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Priority pesticides not covered by GM Ordinance of the Ministry of Health No. 888, of 2021, on water potability standard in Brazil

Agrotóxicos prioritários não abordados pela Portaria GM do Ministério da Saúde nº 888, de 2021, sobre padrão de potabilidade da água no Brasil

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ABSTRACT

The intense use of pesticides can be harmful to the environment and human health, being necessary to monitor the environmental concentrations of pesticides. The legislation on drinking water for human consumption is one of the guiding regulations about monitoring priority. Therefore, a systematic review was carried out to compile information on the contamination of surface water, groundwater, and treated water in Brazil. Thereby, we selected those pesticides which, although they are authorized for use and are among the top-selling pesticides, are not regulated by GM Ordinance of the Ministry of Health (GM/MS) No. 888, of May 4, 2021. The databases used were PubMed, Scielo, Science Direct, Scopus, and Web of Science. Of the 122 pesticides in the market, 11 were selected. Analyses of environmental dynamics, concentration, and health effects were carried out. The Goss methodology and the Groundwater Ubiquity Score (GUS) index were used to estimate the risk of surface water and groundwater contamination, respectively. The concentrations found were compared with the values provided for in the guidelines adopted by international agencies, determining the Brazilian population's margin of exposure (MOE) to the target pesticides. The results indicate a high probability of finding imidacloprid and hexazinone in the water, the prevalence of studies on surface waters, and the need to conduct additional studies as papers on some of the target pesticides were not found. It is concluded that the pesticides studied pose a low risk to human health, however, further studies are still required.

Keywords: legislation; microcontaminants; health; agrochemicals.

RESUMO

O intenso uso de agrotóxicos pode ser prejudicial ao meio ambiente e à saúde humana, tornando necessário o monitoramento de suas concentrações ambientais. Como um dos dispositivos norteadores sobre a prioridade de monitoramento é a legislação de água potável para consumo humano, foi realizada uma revisão sistemática da literatura com o objetivo de compilar informações sobre a contaminação das águas superficiais, subterrâneas e tratadas por agrotóxicos. Foram considerados os agrotóxicos mais vendidos em território brasileiro entre 2009 e 2019 e que possuem autorização de uso, mas que não são regulamentados pela Portaria GM do Ministério da Saúde nº 888, de 4 de maio de 2021. Dos 122 agrotóxicos comercializados, 11 foram selecionados. Analisaram-se a dinâmica ambiental, concentração em águas e efeitos na saúde humana. Na estimativa do risco de contaminação das águas superficiais e subterrâneas, empregou-se a metodologia Goss e o índice *Groundwater Ubiquity Score* (GUS), respectivamente. Uma comparação crítica sobre as concentrações encontradas e os valores-guia adotados por agências internacionais foi realizada, determinando-se a margem de exposição da população brasileira aos agrotóxicos. Os resultados do trabalho mostraram a maior probabilidade de que imidacloprido e hexazinona sejam encontrados em águas; a prevalência de estudos realizados em águas superficiais; e a necessidade de que mais trabalhos sejam realizados, uma vez que não foram encontrados artigos sobre alguns dos compostos-alvo. Conclui-se que os agrotóxicos estudados apresentam baixo risco à saúde, todavia se vê a necessidade de que mais estudos sejam desenvolvidos.

Palavras-chave: legislação; microcontaminantes; saúde; pesticidas.

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Introduction

Pesticides are used to modify the composition of flora or fauna to preserve them from the action of harmful living beings (Brasil, 1989). Historically, since there were problems related to the cultivation process, the Brazilian agricultural production model was based on pesticides (Wahlbrinck et al., 2017). Since 2008 Brazil has been one of the world's largest agricultural producers, the second top exporter of pesticides (Pignati et al., 2017). According to the Brazilian Institute for the Environment and Natural Resources (IBAMA), in 2009, the accumulated sales in Brazil were approximately 270,000 tons of Active Ingredients (AI). In 2019, it was over 560,000, corresponding to a percentage increase of around 108% (IBAMA, 2021).

The current model of agriculture requires the use of pesticides, as they help increase crop productivity (Sharma et al., 2019). However, when they are used excessively, pesticides can be harmful to the environment and contaminate aquatic matrices, the air, and the soil (Lorenzatto et al., 2020). Contamination of aquatic matrices can occur through soil runoff, spray drift, or improper disposal of pesticide containers (Olisah et al., 2020). Once in the aquatic environment, pesticides can bioaccumulate in organisms (Belchior et al., 2014) and may have deleterious effects on the aquatic biota, such as fish (Américo-Pinheiro et al., 2019, 2020). In addition, it is noted that pesticides can evaporate, infiltrate the soil, or be carried through rivers (Souza et al., 2020) and, depending on their properties, they can be transported through the atmospheric process and reach new areas, extending the degree of contamination (Carvalho, 2017). The population can be exposed to the risks of pesticides mainly through food, as humans are at the top of the food chain and depend on resources (i.e., water, land, air) for survival (Belchior et al., 2014).

Considering the aforementioned, it is necessary to analyze the risks associated with human exposure to pesticides. In this context, the risk assessment (RA) methodology stands out. This methodology aims to identify the risks associated with a chemical agent through four steps:

- Hazard identification;
- Dose (concentration) – response (effect) relation;
- Exposure assessment;
- Risk characterization (UNEP, 1999).

The RA methodology is used to establish water potability standards and guidelines worldwide (WHO, 2017), as well as the standards reviewing process (Vigiagua, 2020). Usually, substances are considered potential candidates to integrate the potability standard according to factors like the pattern of occurrence in springs, toxicity, environmental dynamics, persistence/mobility in environmental matrices, and removal in water treatment plants (WTPs).

