Araştırma Makalesi

Potential Human Health Risk from Toxic/Carcinogenic Arsenic in Ripe and Unripe Tomatoes Grown in Municipal Wastewater Treatment Plant Effluents Exposed Zone

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Abstract: The aim of the present study was to investigate the potential risk to human health from toxic/carcinogenic arsenic in ripe (RiTo) and unripe tomatoes (UnRiTo) grown in the municipal wastewater treatment plant effluents exposure zone. The arsenic concentrations were determined in each tissue of RiTo and UnRiTo tomatoes. Arsenic values in tomatoes were root>leaf>unripe tomato>ripe tomato>stem. The maximum ED (exposure dose) value in RiTos was 1.21E-02 mg.kg-1 .day-1 for child, minimum ED value was 4.80E-03 mg.kg⁻¹.day⁻¹ for male. The ED value was calculated as 5.44E-03 mg.kg⁻¹.day⁻¹ for female. The maximum ED value in UnRiTo was 2.12E-02 mg.kg⁻¹.day⁻¹ for child, min ED value was 8.39-03 mg.kg⁻¹.day⁻¹ for male. ED value was calculated as 9.51E-03 mg.kg⁻¹.day⁻¹ for female. EDs in RiTo and UnRiTo were child>female>male. When the HQs (hazard quotient) in RiTo and UnRiTo compared, HQ values in UnRiTo were higher. All of the HQ values were higher than 1. As a result, results of tomatoes analysis show that there was non-carcinogenic and carcinogenic health risks.

Keywords: Arsenic; carcinogenic; health risk; tomatoes; wastewater

Kentsel Atıksu Arıtma Tesisi Çıkış Sularına Maruz Kalan Alanda Yetişen Olgun ve Olgunlaşmamış Domateslerde Toksik/Kanserojen Arseniğin Potansiyel İnsan Sağlığı Riski

Özet: Bu çalışmanın amacı, kentsel atıksu artıma tesisi çıkış sularına maruz kalan bölgede yetiştirilen olgun (Oldo) ve olgunlaşmamış domateslerdeki (Hado) toksik/karsinojenik arseniğin insan sağlığına yönelik potansiyel riskini araştırmaktı. Arsenik konsantrasyonları Oldo ve Hado domateslerinin her dokusunda belirlendi. Domatesteki arsenik değerleri kök>yaprak>olgunlaşmamış domates>olgun domates>gövde şeklinde belirlendi. Oldos'ta maksimum ED (maruz kalma dozu) değeri çocuk için 1.21E-02 mg.kg-1 .gün-1 , minimum ED değeri ise erkek için 4.80E-03 mg.kg-1 .gün-1 idi. Kadınlarda ED değeri 5,44E-03 mg.kg-1 .gün-1 olarak hesaplandı. Hado'da maksimum ED değeri çocuk için 2,12E-02 mg.kg⁻¹.gün⁻¹, minimum ED değeri

ise erkek için 8,39-03 mg.kg⁻¹.gün⁻¹ idi. Kadınlarda ED değeri 9,51E-03 mg.kg⁻¹.gün⁻¹ olarak hesaplandı. Oldo ve Hado'daki ED'ler çocuk>kadın>erkekti. Oldo ve Hado'daki HQ'lar (tehlike bölümü) karşılaştırıldığında, Hado'daki HQ değerleri daha yüksekti. HQ değerlerinin tamamı 1'den yüksek çıkmıştır. Sonuç olarak domates analiz sonuçları kanserojen olmayan ve kanserojen sağlık risklerinin bulunduğunu göstermektedir.

Anahtar Kelimeler: Arsenic; kanserojen; sağlık riski; domates; atıksu

1. Introduction

Environmental pollution by toxic substance is a health concern [1]. The toxic elements can originate from anthropogenic sources such as municipal and sewage discharges [2]. Wastewater treatment plants (WWTP) are established to treat contaminated water and to minimize the concentrations of pollutants it contains and to protect the environment [3,4]. These plants receive used water from municipality and industries, reuse and release effluents and by-products [4-6]. The consumption of food plants contaminated with metal or metalloids is one of the toxic ways humans are exposed to these pollutants [7]. People exposed to toxic metal or metalloids in contaminated areas have increased in recent years, causing serious health problems. Examples of these health effects are disruption of enzyme, nucleic acid, and protein structures [7-9].

