

Do pesticides and mycotoxins in water pose an exposure risk to humans?

¿Los pesticidas y las micotoxinas en el agua representan un riesgo de exposición para los humanos?

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ABSTRACT

This study aimed to evaluate the occurrence of pesticides and mycotoxins in water (e. g., drinking, well, tap and river water) published in the literature from 2008 to 2023 and to estimate the risks of exposure for humans to these contaminants through water consumption. An occurrence survey showed that maximum concentrations of pesticides and mycotoxins were 88,732 and 19,500 ng/L, respectively, in water. Exposure risk assessment estimated by daily intake (DI) of pesticides and mycotoxins showed that children, young people and adults, in descending order, are affected. Therefore, the younger the age group, the greater the exposure risk to contaminants when ingestion of water containing maximum concentrations was analyzed by the occurrence survey.

KEYWORDS: Children, Contaminants, Daily Intake, Water Consumption.

RESUMEN

Este estudio tuvo como objetivo evaluar la presencia de pesticidas y micotoxinas en el agua (por ejemplo, agua potable, de pozo, del grifo y de río) publicada en la literatura de 2008 a 2023 y estimar los riesgos de exposición de los humanos a estos contaminantes a través del consumo de agua. Una encuesta de ocurrencia mostró que las concentraciones máximas de pesticidas y micotoxinas fueron 88.732 y 19.500 ng/L, respectivamente, en el agua. La evaluación del riesgo de exposición estimada por la ingesta diaria (ID) de pesticidas y micotoxinas mostró que los niños, jóvenes y adultos, en orden descendente, se ven afectados. Por lo tanto, cuanto más joven es el grupo de edad, mayor es el riesgo de exposición a contaminantes cuando se analiza la ingestión de agua que contiene concentraciones máximas mediante la encuesta de ocurrencia.

PALABRAS CLAVE: Niños, Contaminantes, Ingesta Diaria, Consumo de Agua.

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Os pesticidas e micotoxinas na água representam um risco de exposição para os seres humanos?

RESUMO

Este estudo teve como objetivo avaliar a ocorrência de agrotóxicos e micotoxinas na água (e.g. potável, de poço, de torneira e de rio) publicada na literatura no período de 2008 a 2023 e estimar os riscos de exposição humana a esses contaminantes por meio do consumo de água. Um levantamento de ocorrência mostrou que as concentrações máximas de agrotóxicos e micotoxinas foram de 88732 e 19500 ng/L, respectivamente, na água. A avaliação do risco de exposição estimado pela ingestão diária (ID) de agrotóxicos e micotoxinas mostrou que crianças, jovens e adultos, em ordem decrescente, são afetados. Portanto, quanto menor a faixa etária, maior o risco de exposição a contaminantes quando a ingestão de água com concentrações máximas foi analisada pelo levantamento de ocorrência.

PALAVRAS-CHAVE: Crianças, Contaminantes, Ingestão Diária, Consumo de Água.

Les pesticides et les mycotoxines dans l'eau présentent-ils un risque d'exposition pour les humains?

RÉSUMÉ

Cette étude visait à évaluer la présence de pesticides et de mycotoxines dans l'eau (e.g. eau de boisson, de puits, du robinet et de rivière) publiée dans la littérature de 2008 à 2023 et à estimer les risques d'exposition pour l'homme à ces contaminants par la consommation d'eau. Une enquête d'occurrence a montré que les concentrations maximales de pesticides et de mycotoxines étaient respectivement

de 88732 et 19500 ng/L dans l'eau. L'évaluation du risque d'exposition estimé par la dose journalière (DI) de pesticides et de mycotoxines a montré que les enfants, les jeunes et les adultes, par ordre décroissant, sont touchés. Par conséquent, plus le groupe d'âge est jeune, plus le risque d'exposition aux contaminants est élevé lorsque l'ingestion d'eau contenant des concentrations maximales a été analysée par l'enquête sur les occurrences.

MOTS CLÉ: Enfants, Contaminants, Apport Journalier, Consommation d'Eau.

I pesticidi e le micotossine nell'acqua rappresentano un rischio di esposizione per l'uomo?

SOMMARIO

Questo studio mirava a valutare la presenza di pesticidi e micotossine nell'acqua (ad es. acqua potabile, di pozzo, di rubinetto e di fiume) pubblicata in letteratura dal 2008 al 2023 e di stimare i rischi di esposizione per l'uomo a questi contaminanti attraverso il consumo di acqua. Un'indagine sugli eventi ha mostrato che le concentrazioni massime di pesticidi e micotossine erano rispettivamente di 88732 e 19500 ng/L nell'acqua. La valutazione del rischio di esposizione stimato in base all'assunzione giornaliera (DI) di pesticidi e micotossine ha mostrato che i bambini, i giovani e gli adulti, in ordine decrescente, ne sono colpiti. Pertanto, più giovane è la fascia di età, maggiore è il rischio di esposizione ai contaminanti quando l'ingestione di acqua contenente le concentrazioni massime è stata analizzata dall'indagine sull'occorrenza.

PAROLE CHIAVE: Bambini, Contaminanti, Assunzione Giornaliera, Consumo di Acqua.