In Brazil, water quality control for human consumption is regulated by Annex XX, of Consolidation Ordinance No. 5, of September 28, 2017, amended by GM Ordinance of the Ministry of Health (MS) No. 888, of May 4, 2021, in which pesticides and other substances harmful to humans are listed (Brasil, 2021). It is worth mentioning that some pesticides, even though they are not listed in the Ordinance, deserve attention. Especially the top-selling ones whose properties increase their occurrence in water matrices.

Therefore, in this study, we aimed to carry out a risk assessment, based on a systematic literature review, of pesticides found in water for human consumption in Brazil, including exposure factors (commercialization, environmental dynamics, and occurrence on the surface, groundwater, and treated water) and chronic toxicity data. To this end, we focused on the top-selling authorized pesticides in Brazil but not listed in the water potability standard.

Material and Methods

Pesticide selection

To identify the top-selling pesticides in Brazil, the data available in IBAMA's current Marketing Reports were compiled (2009-2019) (IBAMA, 2021). Our exclusion criteria were:

- pesticide covered by GM/MS Ordinance No. 888 of 2021 (Brasil, 2021) because the purpose of this study is to evaluate the pesticides not covered by the Brazilian potability ordinance;
- unauthorized pesticides or those that do not have a monograph at the Brazilian Health Surveillance Agency (ANVISA, 2021);
- pesticides with a low percentage of sales — the 70th percentile was applied to the accumulated sales data, and the corresponding value was adopted as the cutoff point;
- adjuvant compounds (those that are used in association with the AI to improve application).

Environmental dynamics

To analyze the probability of pesticides reaching the water, we verified their physicochemical properties: coefficient of adsorption in organic matter (K_{oc}); typical half-life (DT_{50}) in the soil and water phase; solubility in water; octanol-water partition coefficient (K_{ow}); and Henry's law constant (K_H). These properties were obtained through the Pesticides Properties Database (PPDB) (IUPAC, 2020) and, in cases when the information was absent, using the Oregon State University (OSU) Extension Pesticide Properties Database (NPIC, 2020).

The contamination potential of surface water and groundwater was estimated using the Goss methodology (Goss, 1992) and the GUS Index (Gustafson, 1989), respectively.

A systematic review of environmental concentrations in surface water, groundwater, and treated water

A systematic review was carried out using the PRISMA methodology (Moher et al., 2009).

We searched for studies concerning the target pesticides in Brazilian waters using PubMed, Scielo, Science Direct, Scopus, and Web of Science platforms since there is broad literature regarding the subject of this study. The following search codes were used: (pesticides AND water AND Brazil) and ((clomazone OR hexazinone OR "monosodium methyl arsenate" OR MSMA OR tebuthiuron OR cypermethrin OR imidacloprid OR "lambda-cyhalothrin" OR "lambda cyhalothrin" OR methomyl OR azoxystrobin OR "thiophanate-methyl" OR "thiophanate methyl" OR ethephon) AND water AND Brazil). The present review considers articles in English or Portuguese language, published by October 4, 2021. We did not consider review articles since it is expected that the original ones have already been contemplated through the search made. After excluding duplicate articles, screening was performed on two levels: first, by analyzing the title, abstract, and keywords; and second, by reading the entire content of each one of the articles.

We excluded those articles in which at least one of the following pieces of information was absent:

- limit of detection (LOD) and limit of quantitation (LOQ);
- number of samples in which there was detection or quantitation;
- individual concentration of each sample and no information about the frequency of detection/quantitation or the average value.

Also, we did not consider articles that quantified pesticides in mixtures (i.e., with metabolites or other compounds); and when it was not possible to identify the analysis matrix (e.g., raw or treated water). For papers that did not specify the individual environmental concentrations but presented the average and the frequency of detection and/or quantitation, we determined the individual concentrations as follows: concentration = average ÷ number of samples. Due to the occurrence of censored data, lower than the limit of detection (< LOD) or not detected (ND) and/or lower than the limit of quantitation (< LOQ), the substitution method for censored data was applied (Sanford et al., 1993). Therefore, when elaborating the graphical representation of pesticide occurrence, in those studies where the environmental concentration was reported as < LOD or ND, we used LOD/2; and when the concentration was reported as < LOQ, we used LOQ/2. We also considered as outliers (higher concentrations) the values that were at least 1.5 times the interquartile range (Q_3 - Q_1), from the edge of the box (Minitab, 2020), which were not represented due to the graphic scale.

Pesticide occurrence in surface water, groundwater, and treated water

Based on the occurrence data of pesticides in surface water, groundwater, and treated water, we carried out an analysis to identify the most abundant pesticide in each of them. Also, we correlated the detection frequency with the pesticide's position in IBAMA's sales rank, considering total sales from 2009 to 2019.

Human health effects

To analyze the potential effects of pesticides on human health, we gathered information about chronic toxicity data from the International Agency for Research on Cancer (IARC, 2020a) and the United States Environmental Protection Agency (USEPA, 2020a).