Arsenic (As) is an environmental toxicant with human health effects and ranked first on 2017 Priority List of Hazardous Substances [10]. Arsenic enters environmental media either for natural reasons or because of human induced activities [11]. Inorganic arsenic compounds do not contain carbon compared to organic arsenic compounds and are generally composed of simple molecules such as arsenic trioxide. Therefore, inorganic arsenic is highly toxic. Exposure to inorganic arsenic, occurs through arsenic contaminated waters and grains, foods, fruits, and vegetables [12]. Food consumption has been considered as one of the major routes for human exposure to Arsenic, compared with inhalation and dermal contact [13]. Arsenic poses potential human health risk through consumption of crop exposed to water that is arsenic-rich [11]. Exposure of humans to inorganic arsenic can affect multiple organ functions, resulting in different arsenic related diseases including cancer such as bladder, skin, and lung cancer as well as non-cancer diseases, including cardiovascular and dermal lesions disease [7,10,14,15].

Tomatoes are among foods consumed widely in Türkiye. According to Turkish Statistical Institute (TUIK) data, tomato production in 2023 is estimated to be 13.5 million/ton [16]. According to 2018 data, the per capita consumption of tomatoes is 116.9 kg [17]. Tomatoes have a wide variety of uses, especially in the form of frozen foods, canned foods, tomato paste, ketchup, and pickles. However, there is potential human health risk with consumption of the tomatoes contaminated by various pollutants. Tomatoes exposed to the effluents of biological WWTP can pose risk when consumed by human. Therefore, the importance and purpose of the study was to assess the potential health risk of arsenic in tomatoes exposed to effluents from biological WWTP.

2. Material and Method

2.1. Study Area

A study area that takes effluents of WWTP (Elazığ, Türkiye) was selected. Wastewater exposed zone is shown in Figure 1. Schematic flow diagram of WWTP is shown in Figure 2.

Figure 2. Schematic flow diagram of WWTP

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Wastewater from 383.975 people is treated at the plant. WWTP project flow is 1671 L/s for 2020. The WWTP consists of screening, gritting, primary settling, aeration tanks and secondary settling. The WWTP was under revision in 2007 and was in operation in 2008 [18-21]. To determine the coordinate values (X:4271832; Y:529401) were used Magellan eXplorist 510 (Santa Clara, USA).

2.2. Sample Analysis

The tomato samples (TS) (total=1250 g) grown in the wastewater exposed zone were collected from 4 sites (n=12). Tomatoes were harvested by hand. The tomatoes were cleaned in the laboratory with pure water. Separated tissues were dried at 25°C and powdered. Extraction process was implemented as following: sample (1 g) was cold leached with nitric acid (HNO₃). After cooling a modified Aqua Regia solution of equal parts concentrated hydrochloric acid (HCl), HNO₃ and deionized water (DI H2O) were added to samples. The samples diluted with HCl, and then filtered and analyzed by inductively coupled plasma/mass spectrometry. Quality assurance/certificate of analysis (QA/AC) was given in Table 1. Besides, human health risk for arsenic detected in ripe and unripe tomatoes was calculated. The physicochemical properties of arsenic are given in Table 2 [22].

QA: quality assurance, AC: certificate of analysis, QC: quality control, STD V16 and STD TMDA-70.2: standards

2.3. Health Risk Assessment

Tomatoes are among foods commonly consumed by humans. Therefore, it is very important to determine the pollutants in the tissues of tomatoes and to evaluate the carcinogenic risk of the pollutants. In our study, human health risk was evaluated with some calculations in terms of arsenic in RiTo and UnRiTo. The non-carcinogenic risk (HQ) [23];

$$
HQ = \frac{CDI}{RFD}
$$
\n
$$
(2.1)
$$

$$
HQ = \sum_{k=1}^{n} \frac{CDlk}{RFDk}
$$
 (2.2)

where HQ is the expression for non-carcinogenic risk. RFD = reference dose (mg/kg.day) Daily exposure dose (CDI) was obtained as following [24,25]:

$$
CDI_{dietary} = C_{ripe} x \frac{I_{intake} x E F x E D}{BW x A T} \times 10^{-3}
$$
\n
$$
(2.3)
$$

$$
CDI_{dietary} = C_{unripe} x \frac{I_{intake} x E F x E D}{B W x A T} \times 10^{-3}
$$
\n
$$
(2.4)
$$

where CDI_{dietary}: dietary. C_{ripe} : arsenic ripe tomatoes (mg.kg⁻¹), C_{unripe} is arsenic value in unripe tomatoes (mg.kg⁻¹), I_{intake} : intake (g/day), EF and ED: exposure frequency and duration, AT: time (days), BW is weight (kg). Cancer risk (CR) was determined as below [26]:

$$
CR = CDIXSF \tag{2.5}
$$

SF: slope factor $(mg/kg/day)^{-1}$.

2.4. Statistical Analysis

IBM SPSS Statistics 21 was used to investigate correlation among arsenic in both ripe and unripe tomatoes (n=12). If the p-value is less than the significance level ($p = 0.05$), the relationship between arsenic values in ripe and unripe tomatoes are insignificant. The closer the r value is to 1, the greater the relationship.

3. Results and Discussions

3.1. Characteristics of Effluents

pH of the effluents was 7.0-8.3, EC was 1.11-1.22 mS/cm. The arsenic concentrations in WWTP effluents were determined as $5.1\pm0.2 \,\mu$ g/L.

3.2. Arsenic Values in Tomatoes

The arsenic values determined in tomatoes grown in wastewater exposed zone given in Fig. 3 $(n=12)$.

Figure 3. The Arsenic Values

When as was examined, max. As was 1.5 ± 0.08 mg.kg⁻¹ in root and min. As: 0.3 ± 0.01 mg.kg⁻¹ in stem. As values in leaf: 1±0.01 mg/kg. When the arsenic values in RiTo and UnRiTo were compared, the arsenic values in UnRiTo were higher. Arsenic in UnRiTo: 0.7±0.03 mg/kg. As values in tomatoes were root>leaf>unripe tomato>ripe tomato>stem. The arsenic values in RiTo and UnRiTo were compared with reference (As: 0.1 mg/kg) given by Markert [27]. The level of arsenic accumulated by RiTo was determined to be 32 times higher. The arsenic value accumulated by UnRiTo was determined as 35. As can be seen, there was difference in arsenic accumulation between RiTo and UnRiTo.

3.3. Statistics of the Arsenic Values in Tomatoes

Correlations showing the relationship between arsenic values in ripe and unripe tomatoes given in Table 2.

		Ripe	Unripe
Ripe	Pearson Correlation		
Unripe	Pearson Correlation	$,965^*$,035	

Table 2. *Relationship Between Arsenic in Ripe and Unripe Tomatoes*

*. Correlation is significant at the 0.05 level (2-tailed).

The correlations between RiTo and UnRiTo were determined as positive and significant. The correlation between ripe and unripe tomatoes was calculated as r=0.965. The correlation is significant at the 0.05 levels. As a result, a strong relationship was determined between ripe and unripe tomatoes.

3.4. Potential Health Risk in terms of Arsenic in Ripe and Unripe Tomatoes

Arsenic pollution is a serious threat to environmental quality and public health in general due to its persistence and toxicity in the environment [28,29]. ED of arsenic in RiTo and UnRiTo are given in Table 3.

	Ripe tomatoes		Unripe tomatoes
	Value (mg/kg.day)		Value (mg/kg.day)
Male	4.80E-03	Male	8.39E-03
Female	5.44E-03	Female	9.51E-03
Children	1.21E-02	Children	2.12E-02
Total	$2.24E-02$	Total	3.91E-02

Table 3. *Estimated Daily Exposure Doses (mg/kg.day)*

Max. ED value in RiTo was 1.21E-02 mg.kg⁻¹.day⁻¹ for child, minimum ED value was 4.80E-03 mg.kg-1 .day-1 for male. The ED was 5.44E-03 mg/kg.day for female. EDs for humans in RiTo child>female>male, respectively. Total ED in RiTo was calculated as 2.24E-02. The maximum ED value in UnRiTo was 2.12E-02 mg.kg⁻¹.day⁻¹ for child, minimum ED value was 8.39-03 mg.kg⁻¹.day⁻¹ for male. ED value was calculated as 9.51E-03 mg/kg.day for Female. EDs for humans in UnRiTo child>female>male, respectively. Total estimated daily exposure dose in UnRiTo was 3.91E-02. When the ED values in RiTo and UnRiTo were compared, ED values in UnRiTo were higher. Similar to ED values, total estimated daily exposure dose values were also higher in UnRiTo.