Introduction

Population growth promotes the search for efficient production in agricultural sectors¹. The use of chemicals, such as pesticides (e. g., fungicides, herbicides and insecticides), is one of the processes used for increasing agricultural production². Inevitably, pesticides have been widely applied because they mitigate damage to crops caused by fungi, insects, weeds and other pests³. Fungi, which are responsible for causing between 50 and 80 % of crop damage, affect mainly grain production. *Alternaria*, *Aspergillus*, *Fusarium* and *Penicillium* stand out among fungus genera due to their wide geographic distribution, morphological and physiological variability and pathogenicity⁴. However, pesticide application to control fungal diseases may affect and, in some cases, potentiate mycotoxin production by toxicogenic microorganisms⁵.

Another important issue is the fate of pesticides and mycotoxins when they are in the agricultural production chain. Pesticides have been widely studied due to their high toxicity, chemical stability and environmental persistence⁶. Since they are directly applied to the environment, studies have focused on environmental matrices and produced knowledge about their fate and partitioning between environmental compartments. On the other hand, mycotoxins are known for their resistance to physical and chemical treatments in food matrices and little is known about their environmental fate in environmental compartments⁶. Thus, environmental fate of these contaminants is determined by their physicochemical properties, which may allow greater solubility and mobility. As a result, they may be drained and/or leached and spread through the water environment⁷.

The World Health Organization (WHO)⁸ reports that one out of three people in the world does not have access to potable water. In rural areas, this number is even higher, i. e., 8 out of 10 people do not have potable water. They use water from wells (e. g., shallow or artesian wells) or directly from rivers, with high potential of contamination with pesticides and mycotoxins. Thus,

this study aimed at evaluating data on the occurrence of pesticides and mycotoxins in water (e. g., drinking, river, tap and well water) published in the literature and at estimating exposure risks to these contaminants through water consumption associated with described incidence.

Material and methods

Research strategy and data sources

Search for data on the occurrence of pesticides and mycotoxins in water was carried out in electronic databases, including *Embase*, *Google Scholar*, *PubMed* and *Scopus*. The following keywords were used: “occurrence” or “concentration” or “contamination” and “pesticides” or “acaricide” or “bactericide” or “defoliant” or “fungicide” or “herbicide” or “insecticide” or “molluscicides” or “rodenticides” or “crop protection” or “agrochemicals” and “mycotoxins” or “secondary metabolites” and “water” or “drinking water” or “bottled water” or “river” or “wastewater” or “surface water” or “leach” and “continent” or “Africa” or “America” or “Asia” or “Europe” or “Oceania”. In the search strategy, all keywords were associated with primary results to minimize losses of studies. In addition, to complement the automatic search, all references of selected papers and review papers were evaluated in order to find other relevant studies.

Eligibility criteria

To be included in this study of the occurrence of pesticides and mycotoxins, papers should meet the following criteria: (i) uniterms mentioned in the previous item included in the title, abstract or keywords; (ii) data on occurrence of pesticides and/or mycotoxins in water; (iii) published between 2008 and 2023; and (iv) availability of complete data. There were no restrictions regarding the language of the studies. On the other hand, short communications, letters, comments and abstracts in conference proceedings were excluded from the selection.

Exposure risk estimate

Daily intake (DI) is generally used for estimating human exposure to a given contaminant. Thus, DI of pesticides and mycotoxins were estimated by Equation 1, where DI is expressed as µg/kg per day, C is the highest level of

¹ FAO, 2022.

² Fernandes *et al.*, 2019, 1377-1387. Chen *et al.*, 2023, 160637.

³ Elfikrie *et al.*, 2020, 136540. Çelik; Belli; Koçak, 2022, 60-65.

⁴ Gurikar *et al.*, 2022, 1-18.

⁵ Pires *et al.*, 2021, 4533-4541.

⁶ Wu *et al.*, 2022, 114133.

⁷ Juraschek; Kappenberg; Amelung, 2022, 152425.

⁸ WHO, 2022.

contamination of every pesticide and mycotoxin in water in the occurrence survey ($\mu\text{g/L}$), WI is the average water intake (L/day) (for children, young people and adults, values of 1, 1.5 and 2 L, respectively, were assumed), EF is the exposure frequency (350 days/year), EL is exposure length (for children, young people and adults, values of 6, 17 and 64 years, respectively, were assumed), BW is body mass (for children, young people and adults, values of 32, 52, 72 kg, respectively, were assumed) and AT is average life expectancy (for children, young people and adults, values of 2,190, 6,205 and 23,360 days, respectively, were assumed)⁹.

$$DI = \frac{C * WI * EF * EL}{BW * AT} \quad (1)$$

DI calculations were established for drinking, tap, well and river water to demonstrate the quality of this resource in relation to the presence of pesticides and mycotoxins. DI values were compared to reference values and provisional values established by the WHO¹⁰.

Development

Occurrence of pesticides and mycotoxins in water

In the field, the synthesis of mycotoxins may be related to chemical stress that pesticides may cause to fungal species¹¹, which may positively influence concentrations of these metabolites in products from the agricultural production chain¹². Ellner¹³ found that the use of amistar and folicur, pesticides containing strobilurins, potentiated the synthesis of deoxynivalenol (DON) in wheat cultivars. The author describes that the synthesis of DON is independent of the cultivar and time of application of fungicides. In addition, he states that DON synthesis was lower when fungicide application occurred close to flowering, by comparison with the early treatment. Similar behavior was observed by Feksa *et al.*¹⁴ when they evaluated the use of azoxystrobin to control *Gibberella* in wheat grains. The authors report

that the use of azoxystrobin, a pesticide that also contains strobilurins, reduced fungal contamination with increase in DON concentration in grains.

