showing chronic toxic effect by dietary (Wei and Cen, 2020). HQ_{die} values of Co, Sb, V, and La were > 1 for M, F, and C (except M and F for Sb). Non-carcinogenic value greater than 1 is demonstration of potential negative impacts (Lian et al., 2019; Wei and Cen, 2020). The maximum HQ_{die} values in ripe tomatoes were greater in children. HQ_{die} risks of Co, Sb, V, and La in ripe tomatoes were M<F<C. The maximum HI risk value in terms of ripe tomatoes was 31.33 for Co while minimum HI risk value was 3.92 for Sb. HI values in ripe tomatoes were Sb<V<La<Co. HI values in ripe tomatoes were M<F<C. Maximum HI risk value in terms of unripe tomatoes was 52.16 for Co while minimum HI risk value was 2.79 for Sb. THI for ripe tomatoes was 74.23.

Assessment of unripe tomatoes

Co, Sb, V, and La values determined in unripe tomatoes growing in an area contaminated with municipal wastewater are shown in Figure 3.



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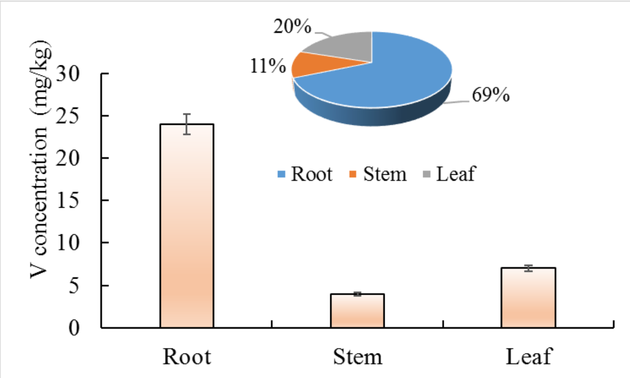

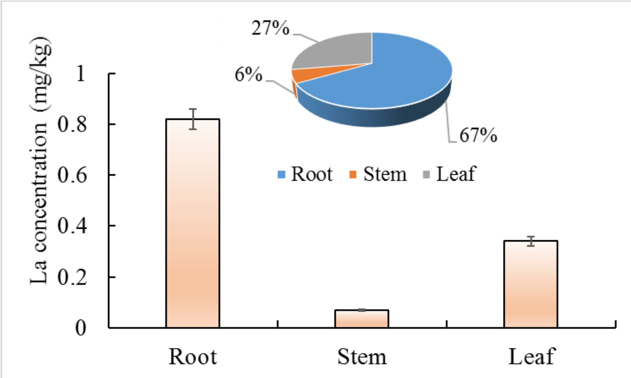

Figure 3. Co, Sb, V, and La values in unripe tomatoes

When Co values were examined, highest Co value was 3.28±0.16 mg/kg in root, minimum Co value was 0.91±0.04 mg/kg in leaf. Co value in stem was 0.93±0.04 mg/kg. Co values for unripe tomatoes were leaf<stem<root. Similarly, Topal et al. (2022) reported that values for Co were leaf< stem< root in grapevines. Co ratios for root, stem, and leaf in unripe tomatoes were 64%, 19%, and 17%, respectively. The highest Sb was 0.12±0.006 mg/kg in root, lowest Sb value was 0.04±0.002 mg/kg in stem. Sb value in leaf was 0.11±0.005 mg/kg. Sb values for unripe tomatoes were stem<leaf<root. Different arrangement was reported by Topal et al. (2022) for grapevines. The values for Sb were stem<root<leaf in grapevines. Sb ratios for root, stem, and leaf in unripe tomatoes were 44%, 15%, and 41%, respectively. The highest V value was 24±1.2 mg/kg in root, lowest V value was 4.0±0.2 mg/kg in stem. V value in leaf was 7.0±0.3 mg/kg. V values for unripe tomatoes were stem<leaf<root. Different arrangement was reported by Topal et al. (2022) for grapevines. The values for V were leaf< stem< root in grapevines. V ratios for root, stem, and leaf in ripe tomatoes were 69%, 11%, and 20%, respectively. The highest La was 0.82±0.04 mg/kg in root, lowest La value was 0.07±0.003 mg/kg in stem. La value in leaf was 0.34±0.002 mg/kg. La values for unripe tomatoes were stem<leaf<root. Similarly, Topal et al. (2022) reported that values for La were stem<leaf<root in grapevines. La ratios for root, stem, and leaf in ripe tomatoes were 67%, 6%, and 27%, respectively. The arrangement of the elements in the root, stem, and leaf of unripe tomatoes was V>Co>La>Sb. According to total element values in the unripe tomatoes; the highest value was 35±1.7 mg/kg for V, the lowest was 0.27±0.01 mg/kg for Sb. Co, Sb, V, and La in unripe tomatoes were compared with references (cobalt:0.2, antimony:0.1, vanadium:0.5 and lanthanum:0.2 mg/kg) given by Markert (1992). Co, Sb, V, and La value accumulated by ripe tomatoes was determined as 25.6 times for Co, 2.7 times for antimony, 70 times for V and 6.15 times for La, respectively. BCF and TF values of Co, Sb, V, and La for ripe tomatoes are given in Table 3.