The HQs were given in Figure 3.

Figure 3. Non-Carcinogenic Risk Values in Tomatoes

Maximum HQ value in RiTo was determined as 40.4 for Child, lowest HQ was 15.99 for male. The HQ was 18.12 for Female. EDs for humans in RiTo were child > female > male, respectively (Fig 3a). Highest HQ in UnRiTo was determined as 70.7 for child, lowest HQ was 27.98 for male. The HQ was 31.71 for Female. EDs for humans in UnRiTo were observed as child>female>male, respectively (Fig 3b). When the HQ values in RiTo and UnRiTo were compared, HQ values in UnRiTo were higher. All the HQ values were higher than 1. HQ values derived from tomatoes dietary exposure reveals that humans consuming these tomatoes is characterized by non-carcinogenic risk.

There is non-carcinogenic human health risk of arsenic in RiTo and UnRiTo grown in wastewater exposure zone. Arsenic accumulated in human may induce neuro behavioral abnormalities during puberty and neuro behavioral changes as adult; other effects for child include intellectual deficiencies, immune suppression, and cognitive [12].

Carcinogenic risk was calculated as 8.46E-03. United States Environmental Protection Agency (USEPA) adopt a risk between 10^{-6} - 10^{-4} to suggest point at which risk management decisions should be taken [30]. The value determined in our study is greater than the ones given. Therefore, there is carcinogenic health risk. The potential carcinogenic risk found is not surprising because of the exposure of the tomatoes to the effluents of the wastewater treatment plant. Inorganic arsenic is considered a carcinogen by the International Agency for Research on Cancer (IARC), causing skin and lung cancers [11]. High arsenic concentrations taken into the body results in decreased arsenic methylation capacity and/or methylarsonic acid in urine. A decreased arsenic methylation capacity with greater proportions of inorganic arsenic and/ or methylarsonic acid in urine is related to increased non-cancer and cancer diseases [12,31].

4. Conclusions

Discharge of effluents from the wastewater treatment plants to the environment can result in excessive accumulation of toxic elements in edible parts of plants grown in this discharge area. Accordingly, consumption of these plants could pose potential health risk to humans consuming them. Tomato plant was chosen in our study since it is grown for agricultural purposes in the region exposed to wastewater. In present research, investigation of human health risk by studying arsenic in tomatoes provides useful information on the status of vegetables exposed to wastewater effluent discharge zone. Human health risk was investigated by assessing arsenic. Results of tomatoes analysis show that there were non-carcinogenic and carcinogenic health risks. The arsenic concentrations were determined in each tissue of RiTo and UnRiTo. Arsenic values in tomatoes were root>leaf>unripe tomato>ripe tomato>stem. The maximum ED value in RiTo was 1.21E-02 mg.kg⁻¹.day⁻¹ for child. The ED value was calculated as 5.44E-03 mg/kg.day for female. The max.ED value in UnRiTo was 2.12E-02 mg.kg⁻¹.day⁻¹ for child. ED value was calculated as 9.51E-03 mg/kg.day for female. EDs for humans in RiTo and UnRiTo were child>female>male. When the HQs in RiTo and UnRiTo were compared, HQ values in UnRiTo were higher. All of the HQ values were higher than 1. As a result, results of tomatoes analysis show that there was non-carcinogenic and carcinogenic health risks. We hope that present research contributes to the health risk assessments, which not only lights today's important problems, but will also give new motivation to attempts that aim to preserve the human and environment health. The limitation of this study is the determination of heavy metal contents and health risks in different plant species in different agricultural areas where wastewater is discharged.

Conflict of interest

The Author reports no conflict of interest relevant to this article

Research and publication ethics statement

The author declares that this study complies with research and publication ethics.