Bellí *et al.*¹⁵ found that the use of fenhexamide and mancozeb increased production of ochratoxin A (OTA) in grapevines in 50 and 80 %, respectively. Costa, Cerqueira and Garda-Buffon¹⁶ evaluated the *in vitro* toxicogenic potential of *Aspergillus carbonarius* in the presence of famoxadone and cresoxim-methyl. The authors found that famoxadone and cresoxim-methyl reduced fungal growth in 76 and 60 %, respectively. However, OTA production doubled in the groups treated with both fungicides, by comparison with the control group.

Despite the scarce number of studies that report increase in mycotoxin synthesis with the use of pesticides, this effect may be observed in several mycotoxins and in different agricultural cultivars. It is justified because some species of toxigenic fungi are able to produce several mycotoxins when subject to stressful situations¹⁷. Even though some toxigenic species belonging to *Aspergillus* and *Penicillium* are able to synthesize OTA, they also produce aflatoxins, such as aflatoxin B₁ (AFB₁), the mycotoxin with the highest toxic potential among aflatoxins¹⁸, classified as carcinogenic for animals and humans by the International Agency for Research on Cancer¹⁹. Production of several mycotoxins by the same fungal genus is related to the fact that they have high adaptive capacity to environments and substrates that they colonize, even when they have low water activity²⁰.

The presence of these contaminants is considered a challenge for quality control and safety in food production in all agricultural production chains. It is noteworthy that around 90 % of pesticides applied to crops does not reach target organisms. Pesticides may be retained in the soil or grains, subject to degradation in different chemical forms, thus, collaborating with fungal stress and enabling greater synthesis of mycotoxins in commodities²¹. The problem related to increase in synthesis of mycotoxins by use of pesticides is not only restricted to the cultivation system. Because they have hydrophilic characteristics, some pesticides and mycotoxins may be disposed of from agricultural fields through the process of leaching and surface runoff, a fact that

⁹ El-Nahhal; El-Nahhal, 2021, 113611. Kruć-Fijałkowska *et al.*, 2022, 3317.

¹⁰ WHO, 2022.

¹¹ Ellner, 2005, 112-115.

¹² Bellí *et al.*, 2006, 1021-1029. Costa; Cerqueira; Garda-Buffon, 2019, 1860-1870.

¹³ Ellner, 2005, 112-115.

¹⁴ Feksa *et al.*, 2019, 128-134.

¹⁵ Bellí *et al.*, 2006, 1021-1029.

¹⁶ Costa; Cerqueira; Garda-Buffon, 2019, 1860-1870.

¹⁷ Richard, 2007, 3-10.

¹⁸ Schmidt-Heydt; Magan; Geisen, 2008, 142-149.

¹⁹ IARC, 2002.

²⁰ Greco *et al.*, 2015, 3512-3537.

²¹ Wang *et al.*, 2021, 2004525.

Table 1. Occurrence of pesticides in water

Matrix	Pesticide (CF in ng/L)	Country	Reference
Drinking water	ATZ (0–4)	Luxembourg	25
Drinking water	IMD (1.22-26.36), CLO (3.89-33.46) and THM (0.26-4.14)	United States	26
Drinking water	IMD (ND-4.8), THD (ND-2.7) and THM (ND-91.7)	Canada	27
Drinking water	ATZ (5-37), AZO (100-192), BEN (30-30), CAR (20-50), CMZ (40-164), CYP (10-14), DIU (40-490), EPX (70-70), IMI (12-15), IMA (12-37), IRG (4-4), PRP (10-10), QUC (124-248) and TBZ (40-460)	Brazil	28
Tap water	ATZ (0–44)	Luxembourg	29
Tap water	FIP (<0.1-5) and IMD (<0.1-0.2)	Canada	30
Tap water	ACE (<0.002-69.2), CLO (<0.005-104), DIN (<0.003-312), IMD (<0.02-68.3), THD (<0.002-74.2) and THM (<0.03-214)	China	31
River water	ATZ (100-7300)	United States	32
River water	DIU (ND-86.7), DIN (ND-1.6) and IMI (ND-35.3)	Georgia	33
River water	ACE (ND-1.4), CLO (ND-12), DIN (3.7-100), IMD (ND-25) and THM (ND-11)	Japan	34
River water	IMD (5-28000)	Netherlands	35
River water	ACE (ND-380), CLO (ND-420), IMD (ND-4560), THD (ND-400) and THM (ND-200)	Australia	36
River water	FIP (0.24–0.92), FIPD (<0.08–0.37) and FIPS (0.16–0.39)	Germany	37
River water	2,4-D (2625-88732), ATZ (80-10560), CBD (20-1396), EPX (50-261), IMD (20-1437), PRO (20-130), MEM (2-29), MTR (200-421), NIC (7-175), PRS (4-12), SIM (50-2905), TBZ (15-737), THI (36-79)	Brazil	38
River water	ACE (0.62-308.96), CLO (ND-12.78), DIN (ND-6.2), IMD (0.03-30.78), NIT (ND-5.31), THD (ND-0.93) and THM (ND-9.69)	China	39
Well water	DIC (ND-69), FEB (ND-110), FEN (2-476) and IMD (nd-153)	Vietnam	40
Well water	CHL (5-32), IMD (17-43), ISO (7-18), MZC (15-15) and NIC (12-30)	Poland	41