Critical comparison of environmental occurrence and maximum acceptable values in drinking water

We searched for information about the target pesticides presence on international agencies and guidelines for drinking water quality to obtain the maximum acceptable values (MAV) on drinking water. We selected USEPA and the World Health Organization (WHO) guidelines, as they are considered the main references used on drinking water standards in several countries (Araújo, 2018); New Zealand, Canada, and Australia guidelines that are also international references and employ the risk assessment methodology; and the European Environmental Agency (EEA), considering its high restrictiveness (Souza et al., 2019). Based on the occurrence data and the MAV in drinking water, we made a critical comparison of the environmental concentrations to identify its potential risk for human health. According to USEPA, the occurrence value (OV) can be obtained by the 90th, 95th or 99th percentile of the concentrations found or through the maximum value detected in drinking water (USEPA, 2016a). On the other hand, the Australian Drinking Water Guidelines use only the maximum value found in drinking water (NHMRC, 2021). Given the impossibility of calculating the percentile for some pesticides due to the reduced amount of data, we chose to use the recommendation proposed by the Australian guidelines, with some modifications. Thus, to obtain the MOE, we calculated the ratio between MAV and OV in each of the matrices — and not only for drinking water, as the methodology proposes. This approach was adopted considering a conservative view on those cases in which the water resources are used for public supply and considering that water treatment would not effectively remove residual pesticides. The OV of each pesticide was obtained using the maximum concentration found in each matrix (disregarding outliers). In cases where more than one MAV was available, we used the most restrictive one. From the values obtained, the MOE was stipulated: MOE ≤ 1: the pesticide poses a risk to human health; 1 ≤ MOE ≤ 10: the pesticide deserves attention since its occurrence is in the same order of magnitude as the concentrations that would represent a risk to human health; and MOE ≥ 10: the pesticide is less likely to cause adverse health effects.

Results and Discussion

Pesticide selection

The research started with 122 pesticides and, based on the application of the criteria, 111 were excluded: 32 according to criteria 1 (covered by GM/MS Ordinance No. 888 of 2021); 8 according to criteria 2 (ANVISA monograph absent/excluded); 66 based on criteria 3 (total sales were less than 12128t); and 5 according to criteria 4 (adjuvants). Finally, a total of 11 pesticides remained in the study: clomazone, hexazinone, monosodium methyl arsonate (MSMA), and tebuthiuron (herbicides); cypermethrin, imidacloprid, lambda-cyhalothrin and methomyl (insecticides); azoxystrobin and thiophanate-methyl (fungicides); and ethephon (growth regulator).

Environmental dynamics

The physicochemical properties of the pesticides influence their environmental dynamics, defining major or minor tendencies to reach water matrices. Using the International Union of Pure and Applied Chemistry (IUPAC, 2020) and OSU (NPIC, 2020) data, we evaluated the water contamination potential of pesticides. Among the regarded pesticides, hexazinone and imidacloprid have greater contamination probability, as they have high solubility (33,000 and 2,500 mg/L, respectively), showing a tendency for surface runoff (Elias et al., 2018) and high $DT_{50\ (soil)}$ (105 and 191 days, respectively). These properties, although being influenced by soil type and climate conditions (New Zealand, 2020), indicate that these pesticides are persistent in the environment. Furthermore, hexazinone and imidacloprid have low K_{oc} (54 and 13 ml/g, respectively), i.e., they are poorly retained on soil particles (Pérez-Lucas et al., 2021); low K_{ow} (1.17 and 0.57, respectively), an indication that they can easily pass into the aqueous phase (Yang et al., 2018), and low K_H (1.10×10^{-7} and 1.7×10^{-10} Pa m^3/mol, respectively), which means they do not volatilize easily, remaining in the aquatic environment for longer periods (Chao et al., 2017). In addition, methomyl has high solubility (55,000 mg/L) and low K_{oc} (72 ml/g); MSMA is strongly retained on soil particles (200 days) and shows low log K_{ow} (-3.1), an indication that it has a higher affinity to the water phase.

Otherwise, some pesticides did not show a tendency for contamination: cypermethrin, which has low solubility (0.009 mg/L), is strongly adsorbed to the soil matrix (3×10^5 ml/g), shows volatilization tendency (0.31 Pa m^3/mol), and has high log K_{ow} (5.55), with a less pronounced hydrophilic characteristic; lambda-cyhalothrin shows low solubility (0.005 mg/L) and is strongly retained to the soil (K_{oc} = 283,707 ml/g and $DT_{50\ (soil)}$ = 175 days); methomyl, which in addition to having high solubility (55,000 mg/L) and low K_{oc} (72 ml/g), shows low $DT_{50\ (water)}$ (2.9 days), an indication that it is poorly persistent in the environment; tebuthiuron that despite showing high soil permanency (400 days) and low log K_{ow} (1.79), tends to volatilize (K_H = 2.47×10^{-5} Pa m^3/mol); clomazone and ethephon are not persistent in the soil since they have $DT_{50\ (soil)}$ equal to 22.6 and 13.1 days, respectively. Also, ethephon is poorly persistent in the water matrix ($DT_{50\ (water)}$ = 2.4 days).

It is worth mentioning the fungicide class, since both azoxystrobin and thiophanate-methyl have low solubility (6.7 and 18.5 mg/L, respectively) and are slightly mobile on the solid surface (K_{oc} = 589 and 1830 ml/g, respectively), tending to remain retained to the soil matrix. Also, they have $DT_{50\ (water)}$ equal to 6.1 and 3 days, respectively, indicating that they are slightly persistent in the water matrix.

According to the Goss methodology (Goss, 1992), hexazinone, tebuthiuron, and azoxystrobin have a high potential for water contamination, considering their transportation as dissolved in the water; and lambda-cyhalothrin is a potential contaminant considering its transportation in the soil. MSMA has a high contamination potential through both water and soil transportation.

The other target pesticides have a moderate to low probability of surface water contamination.