Table 3. *BCF and TF values of in unripe tomatoes*

	BCF1 (root/soil)	BCF2 (stem/soil)	BCF3 (stem/water)	BCF4 (root/water)	BCF5 (fruit/soil)	TF1 (leaf/root)	TF2 (stem/root)	TF3 (leaf/stem)
Co	0.21	0.06	3.58	12.62	0.02	0.28	0.28	0.98
Sb	0.48	0.16	0.11	0.32	0.16	0.92	0.33	2.75
V	0.20	0.03	0.56	3.33	0.03	0.29	0.17	1.75
La	0.18	0.02	3.50	41.00	0.01	0.41	0.09	4.86

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BCF1, BCF2, and BCF5 in ripe tomatoes were < 1. This indicates that Co, Sb, V, and La do not accumulate well from the soil to the roots, stems and fruits. BCF3 was >1 for Co and La. This indicates that Co and La accumulate well from wastewater to the stems. BCF4 was >1 for Co, V, and La. This indicates that Co, V, and La accumulate well from wastewater to the roots. The highest TF value was 4.86 for La, minimum TF was 0.09 for lanthanum. TF1s were between 0.28 and 0.92. TF2s were between 0.09 and 0.33. TF3s were between 0.98 and 4.86. Co, Sb, V, and La values were <1 for TF1 and TF2. Co value was<1 for TF3. Sb, V, and La values were>1 for TF3. TF values greater than 1 indicate a good translocation of Sb, V, and La in unripe tomato organs (stem, leaf, and root). EDs of Co, Sb, V, and La in unripe tomatoes are shown in Table 4.

Table 4. *Estimated daily exposure doses in unripe tomatoes (mg/kg.day)*

	Unripe tomatoes			
	Co	Sb	V	La
Male	3.36E-03	2.40E-04	2.40E-02	3.60E-04
Female	3.80E-03	2.72E-04	2.72E-02	4.08E-04
Children	8.48E-03	6.06E-04	6.06E-02	9.09E-04
Total	1.56E-02	1.12E-03	1.12E-01	1.68E-03

Maximum TED for humans in unripe tomatoes were 1.12E-01 mg/kg.day for V, minimum TED were 1.12E-03 mg/kg.day for Sb. TED values for humans in unripe tomatoes were Sb<La<Co<V, respectively. Max. ED for M, F, and C in unripe tomatoes were determined as 2.40E-02, 2.72E-02 and 6.06E-02 mg/kg.day for V, minimum EDs were 2.40E-04, 2.72E-04 and 6.06E-04 mg/kg.day for Sb, respectively. Total Co, Sb, V, and La values for C, M, and F, were 7.06E-02, 2.80E-02, and 3.17E-02 mg/kg.day, respectively. Total Co, Sb, V, and La in unripe tomatoes were male<female<children. The highest ED and TED values were calculated for vanadium. Vanadium causes various symptoms as reported by Ścibior et al. (2020). Important symptoms of vanadium exposure via the oral route include abdominal pain, gastrointestinal disorders, nausea, diarrhea, vomiting, loss of appetite, green-black tongue, and weight reduction (Ścibior et al., 2020). HQ risks for unripe tomatoes are shown in Fig 4.