2,4-D = 2,4-dichlorophenoxyacetic acid, ACE = acetamiprid, ATZ = atrazine, AZO = azoxystrobin, BEN = bentazone, CAR = carbofuran, CBD = carbendazim, CF = contamination range, CHL = chlorotoluron, CLO = clothianidin, CMZ = clomazone, CYP = cyproconazole, DIC = dichlorvos, DIN = dinotefuran, DIU = diuron, EPX = epoxiconazole, FEB = fenobucarb, FEN = fenitrothion, FIP = fipronil, FIPD = fipronil-desulfinyl, FIPS = fipronil-sulfone, IMD = imidacloprid, IMA = imazethapyr, IMI = imazapic, IRG = irgarol, ISO = Isoproturon, ND = not detected, MEM = mesosulfuron-methyl, MTR = mesotrione, MZC = metazachlor, NIC = nicosulfuron, NIT = nitenpyram, PRO = propoxur, PRP = propanil, PRS = prosulfuron, QUC = quinclorac, SIM = simazine, TBZ = tebuconazole, THD = thiacloprid, THI = thifensulfuron-methyl, THM = thiamethoxam.

Source: own elaboration.

contributes to their increasingly occurrence in surface and groundwater, including drinking water intended for human consumption (Table 1 and Table 2).

The occurrence survey in Table 1 shows that IMD has higher occurrence in different matrices, followed by THM and CLO. IMD has higher occurrence than other pesticides when matrices are evaluated individually. In Table 2, ZEN has the highest occurrence in different matrices, followed by DON and AFB₁. AFB₁ has higher occurrence in drinking and tap water while ZEN occurs in river water. In well water, a single study reports the occurrence of a single mycotoxin, ZEN. Kolpin *et al.*²² were the only authors to report the co-occurrence of ATZ, DON and ZEN in river water samples. Contamination of water bodies with pesticides and mycotoxins through leaching may be considered a problem, especially in tropical and equatorial regions, where there is high rainfall²³. Considering that water is an important

route of exposure to various contaminants for humans and that conventional water treatment processes are not 100 % effective, contamination of water resources has become a worldwide concern due to the toxic effects that they may cause²⁴.

²³ Meyer-Wolfarth *et al.*, 2021, 249-263.

²⁴ IARC, 2002. Kruć-Fijałkowska *et al.*, 2022, 3317.

²⁵ Bohn *et al.*, 2011, 1041-1054.

²⁶ Klarich *et al.*, 2017, 168-173.

²⁷ Sultana *et al.*, 2018, 506-513.

²⁸ Caldas *et al.*, 2019, 71-80.

²⁹ Bohn *et al.*, 2011, 1041-1054.

³⁰ Montiel-León *et al.*, 2018, 2765-2779.

³¹ He *et al.*, 2021, 118117.

³² Kolpin *et al.*, 2010, 2089-2099.

³³ Hladik; Calhoun, 2012, 3-9.

³⁴ Yamamoto *et al.*, 2012, 2189-2194.

³⁵ Dijk; Staalduinen; Sluijs, 2013, e62374.

³⁶ Sánchez-Bayo; Hyne, 2014, 143-151.

³⁷ Michel *et al.*, 2016, 171-179.

³⁸ Lima *et al.*, 2020, 10581-10598.

³⁹ Jia *et al.*, 2023, 109836.

⁴⁰ Lamers *et al.*, 2011, 356-361.

⁴¹ Kruć-Fijałkowska *et al.*, 2022, 3317.

²² Kolpin *et al.*, 2010, 2089-2099.

Table 2. Occurrence of mycotoxins in water

Matrix	Mycotoxin (CF in ng/L)	Country	Reference
Drinking water	AFB ₁ (0.22-0.70), AFB ₂ (0.16-0.48), AFG ₁ (0.42-0.60) and OTA (0.22-0.26)	Portugal	42
Drinking water	AFB ₁ (0.052-0.075)	India	43
Drinking water	AFB ₁ (260-470) and KJA (300-4100)	Spain	44
Tap water	3-ADON (18.74-145.69), 15-ADON (15.14-71.61), AFB ₁ (3.083-3.083), AFM ₁ (0.099-0.099), AFG ₁ (0.013-0.013), AFG ₂ (3.05-3.18), DON (8.40-71.61) and STC (0.223-0.223)	South Africa	45
Tap water	AFB ₁ (200-19500) and OTA (300-14400)	Egypt	46
River water	DON (ND-22)	Switzerland	47
River water	ZEN (0.7-43.7)	Poland	48
River water	DON (11-583) and ZEN (8-47)	United States	49
River water	ZEN (2-25)	Poland	50
River water	3-ADON (ND-49.3), α -ZEL (ND-1701), β -ZEL (ND-1828), DON (5-1662), NIV (ND-43.7), VERA (ND-42.3) and ZEN (ND-96)	United States	51
River water	ZEN (17-17) and β -ZEL (168-168)	Brazil	52
Well water	ZEN (<0.3-0.5)	Poland	53

3-ADON = 3-acetyldeoxynivalenol, 15-ADON = 15-acetyldeoxynivalenol, α -ZEL = α -zearalenol, β -ZEL = β -zearalenol, AFB₁ = Aflatoxin B₁, AFB₂ = Aflatoxin B₂, AFG₁ = Aflatoxin G₁, AFM₁ = Aflatoxin M₁, BEA = beauvericin, CF = contamination range, DON = deoxynivalenol, FB₁ = fumonisin B₁, FB₂ = fumonisin B₂, FB₃ = fumonisin B₃, KJA = kojic acid, ND = not detected, NIV = nivalenol, STC = terigmatocystin, VERA = verrucarín A, ZEN = zearalenone. Source: own elaboration.