Regarding groundwater contamination, we verified that hexazinone and tebuthiuron tend to contaminate groundwater, according to the GUS index (Gustafson, 1989). Moreover, clomazone, methomyl, azoxystrobin, and ethephon can also be potential contaminants since they are at the transition state. The other pesticides have little contamination probability. However, it is worth noting that even those compounds that are unlikely to reach water matrices, given their properties, could also be potential contaminants since climate and soil characteristics can be favorable to leach (Pérez-Lucas et al., 2019). We were not able to calculate the contamination probability of imidacloprid for both surface water and groundwater since its K_{oc} value is absent in the PPDB (IUPAC, 2020), and this insecticide is not listed in the OSU Extension Pesticide Properties Database (NPIC, 2020).

A systematic review of concentrations in surface water, groundwater, and treated water

A total of 1,775 articles were found (number of articles = N = 1,775), 104 from PubMed, 40 from Scielo, 197 from Science Direct, 870 from Scopus, and 564 from Web of Science (Figure 1). After screening, only 30 articles were included in our analysis based on the inclusion and exclusion criteria.

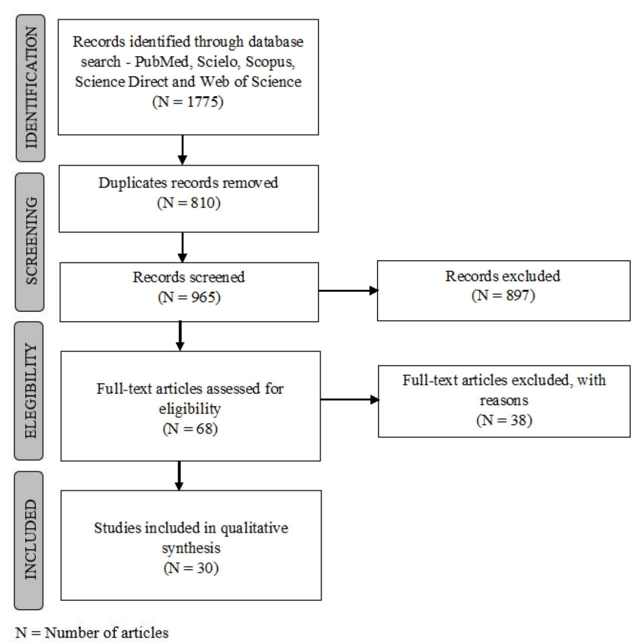


Figure 1 – Flowchart of the systematic review.
Source: adapted from PRISMA (Moher et al., 2009).

Usually, the articles found evaluated the occurrence of more than one pesticide in waters.

The most studied pesticide was clomazone (N = 17), followed by imidacloprid (N = 12), azoxystrobin (N = 10), tebuthiuron (N = 5), hexazinone (N = 4), and lambda-cyhalothrin (N = 2). Cypermethrin and methomyl were studied in only one article each. We did not find articles regarding ethephon, MSMA, and thiophanate-methyl. About 57% of the studies referred to the occurrence of pesticides in surface water, approximately 3% in groundwater matrices, and the same percentage in drinking water. The remaining percentage referred to the occurrence in more than one matrix (e.g., surface and groundwater). We observe a larger number of studies related to both surface and treated water, approximately 23%.

Establishing a comparison between scientific production and commercialization over the years, it was possible to note a growing trend (Figure 2). It is worth noting that the 2020 and 2021 sales data were not plotted because they were not available yet (IBAMA, 2021).

Although scientific production showed some periods of decline, a growth tendency is observed since 2018, as suggested by the trendline (Figure 2).

Most of the studies were carried out in the South (N = 19) and Southeast (N = 8) regions of Brazil, where the trade of agricultural products is highly significant (Oliveira and Rodrigues, 2019). The Midwest region showed two articles. The North and Northeast regions, which have little participation in the Brazilian agribusiness (Oliveira and Rodrigues, 2019), had only one study each.

Pesticide occurrence in Brazilian surface water

We found 27 articles related to surface water contamination in Brazil. Most of them was about clomazone (N = 16), imidacloprid (N = 11), and azoxystrobin (N = 9); followed by tebuthiuron (N = 5), hexazinone (N = 4), and lambda-cyhalothrin (N = 2). Cypermethrin and methomyl were reported by only one article each. Figure 3 shows pesticide concentration in Brazilian surface water.

Among the target pesticides of this study, we observed that imidacloprid was the top-selling product and also the most detected in surface waters (F = 27.3%). Likewise, the least selling, cypermethrin, was not detected (Figure 3). These results are in line with the expectations, as top-selling pesticides are more likely to have a higher detection percentage.

Azoxystrobin is one of the most widely used fungicides worldwide (Uçkun and Öz, 2021) and it is applied mainly against *brusone* (Pyricularia oryzae), the main fungal disease that affects irrigated rice (Back et al., 2016). Approximately 2900 tons of this fungicide are sold annually in Brazil. Concentrations of this pesticide were found in the range of 0.001 to 0.125 μg L^{-1} (Figure 3) in Rio Grande do Sul (RS) (Amaral et al., 2020; Severo et al., 2020) and São Paulo (SP) states (López-Doval et al., 2017; Montagner et al., 2014, 2019). In Montagner et al. (2019), an outlier of 0.431 μg L^{-1} was observed in the sample collected in the city of Indaiatuba (SP). In the region of Londrina, Paraná (PR), azoxystrobin was quantified at an average concentration of 0.027 μg L^{-1} in 15 of the 24 samples analyzed (Souza et al., 2019). In other studies carried out in the southern region of Brazil, it was not found at quantifiable levels (Amaral et al., 2018; Almeida et al., 2019) and it was not detected in the Camanducaia River and its tributaries (SP) (Barizon et al., 2020).