References

[1] Gunawardena, S.A., Gunawardana, J.W., Chandrajith, R., Thoradeniya, T., Jayasinghe, S. (2020). Renal bioaccumulation of trace elements in urban and rural Sri Lankan populations: A preliminary study based on post mortem tissue analysis, *Journal of Trace Elements in Medicine and Biology*, 61: Article 126565.

[2] Anandkumar, A., Li, J., Prabakaran, K., Jia, Z.X., Du, D. (2020). Accumulation of toxic elements in an invasive crayfish species (Procambarus clarkii) and its health risk assessment to humans, *Journal of Food Composition and Analysis*, 88: Article 103449.

[3] USEPA, (2004). U.S.E.P.A, Primer for Municipal Wastewater Treatment Systems, US Environmental Protection Agency Municipal Support, Division Office.

[4] Moloi, M., Ogbeide, O., Otomo, P.V. (2020). Probabilistic health risk assessment of heavy metals at wastewater discharge points within the Vaal River Basin, South Africa, *International Journal of Hygiene and Environmental Health*, 224:Article 113421.

[5] Edokpayi, J., Odiyo, J., Msagati, T., Popoola, E. (2015). Removal efficiency of faecal indicator organisms, nutrients and heavy metals from a peri-urban wastewater treatment plant in thohoyandou, Limpopo Province, South Africa, *Int. J. Environ. Res. Public Health*, 12: 7300-7320.

[6] Mosolloane, P.M., Bredenhand, E., Otomo, P.V. (2019). Laboratory assessment of the ecotoxic effects of sewage sludge from the Maluti-Drakensberg region on a terrestrial oligochaete species, *Ecotoxicology*, 28:86-91.

[7] Sun, Z., Hu, Y., Cheng, H. (2020). Public health risk of toxic metal(loid) pollution to the population living near an abandoned small-scale polymetallic mine, *Science of The Total Environment*, 718:Article 137434.

[8] Hough, R.L., Breward, N., Young, S.D., Crout, N.M.J., Tye, A.M., Moir, A.M., Thornton, I. (2004). Assessing potential risk of heavy metal exposure from consumption of home-produced vegetables by urban populations, *Environ. Health Persp*., 112: 215-221.

[9] Nachman, K.E., Punshon, T., Rardin, L., Signes-Pastor, A.J., Murray, C.J., Karagas, M.R. 2018. Opportunities and challenges for dietary arsenic intervention, *Environ. Health Persp*., 126: Article 084503.

[10] Cui, D., Zhang, P., Li, H., Zhang, Z., Yang, Z. (2020). Biotransformation of dietary inorganic arsenic in a freshwater fish Carassius auratus and the unique association between arsenic dimethylation and oxidative damage*, Journal of Hazardous Materials*, 391: Article 122153.

[11] Zhao, Y., Zhen, Z., Wang, Z., Zeng, L., Yan, C. (2020). Influence of environmental factors on arsenic accumulation and biotransformation using the aquatic plant species Hydrilla verticillata, *Journal of Environmental Sciences*, 90: 244-252.

[12] Bocca, B., Pino, A., Brumatti, L. V., Rosolen, V., Ronfani, L. (2020). Children exposure to inorganic and organic arsenic metabolites: A cohort study in Northeast Italy, *Environmental Pollution*, 265: 114826.

[13] Lyu, R., Gao, Z., Li, D., Yang, Z., Zhang, T. (2020). Bioaccessibility of arsenic from gastropod along the Xiangjiang River: Assessing human health risks using an in vitro digestion model, *Ecotoxicology and Environmental Safety*, 193: Article 110334.

[14] Manthari, R.K., Tikka, C., Ommati, M.M., Niu, R., Sun, Z., Wang, J. (2018). Arsenic-induced autophagy in the developing mouse cerebellum: involvement of the blood-brain barrier's tight-junction proteins and the PI3K-Akt-mTOR signaling pathway, *J. Agric. Food Chem*., 66: 8602-8614.

[15] Signes-Pastor, A.J., Mitra, K., Sarkhel, S., Hobbes, M., Burlo, F., de Groot,W.T. (2008). Arsenic speciation in food and estimation of the dietary intake of inorganic arsenic in a rural village of West Bengal, India, *J. Agric. Food Chem*., 56:9469-9474.