Estimate of risk to human health due to consumption of water with pesticides and mycotoxins

Humans are constantly exposed to various toxic chemicals in food and drink consumed on a daily basis. Therefore, considering that water is essential for life, estimating the risk to human health caused by contaminants is important to support actions that guarantee its safe supply to the population. In the case of pesticides and mycotoxins in water, DI estimates concentrations of these contaminants that different age groups are exposed to daily. The highest DIs of pesticides and mycotoxins were in a descending order for children, young people and adults (Table 3). Thus, young individuals are exposed to higher concentrations of pesticides and mycotoxins when they drink water at concentrations analyzed by the occurrence survey.

Regarding pesticides, the highest DIs (children/young people/adults) were observed for 2,4-D (2.6589/0.0735/0.0020 $\mu\text{g/kg}$), IMD (0.8390/0.0232/0.0006 $\mu\text{g/kg}$) and ATZ (0.3168/0.0088 /0.0002 $\mu\text{g/kg}$) in river water, followed by IUD (0.0147/0.0004/1.08E-05 $\mu\text{g/kg}$), TBZ (0.0138/0.0004/1.02E-5 $\mu\text{g/kg}$) and QUC (0.0074/0.0002/5.48 E-6 $\mu\text{g/kg}$) in drinking water, DIN (0.0093/0.0003/6.89E-6 $\mu\text{g/kg}$), THM (0.0022/6.15E-5/1.64E-6 $\mu\text{g/kg}$) and CLO (0.0031/8.62 E-5/2.30E-6 $\mu\text{g/kg}$) in tap water and FEN (0.0143/0.0004/1.05E-5 $\mu\text{g/kg}$), IMD (0.0046/0.0001/0.38E-6 $\mu\text{g/kg}$) and FEB (0.0033 /9.12E-5/2.43E-6 $\mu\text{g/kg}$) in well water. Concerning mycotoxins, the highest IDs were observed for AFB₁ (0.5843/0.0162/0.004 $\mu\text{g/kg}$), OTA (0.4315/0.0119/0.0003 $\mu\text{g/kg}$) and 3-ADON (0.0044/0.0001/3.22E-6 $\mu\text{g/kg}$) in tap water, followed by KJA (0.1229/0.0034/9.05E-5 $\mu\text{g/kg}$), AFB₁ (0.0141/0.0004/1.04E-5 $\mu\text{g/kg}$) and AFG₁ (1.80E-5/ 4.97E-7/1.32 E-8 $\mu\text{g/kg}$) in drinking water, β -ZEL (0.0548/0.0015/4.04E-5 $\mu\text{g/kg}$), α -ZEL (0.0510/0.0014/3.76E-5 $\mu\text{g/kg}$) and DON (0.0498/0.0014 /3.67E-5 $\mu\text{g/kg}$) in river water and ZEN (1.50E-5/4.14E-7/1.10E-8 $\mu\text{g/kg}$) in well water. DIs did not represent any exposure risk, according to the WHO⁵⁴. However, tolerable daily intake (TDI), i.e., concentrations that can be

⁴² Mata *et al.*, 2015, 455-464.

⁴³ Banu; Sadagopan, 2016, 207-217.

⁴⁴ Picardo *et al.*, 2020, 127888.

⁴⁵ Mhlango *et al.*, 2020, 519.

⁴⁶ Diab *et al.*, 2021, 75-102.

⁴⁷ Bucheli *et al.*, 2008, 1029-1034.

⁴⁸ Gromadzka *et al.*, 2009, 1051-1059.

⁴⁹ Kolpin *et al.*, 2010, 2089-2099.

⁵⁰ Waskiewicz *et al.*, 2012, 429-435.

⁵¹ Kolpin *et al.*, 2014, 669-676.

⁵² Emídio; Silva; Marchi, 2015, 1-8.

⁵³ Gromadzka *et al.*, 2009, 1051-1059.

⁵⁴ WHO, 2022.

Table 3. Estimated daily intake (DI) ($\mu\text{g/kg}$) of pesticides and mycotoxins in terms of maximum concentrations in water