Cypermethrin, a synthetic pyrethroid used against agricultural and domestic pests (Bhatt et al., 2020), has average annual sales in Brazil of about 1230 tons. It was not detected in any of the 10 samples collected in Minas Gerais (MG) in a study that showed relatively high LOD and LOQ (1.5 and 5 μg L^{-1}, respectively) (Rodrigues et al., 2018).

Clomazone has average annual sales in Brazil of approximately 5164 tons and it is widely used in rice crops (Guo et al., 2021). Studies on this herbicide were conducted in RS, PR, and SP, being found in quantifiable levels in 11 (Zanella et al., 2002; Bortoluzzi et al., 2006, 2007; Armas et al., 2007; Silva et al., 2009; Primel et al., 2010; Marchesan et al., 2007, 2010; Caldas et al., 2013; Severo et al., 2020; Guarda et al., 2020b) of the 16 articles considered in at least one sample analyzed in each of the studies, totaling 218 of 1064 samples (Figure 3).

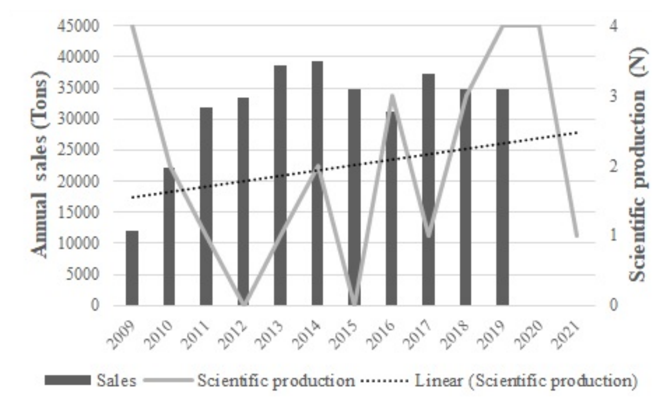
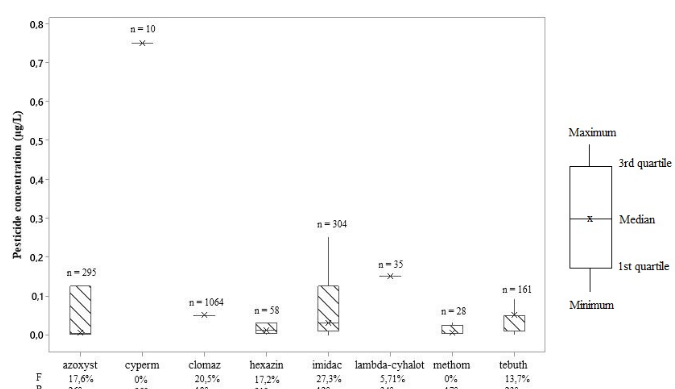


Figure 2 – Annual sales (2009-2019) and Scientific production (2009-2021)*.
*2020 and 2021 sales data are still not available by IBAMA.



n = total number of samples; F = frequency of detection; R = position in the sales ranking

* outilers were not represented in the Figure due to the scale used

Figure 3 – Pesticide occurrence in Brazilian surface water.

Of this amount, about 41% were between 0.002 and 0.1 µg L^{-1}; and approximately 50% were found between 0.15 and 1.72 µg L^{-1}. Outliers of 3.21 and 15.69 µg L^{-1} were identified, associated with the increased use of this herbicide and reduced manual weed control (Bortoluzzi et al., 2007). Moreover, outliers between 5.4 and 23 µg L^{-1} were found, possibly because clomazone has high water stability and is widely used in the study area (Primel et al., 2010). There was no detection/quantitation in other studies (Vieira et al., 2016; López-Doval et al., 2017; Vieira et al., 2017; Souza et al., 2019; Barizon et al., 2020).

Hexazinone, widely used in sugarcane crops (Acayaba et al., 2021), has average annual sales in Brazil of approximately 1374 tons. A study carried out in Mato Grosso (MT) identified this pesticide in two of the 18 samples collected, at concentrations of 0.009 and 0.02 µg L^{-1} (Sposito et al., 2018) (Figure 3). In PR, it was quantified in the range of 0.01 and 0.03 µg L^{-1} (Figure 3) and outliers from 0.07 to 0.14 µg L^{-1} (Almeida et al., 2019). There was no detection in MT (Duarte et al., 2016) and no quantitation in PR (Souza et al., 2019).

Imidacloprid, of which about 7659 tons are sold per year in Brazil, is a neonicotinoid used against a variety of insects (Tuelher et al., 2018) and it was found at concentrations between 0.001 and 0.125 µg L^{-1} in RS (Amaral et al., 2018, 2020; Severo et al., 2020), SP (López-Doval et al., 2017), MT (Sposito et al., 2018), PR (Almeida et al., 2019; Souza et al., 2019) and Tocantins (TO) (Guarda et al., 2020b) (Figure 3). Studies carried out in RS detected outliers between 0.38 and 2.18 µg L^{-1} (Bortoluzzi et al., 2006), from 0.55 to 2.59 µg L^{-1} (Bortoluzzi et al., 2007) and from 0.17 to 0.82 µg L^{-1} (Severo et al., 2020). In Bortoluzzi et al. (2006, 2007), the high concentrations found were justified by the increase in the use of imidacloprid to replace other insecticides that were used in tobacco cultivation; whereas in Severo et al. (2020), although the meteorological conditions of the collection were not reported, it was possible that extreme rainfall events had occurred, since high concentrations can be recorded after heavy rainfall (Pérez et al., 2017). There was no detection in a study carried out in SP (Barizon et al., 2020).