 $TMAF,$ (2023). https://arastirma.tarimorman.gov.tr/tepge/Belgeler/PDF%20Tar%C4%B1m%20%C3%9Cr%C3%BCn leri%20Piyasalar%C4%B1/2023-Temmuz%20Tar%C4%B1m%20%C3%9Cr%C3%BCnleri%20Rapo ru/DOMATES%20T%C3%9CP%20HAZ%C4%B0RAN%202023-TEPGE.pdf.

[17] TUİK, (2020). Turkish Statistical Institute, 2020. https://www.tuik.gov.tr/ Acessed: 10.11.2020.

[18] Topal, M. , Aşcı Toraman, Z. , Arslan Topal, E. I. , Sel, C. & Öbek, E. (2021). Investigation of SARS-CoV-2 and gastrointestinal pathogens in a municipal wastewater treatment plant in Turkey . *International Journal of Pure and Applied Sciences* , 7 (3) , 500-508 . DOI: 10.29132/ijpas.956919

[19] Topal, M., Arslan Topal, E.I., (2011). Evaluation of the Elazığ municipal wastewater treatment plant with some parameters in 2010-2011 Winter season, *Cumhur. Sci. J*., 32: 1-12.

[20] Topal, M., Uslu, G., Öbek, E., Arslan Topal, E.I., (2014). Evaluation of Elazığ municipal wastewater treatment plant with physicochemical parameters, Eurasia 2014 Waste Management Symposium, p.1169–1176, İstanbul, Turkey.

[21] Topal, M., Uslu, G., Öbek, E., Arslan Topal, E.I., (2016). Investigation of relationships between removals of tetracycline and degradation products and physicochemical parameters in municipal wastewater treatment plant*, Journal of Environmental Management*, 173:1-9.

[22] Lenntech, "Chemical properties of arsenic - Health effects of arsenic - Environmental effects of arsenic" [online document], (2023). Available: https://www.lenntech.com/periodic/elements/as.htm [Accessed: Sep 14, 2023].

[23] Lian, M.; Wang, J.; Sun, L.; Xu, Z.; Tang, J.; Yan, J.; Zeng, X. (2019). Profiles and potential health risks of heavy metals in soil and crops from the watershed of Xi River in Northeast China. Ecotoxicol. *Environ.Saf.,* 169, 442-448.

[24] USEPA. (2001). Supplemental Guidance for Developing Soil Screening Levels for Superfund Sites [R]. Office of Solid Waste and Emergency Response, Washington, DC [OSWER9355.4e24].

[25] USEPA. (2011). United States Environmental Protection Agency. Exposure Factors Handbook. National Center for Environmental Assessment. Washington, DC (EPA/600/R-09/ 052F), https://cfpub.epa.gov/ncea/risk/recordisplay.cfm?deid=236252.

[26] USEPA. (1989). Risk assessment guidance for Superfund Human health evaluation manual, (part A) [R], vol. 1, Office of emergency and remedial response, Washington, DC (1989) [EPA/540/1-89/002].

[27] Markert, B. (1992). Establishing of Reference Plant for Inorganic Characterization of Different Plant Species By Chemical Fingerprinting. *Water Air Soil Pollut*. 64:533-538.

[28] Bhattacharya, P., Welch, A.H., Stollenwerk, K.G., McLaughlin, M.J., Bundschuh, J., Panaullah, G. (2007). Arsenic in the environment: biology and chemistry, *Science of the Total Environment*, 379:109-120.

[29] Naveed, S., Yu, Q., Zhang, C., Ge, Y., (2020). Extracellular polymeric substances alter cell surface properties, toxicity, and accumulation of arsenic in Synechocystis PCC6803, *Environmental Pollution*, 261:Article 114233.

[30] Zuzolo, D., Cicchella, D., Demetriades, A., Birke, M. (2020). Arsenic: Geochemical distribution and age-related health risk in Italy, *Environmental Research*, 182:Article 109076.

[31] Hsueh, Y.M., Chen, W.J., Lee, C.Y., Chien, S.N., Shiue, H.S., Huang, S.R. (2016). Association of arsenic methylation capacity with developmental delays and health status in children: a prospective case–control trial, *Sci. Rep*., 6: 37287.