Pesticide	Age group	DI ($\mu\text{g/kg}$)			
		Drinking water	Tap water	Well water	River water
2,4-D	Child	*	*	*	2.6589
	Young	*	*	*	0.0735
	Adult	*	*	*	0.0020
ACE	Child	*	0.0021	*	0.0114
	Young	*	5.74E-5	*	0.0003
	Adult	*	1.53E-6	*	8.39E-6
ATZ	Child	0.0011	0.0013	*	0.3164
	Young	3.07E-5	3.65E-5	*	0.0088
	Adult	8.17E-7	9.71E-7	*	0.0002
AZO	Child	0.0058	*	*	*
	Young	0.0002	*	*	*
	Adult	4.24E-6	*	*	*
BEM	Child	0.0009	*	*	*
	Young	2.49E-5	*	*	*
	Adult	6.62E-7	*	*	*
CAR	Child	0.0015	*	*	*
	Young	4.14E-5	*	*	*
	Adult	1.10E-6	*	*	*
CBD	Child	*	*	*	0.0418
	Young	*	*	*	0.0012
	Adult	*	*	*	3.08E-5
CHL	Child	*	*	0.0010	*
	Young	*	*	2.65E-5	*
	Adult	*	*	7.06E-7	*
CLO	Child	0.0010	0.0031	*	0.0126
	Young	2.77E-5	8.62E-5	*	0.0003
	Adult	7.39E-7	2.30E-6	*	9.27E-6
CMZ	Child	0.0049	*	*	*
	Young	0.0001	*	*	*
	Adult	3.62E-6	*	*	*
CYP	Child	0.0004	*	*	*
	Young	1.15E-5	*	*	*
	Adult	3.09E-7	*	*	*
DIC	Child	*	*	0.0021	*
	Young	*	*	5.72E-5	*
	Adult	*	*	1.52E-6	*
DIN	Child	*	0.0093	*	0.0030
	Young	*	0.0003	*	8.29E-5

Pesticide	Age group	DI ($\mu\text{g/kg}$)			
		Drinking water	Tap water	Well water	River water
DIU	Adult	*	6.89E-6	*	2.21E-6
	Child	0.0147	*	*	0.0026
	Young	0.0004	*	*	7.19E-5
EPX	Adult	1.08E-5	*	*	1.91E-6
	Child	0.0021	*	*	0.0078
	Young	5.80E-5	*	*	0.0002
FEB	Adult	1.55E-6	*	*	5.76E-6
	Child	*	*	0.0033	*
	Young	*	*	9.12E-5	*
FEN	Adult	*	*	2.43E-6	*
	Child	*	*	0.0143	*
	Young	*	*	0.0004	*
FIP	Adult	*	*	1.05E-5	*
	Child	*	0.0001	*	2.76E-5
	Young	*	4.14E-6	*	7.63E-7
FPID	Adult	*	1.10E-7	*	2.03E-8
	Child	*	*	*	1.11E-5
	Young	*	*	*	3.07E-7
FIPS	Adult	*	*	*	8.17E-9
	Child	*	*	*	1.17E-5
	Young	*	*	*	3.23E-7
IMA	Adult	*	*	*	8.61E-9
	Child	0.0004	*	*	*
	Young	1.24E-5	*	*	*
IMD	Adult	3.31E-7	*	*	*
	Child	0.0008	0.0020	0.0046	0.8390
	Young	2.18E-5	5.66E-5	0.0001	0.0232
IMI	Adult	5.82E-7	1.51E-6	3.38E-6	0.0006
	Child	*	*	*	0.0011
	Young	*	*	*	2.93E-5
IRG	Adult	*	*	*	7.79E-7
	Child	0.0001	*	*	*
	Young	3.32E-6	*	*	*
ISSO	Adult	8.83E-8	*	*	*
	Child	*	*	0.0005	*
	Young	*	*	1.49E-5	*
MEM	Adult	*	*	3.97E-7	*
	Child	*	*	*	0.0009
	Young	*	*	*	2.40E-5
	Adult	*	*	*	6.4E-7

(continued)

Table 3. Estimated daily intake (DI) (µg/kg) of pesticides and mycotoxins in terms of maximum concentrations in water (continued)

Pesticide	Age group	DI (µg/kg)			
		Drinking water	Tap water	Well water	River water
MTR	Child	*	*	*	0.0126
	Young	*	*	*	0.0003
	Adult	*	*	*	9.29E-6
MZC	Child	*	*	0.0004	*
	Young	*	*	1.24E-5	*
	Adult	*	*	3.31E-7	*
NIC	Child	*	*	0.0009	0.0052
	Young	*	*	2.49E-5	0.0001
	Adult	*	*	6.62E-7	3.86E-6
NIT	Child	*	*	*	0.0002
	Young	*	*	*	4.40E-6
	Adult	*	*	*	1.17E-7
PRO	Child	*	*	*	0.0039
	Young	*	*	*	0.0001
	Adult	*	*	*	2.87E-6
PRP	Child	0.0003	*	*	*
	Young	8.29E-6	*	*	*
	Adult	2.21E-7	*	*	*
PRS	Child	*	*	*	0.0004
	Young	*	*	*	9.95E-6
	Adult	*	*	*	2.65E-7
QUC	Child	0.0074	*	*	*
	Young	0.0002	*	*	*
	Adult	5.48E-6	*	*	*
SIM	Child	*	*	*	0.0628
	Young	*	*	*	0.0017
	Adult	*	*	*	4.63E-5
TBZ	Child	0.0138	*	*	0.0221
	Young	0.0004	*	*	0.0006
	Adult	1.02E-5	*	*	1.63E-5
THD	Child	8.09E-5	0.0022	*	0.0120
	Young	2.24E-6	6.15E-5	*	0.0003
	Adult	5.96E-8	1.64E-6	*	8.83E-6
THI	Child	*	*	*	0.0024
	Young	*	*	*	6.55E-5
	Adult	*	*	*	1.74E-6
THM	Child	0.0027	0.0064	*	0.0060
	Young	7.60E-5	0.0002	*	0.0002