Lambda-cyhalothrin, a synthetic pyrethroid insecticide that mimics the insecticidal properties of natural pyrethrin (Sharma et al., 2021), has annual sales in Brazil of approximately 1241 tons. It was detected in the region of Guaíra (SP) at concentrations of 0.1 and 0.2 µg L^{-1} and an outlier of 5.66 µg L^{-1} (Filizola et al., 2002). There was no detection in a study carried out in Sergipe (SE) (Pinheiro and Andrade, 2009).

Methomyl is widely used due to its broad-spectrum properties (He et al., 2022) and has average annual sales in Brazil of 6106 tons. It was not detected in any of the 28 samples collected in Formoso River (PR) (Guarda et al., 2020c).

Tebuthiuron, an herbicide widely used in sugarcane crops (Teixeira et al., 2018), has average annual sales in Brazil of 3475 tons. Its occurrence was reported in SP (Monteiro et al., 2014), PR (Almeida et al., 2019), and MT (Sposito et al., 2018) at concentrations between 0.01 and 0.05 µg L^{-1} (Figure 3) and outliers from 0.06 to 0.18 µg L^{-1} (Almeida et al., 2019). There was no detection in another study carried out in SP (Barizon et al., 2020) and no quantitation in PR (Souza et al., 2019).

Pesticide occurrence in Brazilian groundwater

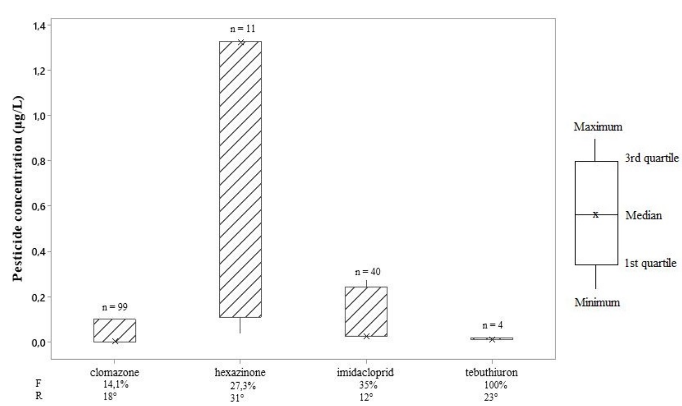
The risk of groundwater contamination depends on the physicochemical properties of pesticides, soil properties, hydrological and climatic conditions, and the management practices adopted in the crops (Gaona et al., 2019). We found a total of four studies carried out in groundwater matrices. Clomazone, hexazinone, and imidacloprid had two articles each; azoxystrobin and tebuthiuron only one; and no articles were found on the other pesticides. Among the pesticides that are more likely to be found in groundwater due to their high leaching potential, clomazone, hexazinone, and tebuthiuron were detected. Tebuthiuron was the most detected (F = 100%), although its total number of samples (n = 4) is much lower than the second most found, imidacloprid (F = 35%; n = 40) (Figure 4).

Clomazone was quantified in the range of 0.001 to 0.008 µg L^{-1} in the southern region of Brazil (Silva et al., 2011) (Figure 4) and in outliers of 2.68 and 10.84 µg L^{-1} (Bortoluzzi et al., 2007), possibly related to the expansion of tobacco farming in RS and the reduction of manual weed control (Bortoluzzi et al., 2007).

Hexazinone was quantified in PR at concentrations of 0.04 to 0.11 µg L^{-1} (Almeida et al., 2019), not being detected in a study carried out in MT, in which the LOD and LOQ were 2.65 and 8.04 µg L^{-1}, respectively (Duarte et al., 2016).

Imidacloprid was detected in PR at concentrations between 0.05 and 0.16 µg L^{-1} (Almeida et al., 2019); and in RS in 10 of the 36 samples analyzed, in which outliers between 0.67 and 6.22 µg L^{-1} were identified, possibly due to the increased use of this insecticide in the cultivation of tobacco (Bortoluzzi et al., 2007) (Figure 4).

The occurrence of tebuthiuron has been reported in PR at concentrations between 0.01 and 0.02 µg L^{-1} (Almeida et al., 2019) (Figure 4).



n = total number of samples; F = frequency of detection; R = position in the sales ranking

* outilers were not represented in the Figure due to the scale used

Figure 4 – Pesticide occurrence in Brazilian groundwater.

Pesticide occurrence in Brazilian treated water

Pesticides can be leached from soils (Singh et al., 2018) and since conventional treatment processes are generally not effective enough in removing residual pesticides (Elfikrie et al., 2020), they may be found in drinking water. We found eight studies on the target pesticides in treated water: azoxystrobin (N = 5); clomazone, imidacloprid, and tebuthiuron (N = 3); hexazinone (N = 2); and cypermethrin (N = 1). Cypermethrin data were not plotted because they comprise two samples only. No studies were found on the other pesticides. It is worth mentioning that the frequency of detection in treated water was lower than in the two environmental matrices previously addressed.

The top-selling pesticide, imidacloprid, had the second-highest frequency of detection (F = 12.8%) and, as in surface water, it was observed that the least selling product, in this case, hexazinone, was not detected (Figure 5). Once again, these results were in line with the expectations since less intense commercialization implies a lower probability that the pesticide will be found in the environment.

Azoxystrobin was found at concentrations between 0.001 and 0.002 μg L^{-1} in PR (Souza et al., 2019) and SP states (Montagner et al., 2019). This fungicide was not quantified in other studies carried out in PR (Almeida et al., 2019), SP (Montagner et al., 2014), and RS (von Ameln Lovison et al., 2021) (Figure 5).