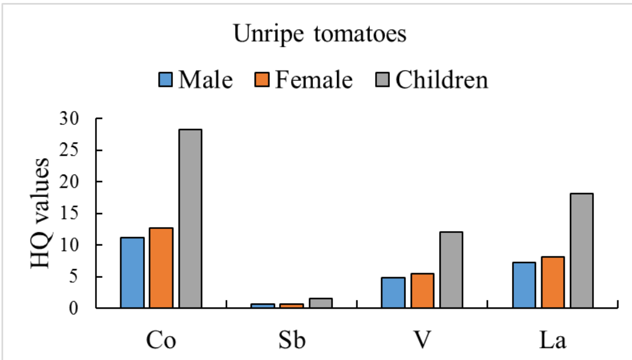

Figure 4. HQ values in unripe tomatoes

Maximum HQ_{die} for M in unripe tomatoes was observed as 11.19 for Co, while minimum HQ_{die} was 0.59 for Sb. When the HQ_{die} for F in unripe tomatoes were examined, maximum HQ_{die} was 12.68 for Co, while minimum HQ_{die} was 0.68 for Sb. When the HQ_{die} for C in unripe tomatoes were examined, maximum HQ_{die} was 28.28 for Co and minimum HQ_{die} was 1.51 for Sb. HQ_{die} values for C, M, and F for unripe tomatoes were Sb<La<V<Co. HQ_{die} values for C, M, and F in unripe tomatoes were>10.0 for Co, V and La showing chronic toxic effect via dietary (Wei and Cen, 2020). HQ_{die} values of CRMs were > 1 for M, F, and C (except male and female for Sb). Non-carcinogenic value greater than 1 is demonstration of potential negative impacts (Lian et

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al., 2019; Wei and Cen, 2020). The maximum HQ_{die} values in unripe tomatoes were greater in children. HQ_{die} risks of Co, Sb, V, and La in unripe tomatoes were M<F<C. The maximum HI risk value in terms of unripe tomatoes was 52.16 for Co while minimum HI risk value was 2.79 for Sb. HI values of Co, Sb, V, and La in unripe tomatoes were Sb<V<La<Co. Also, HI values of Co, Sb, V, and La in unripe tomatoes were M<F<C. THIs in unripe tomatoes were 110.66.

CONCLUSION

Tomatoes are among the foods consumed by people. Especially unripe tomatoes are used in pickling. Ripe tomatoes are consumed by people such as breakfast, tomato paste, and etc. Some health risks arise as a result of tomato consumption exposed to contaminants. Hence, identification of pollutants that can cause any health risks in the content of tomatoes consumed by humans is important. Accumulations and health risks were investigated due to the Co, Sb, V, and La in tomatoes growing in an area contaminated with municipal wastewater. The Co, Sb, V, and La concentrations were determined in each organ (stem, root and leaf) of ripe and unripe tomatoes. Maximum TED for humans in ripe and unripe tomatoes were determined as 1.68E-01 and 1.12E-01 mg/kg.day for V, respectively. Total Co, Sb, V, and La in ripe and unripe tomatoes were C>F>M. The maximum HQ values in ripe and unripe tomatoes were greather in C. The HQ and HI values of Co, Sb, V, and La in ripe and unripe tomatoes were M<F<C. HI values of Co and La were observed as unripe>ripe. HIs of Sb and V were observed as ripe>unripe. HQ values for F and C in ripe tomatoes were>10.0 for Co. HQ values for C, M, and F in unripe tomatoes were>10.0 for Co, V and La. This situation showed chronic toxic effect via dietary. When total hazard index (THI) values were exaimed, THI values in ripe and unripe tomatoes were 74.23 and 110.66, respectively. HIs and THIs were > 1 for cobalt, vanadium, antimony and lanthanum concentrations in tomatoes. Therefore, tomatoes were found to accumulate Co, Sb, V, and La well, and hence a non-carcinogenic health risk to tomatoes growing in an area contaminated with municipal wastewater.

CONFLICT OF INTEREST

The Authors report no conflict of interest relevant to this article.

RESEARCH AND PUBLICATION ETHICS STATEMENT

The authors declare that this study complies with research and publication ethics.

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