Mycotoxin	Age group	DI (µg/kg)			
		Drinking water	Tap water	Well water	River water
3-ADON	Adult	2.02E-6	4.72E-6	*	4.42E-6
	Child	*	0.0044	*	0.0015
	Young	*	0.0001	*	4.09E-5
15-ADON	Adult	*	3.22E-6	*	1.09E-6
	Child	*	0.0021	*	*
	Young	*	5.94E-5	*	*
α-ZEL	Adult	*	1.58E-6	*	*
	Child	*	*	*	0.0510
	Young	*	*	*	0.0014
β-ZEL	Adult	*	*	*	3.76E-5
	Child	*	*	*	0.0548
	Young	*	*	*	0.0015
AFB ₁	Adult	*	*	*	4.04E-5
	Child	0.0141	0.5843	*	*
	Young	0.0004	0.0162	*	*
AFB ₂	Adult	1.04E-5	0.0004	*	*
	Child	1.44E-5	*	*	*
	Young	3.98E-7	*	*	*
AFG ₁	Adult	1.06E-8	*	*	*
	Child	1.80E-5	3.90E-7	*	*
	Young	4.97E-7	1.08E-8	*	*
AFG ₂	Adult	1.32E-8	2.87E-10	*	*
	Child	*	9.53E-5	*	*
	Young	*	2.64E-6	*	*
AFM ₁	Adult	*	7.02E-8	*	*
	Child	*	2.97E-6	*	*
	Young	*	8.21E-8	*	*
DON	Adult	*	2.19E-9	*	*
	Child	*	0.0021	*	0.0498
	Young	*	5.94E-5	*	0.0014
KJA	Adult	*	1.58E-6	*	3.67E-5
	Child	0.1229	*	*	*
	Young	0.0034	*	*	*
NIV	Adult	9.05E-5	*	*	*
	Child	*	*	*	0.0013
	Young	*	*	*	3.63E-5
OTA	Adult	*	*	*	9.65E-7
	Child	7.79E-6	0.4315	*	*
	Young	2.16E-7	0.0119	*	*
STC	Adult	5.74E-9	0.0003	*	*
	Child	*	6.68E-6	*	*

Table 3. Estimated daily intake (DI) ($\mu\text{g/kg}$) of pesticides and mycotoxins in terms of maximum concentrations in water (continued)

Mycotoxin	Age group	DI ($\mu\text{g/kg}$)			
		Drinking water	Tap water	Well water	River water
VERA	Young	*	1.85E-7	*	*
	Adult	*	4.92E-9	*	*
	Child	*	*	*	0.0013
	Young	*	*	*	3.51E-5
	Adult	*	*	*	9.34E-7
ZEN	Child	*	*	1.50E-5	0.0029
	Young	*	*	4.14E-7	7.96E-5
	Adult	*	*	1.10E-8	2.12E-6

* = not reported by the occurrence survey.

Source: own elaboration.

ingested without risk to health and with a safety margin, established by the WHO are defined only for ATZ, BEM, CAR, CHL, 2,4-D, DIC, ISO and SIM in potable water. i. e., 20, 9, 2, 11300, 10, 4, 3 and $0.52 \mu\text{g/kg}$, respectively. The other pesticides reported in the occurrence survey had no established reference values of TDI. Regarding mycotoxins, no legislation establishes TDI values related to water consumption.

According to WHO⁵⁵, DI values of pesticides calculated do not pose any exposure risk. In the case of mycotoxins, it is important to say that the European Commission warns that AFB₁ consumption of concentrations below 1 ng/kg/day may cause carcinogenic effects⁵⁶. Additionally, their incidence in water at low concentrations without any acute toxic effect, bioaccumulation in the food chain and simultaneous ingestion of these contaminants may result in toxic synergism. Michel *et al.*⁵⁷ verified not only the occurrence of FIP and its metabolites FIPD and FIPS in river water samples but also their occurrence in muscle tissue of eels captured downstream from collection spots of water samples. FIP was predominant in all water samples at concentrations ranging from 0.24 to 0.92 ng/L , followed by FIPS, from 0.16 to 0.39 ng/L , and FIPD, from <0.08 to 0.37 ng/L . In muscle samples, concentrations of FIP, FIPD and FIPS ranged from 0.04 to 0.32 , 0.02 to 0.13 and

0.52 to $11.24 \mu\text{g/kg}$, respectively. Gonkowski *et al.*⁵⁸ evaluated the occurrence of ZEN and its metabolites α -ZEL and β -ZEL in dry fish and in river water where the species was captured. Data on ZEN levels in dry fish ranged from 27.2 to $53.9 \mu\text{g/kg}$ and <2000 to 18000 ng/L in water. In both studies, the authors concluded that these contaminants may contribute to consumers' exposure and lead to public health problems.

Other studies also report bioaccumulation of pesticides carbaryl, famoxadone, fenpyroximate, thiamethoxam, boscalid and difenoconazole in ground beef at concentrations ranging from 10 to $20 \mu\text{g/kg}$ ⁵⁹, chlorpyrifos ($1000 \mu\text{g/kg}$) and phenthoate ($5 \mu\text{g/kg}$) in animal fat⁶⁰ and 2,4-D (13400 - $26300 \mu\text{g/kg}$) in fish meat⁶¹. Concerning mycotoxins enniatin A₁ (1.7 - $29 \mu\text{g/kg}$) enniatin B (1.3 - $103 \mu\text{g/kg}$), enniatin B₁ (1.4 - $94 \mu\text{g/kg}$)⁶² and AFB₁, their bioaccumulation was reported in fish muscle (0 - $264.73 \mu\text{g/kg}$)⁶³, AFB₁ (40 - 600 ng/L) and AFM₁ (40 - 3670 ng/L) in milk⁶⁴, AFM₁ (0.20 - $1.19 \mu\text{g/kg}$) in powdered milk⁶⁵, OTA (0.3 - $1.9 \mu\text{g/kg}$) and ZEN (5 - $317.3 \mu\text{g/kg}$) in seafood⁶⁶.