Clomazone was quantified in RS at an average concentration of 0.063 μg L^{-1} in 4 of the 10 samples analyzed (Caldas et al., 2013). It was not detected in other studies carried out in the southern region (Primel et al., 2010; Souza et al., 2019) (Figure 5).

Hexazinone was not quantified in any of the 24 samples collected in the Tibagi River (PR) (Souza et al., 2019). Imidacloprid was found at concentrations between 0.01 and 0.02 μg L^{-1} in studies carried out in PR (Almeida et al., 2019; Souza et al., 2019), and it was not quantified in RS (von Ameln Lovison et al., 2021) (Figure 5).

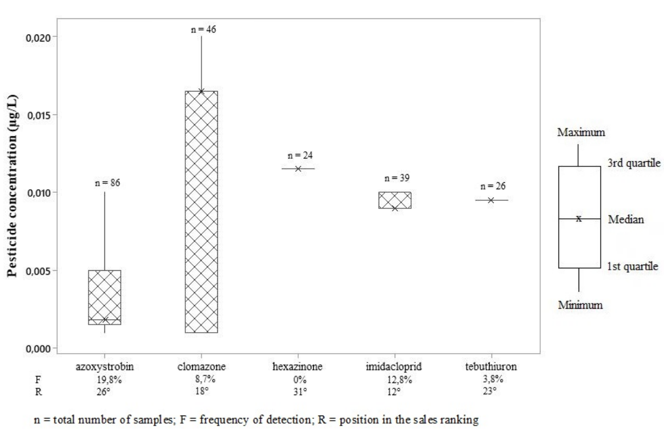


Figure 5 – Pesticide occurrence in Brazilian treated water.

Cypermethrin was not detected in any of the two samples collected in MG (Rodrigues et al., 2018). Studies related to tebuthiuron were conducted in PR (Souza et al., 2019) and SP (Monteiro et al., 2014); however, it was only quantified in the SP study (at a concentration of 0.01 μg L– 1, in filtered water). After treatment, tebuthiuron was at levels lower than LOQ (Monteiro et al., 2014).

Human health effects

Pesticides are considered highly toxic as they persist in the environment and tend to accumulate in organisms (Porter et al., 2018). In humans, the effects are diverse, such as cancer, malformation, and chromosomal alterations (Sabarwal et al., 2018). Cypermethrin, an endocrine disruptor (IARC, 2020b) that poses risks to the gastrointestinal system (USEPA, 2020a), is a potential human carcinogen (USEPA, 2016b). Ethephon can affect the nervous system, and thiophanate-methyl the endocrine and reproductive systems (USEPA, 2020a). Methomyl, although it can affect the urinary and immune systems (USEPA, 2020a), showed evidence of non-carcinogenicity in humans, as did hexazinone and tebuthiuron, which are non-carcinogenic (USEPA, 2020b). While it is not likely to be carcinogenic to humans, lambda-cyhalothrin is neurotoxic (USEPA, 2017). We did not find information on the other pesticides.

Due to the adverse effects pesticides can have on human health, it is necessary to remove these contaminants before water is distributed to the population (Mekonen et al., 2016). However, most pesticides are not effectively removed in conventional WTPs (Elfikrie et al., 2020). Therefore, advanced technologies are required, which must be chosen based on the characteristics of the contaminant (Rodriguez-Narvaez et al., 2017), such as zeolite coated with zero-valent iron nanoparticles (Rashtbari et al., 2020), gamma irradiation (Khedr et al., 2019), membrane filtration (Fini et al., 2019), advanced oxidative processes (Malakootian et al., 2020), adsorption (Salomão et al., 2021), and ozonation (Cruz-Alcalde et al., 2017).

A critical comparison between environmental occurrence and maximum acceptable values in drinking water

The compilation of pesticide occurrence data in Brazilian aquatic matrices showed that they are usually present at low concentrations. However, even small concentrations can be harmful to the health of the population since the toxic potential of pesticides can be increased through bioaccumulation and/or biomagnification (Guarda et al., 2020a). Thus, pesticide toxicity must be analyzed and reference values should be established for the Brazilian reality. The reference values for drinking water obtained from international water quality agencies and guidelines are shown in Table 1.

Four of the target pesticides of this study are listed in at least one of the water quality agencies/guidelines considered (Table 1).

Table 1 – Reference Values (μg/L), maximum concentration found, and margin of exposure in drinking water.

Pesticides	WHO	US EPA	EU	Australia	Canada	NZ	Surface water		Groundwater		Treated water	
							MC	MOE	MC	MOE	MC	MOE
Cypermethrin	*	-	-	200	-	-	ND		WS		ND	
Hexazinone	-	-	-	400	-	400	0.03	13333.3	0.11	3636.36	NQ	
Methomyl	*	-	-	20	-	-	ND		WS		WS	
Thiophanate methyl	-	-	-	90	-	-	WS		WS		WS	

EU: European Union; NZ: New Zealand; MC: Maximum concentration found; MOE: Margin of exposure; -guide value not presented/not included in the legislation; *pesticide has no guide value as it is unlikely to be found in drinking water; ND: not detected; NQ: not quantified; WS: without studies in the matrix of interest.
Source: WHO (2017), European Parliament (2020), Health Canada (2020), New Zealand (2020), NHMRC (2021) and USEPA (2021).