Many contaminants have chemical structures that, after injection, interact with cellular organelles and macromolecules and induce toxic effects in mammals (e.g., cytotoxic, estrogenic, immunosuppressive, nephrotoxic, neurotoxic and carcinogenic)⁶⁷. In addition, some pesticides may reduce intelligence and impair short-term memory, especially in children and adolescents⁶⁸. It is noteworthy that, the higher the DIs of pesticides and mycotoxins in river water, followed by tap water, the more exposed to their negative effects is the population that uses this resource.

Thus, risks to human health posed by consumption of water contaminated with pesticides and mycotoxins cannot be ignored. However, their control has several challenges, such as different groups of pollutants that require distinct chemical processes, remediation technologies and objective treatment. Therefore, specific legislation that determines the lowest concentrations of the metabolites in water which does not cause any

⁵⁸ Gonkowski *et al.*, 2018, 1046-1050.

⁵⁹ Song *et al.*, 2020, 1306-1315.

⁶⁰ Kang *et al.*, 2020, 1573-1586.

⁶¹ Al-Amri *et al.*, 2021, 709-720.

⁶² Tolosa *et al.*, 2017, 67-74.

⁶³ Michelin *et al.*, 2016, 265-272. Deng *et al.*, 2020, 735055.

⁶⁴ Gonçalves *et al.*, 2018, 260-264.

⁶⁵ Sibaja *et al.*, 2019, 97-104.

⁶⁶ Sun *et al.*, 2015, 42-48.

⁶⁷ IARC, 2002. Eagles *et al.*, 2021, 129279. Kruć-Fijałkowska *et al.*, 2022, 3317.

⁶⁸ Yadav; Sankhla; Kumar, 2019, 243-245.

⁵⁵ WHO, 2022.

⁵⁶ European Commission, 1996.

⁵⁷ Michel *et al.*, 2016, 171-179.

adverse effects must be established. Thus, regulatory agencies of each country establish guidelines on water quality parameters for consumption by its human population⁶⁹. The WHO also establish its guidelines for drinking water quality⁷⁰.

In addition, effective strategies to control or mitigate them must be developed and applied so that effective treatments may decrease adverse effects on humans. Physical, chemical, and biological methods have been applied to mitigate these contaminants in liquid matrices, such as the application of UV light radiation to mitigate aflatoxin M1 in milk⁷¹, ozone to mitigate patulin in apple juice⁷² and the enzyme peroxidase to mitigate OTA and ZEA in beer⁷³, respectively. For pesticides, the best results are achieved by chemical method using photocatalysis resulting in 100 % degradation of monocrotophos in water⁷⁴. In relation to the physical method, the best result is reached by reverse osmosis membrane and bio-filtration methodology with degradation value of 97 %⁷⁵, while the biological method that has the best result is the hybrid membrane bioreactor treatment, which reached 99 % degradation⁷⁶.

All methods (e.g., chemical, physical and biological ones) have good efficiency at mitigating mycotoxins and good variability in application because, even when methodologies are applied to several mycotoxins, mitigation ranged from 27 to 100 %⁷⁷. Although there are no studies of degradation and mitigation of mycotoxins in environmental matrices, the methods presented can be the starting point for applications to water.

Conclusion

A large variety of pesticides and mycotoxins may be detected in drinking, waste, river and tap water. Data compilation from the literature and assessment of DI enabled to state that young individuals are exposed to higher concentrations of both groups of contaminants. In addition, the highest DI was observed in river water, followed by tap water. It means that the population that drinks water from these sources is more exposed

to the deleterious effects of the contaminants. Even though intake values are below those established by the WHO for pesticides, their simultaneous ingestion may result in bioaccumulation in the food chain and in toxic synergism. To circumvent this problem and risk of exposure, it's necessary that studies aiming at the degradation of mycotoxins and pesticides in water be carried out. Physical, chemical and biological methods can be tested, with or without a combination of them, and applied to minimize contamination and increase water quality, ensuring safe water for animals and humans. Furthermore, this study demonstrates the need to establish concentrations that can be ingested without health risks for mycotoxins and also for the pesticides that do not contain them.

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⁶⁹ Brasil, 2021. USEPA, 2009. China, 2006. European Union, 2020.

⁷⁰ WHO, 2022.

⁷¹ Khoori *et al.*, 2020, 14729.

⁷² Diao *et al.*, 2019, 957.

⁷³ Garcia *et al.*, 2020, 109039.

⁷⁴ Sraw *et al.*, 2022, 1265.

⁷⁵ Schotag *et al.* 2022, 118352.

⁷⁶ Navaratna; Shu; Jegatheesan, 2016, 795-803.

⁷⁷ Garcia *et al.*, 2020, 109039. Dudziak, 2012, 779-785. Bosch *et al.*, 2017, 97.

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