MOE calculation was not possible for pesticides that did not have a MAV (azoxystrobin, clomazone, ethephon, imidacloprid, lambda-cyhalothrin, MSMA, and tebuthiuron). It is worth mentioning that in some cases, even when a MAV was available, we could not calculate the MOE in cases with no detection/quantitation (cypermethrin and methomyl); when the only detectable concentration referred to an outlier; and when associated studies were lacking (thiophanate-methyl) (Table 1). It was only possible to establish the MOE for hexazinone and, for both surface water and groundwater, the values were above 10 (Table 1), indicating a small probability that adverse health effects will occur (USEPA, 2016a). This result is possibly due to concentrations as high as MAV were not reported and, for cases in which the occurrence was higher, as for imidacloprid, no associated MAV was found. Considering that none of the OV exceeded the reference values, and the analysis referring to the MOE showed a satisfactory result, it would be possible to infer that the concentrations found would not be harmful to the population's health. However, despite the occurrence at low levels having the potential to be dangerous, pesticides are not found alone in the environment, and the interaction between them and other substances can increase the adverse effects (Lei et al., 2015).

Conclusions

The systematic review showed more studies carried out on surface water, followed by treated water and groundwater. We noted that some pesticides had more studies than others, highlighting clomazone in the surface water matrix, and azoxystrobin in the treated water one. No monitoring data were found for ethephon and thiophanate-methyl, probably due to unfavorable environmental dynamics, which reduces their probability of environmental occurrence. Imidacloprid and hexazinone are the most likely to be found in aquatic matrices. However, the MOE of the Brazilian population to hexazinone showed that this compound was not found at levels that would potentially cause harm to the population's health. Nevertheless, it is recommended to continue monitoring this and other pesticides in the water and analyze the risks associated with a mixture of pesticides. We conclude that the target pesticides pose a low risk to human health. However, some objections must be raised, especially for cypermethrin, because it is a potential carcinogen. Due to MSMA's favorable environmental dynamics, it is necessary to monitor it. Furthermore, it is important to carry out toxicological studies for pesticides for which a MAV has not been found, such as imidacloprid.

Contribution of authors:

De Deus, B.C.T.: Conceptualization, Data Curation, Formal Analysis, Investigation, Methodology, Project Administration, Validation, Visualization, Writing — Original Draft, Writing — Review and Editing. Pereira, R.O.: Conceptualization, Formal Analysis, Methodology, Supervision, Validation, Writing – Review and Editing. Brandt, E.M.F.: Conceptualization, Formal Analysis, Methodology.

References

Acayaba, R.D.; Albuquerque, A.F.; Ribessi, R.L.; Umbuzeiro, G.A.; Montagner, C.C., 2021. Occurrence of pesticides in waters from the largest sugar cane plantation region in the world. Environmental Science and Pollution Research International, v. 28, (8), 9824-9835. https://doi.org/10.1007/s11356-020-11428-1.

Agência Nacional de Vigilância Sanitária (ANVISA), 2021. Monografias Autorizadas. Ministério da Saúde, Brasil (Accessed October 5, 2021) at:. https://www.gov.br/anvisa/pt-br/setorregulado/regularizacao/agrotoxicos/monografias/monografias-autorizadas-por-letra.

Almeida, M.B.; Madeira, T.B.; Watanabe, L.S.; Meletti, P.C.; Nixdorf, S.L., 2019. Pesticide determination in water samples from a rural area by multi-target method applying liquid chromatography-tandem mass spectrometry. Journal of the Brazilian Chemical Society, v. 30, (8), 1657-1666. https://doi.org/10.21577/0103-5053.20190066.

Amaral, A.M.B.; Gomes, J.L.C.; Weimer, G.H.; Marins, A.T.; Loro, V.L.; Zanella, R., 2018. Seasonal implications on toxicity biomarkers of loricariichthys anus (Valenciennes, 1835) from a subtropical reservoir. Chemosphere, v. 191, 876-885. https://doi.org/10.1016/j.chemosphere.2017.10.114.

Amaral, A.M.B.; Moura, L.K.; Pellegrin, D.; Guerra, L.J.; Cerezer, F.O.; Saibt, N.; Prestes, O.D.; Zanella, R.; Loro, V.L.; Clasen, B., 2020. Seasonal factors driving biochemical biomarkers in two fish species from a subtropical reservoir in southern Brazil: An integrated approach. Environmental Pollution, v. 266, part 3, 115168. https://doi.org/10.1016/j.envpol.2020.115168.

Américo-Pinheiro, J.H.P.; Cruz, C.; Aguiar, M.M.; Torres, N.H.; Ferreira, L.F.R.; Machado-Neto, J.G., 2019. Sublethal effects of imidacloprid in hematological parameters of tilapia (Oreochromis Niloticus). Water, Air, and Soil Pollution, v. 230, (8), 193. https://doi.org/10.1007/s11270-019-4256-0.

Américo-Pinheiro, J.H.P.; Machado, A.A.; Cruz, C.; Aguiar, M.M.; Ferreira, L.F.R.; Torres, N.H.; Machado-Neto, J.G., 2020. Histological changes in targeted organs of nile tilapia (Oreochromis Niloticus) exposed to sublethal concentrations of the pesticide carbofuran. Water, Air, and Soil Pollution, v. 231, (5), 228. https://doi.org/10.1007/s11270-020-04628-5.

Araújo, A.S., 2018. Comparação entre os padrões de potabilidade nacional e internacional quanto à presença de agrotóxicos. Specialization monograph, Instituto de Ciências Biológicas, Universidade Federal de Minas Gerais, Minas Gerais. Retrieved 2021-10-24, from https://repositorio.ufmg.br/handle/1843/BUOS-BCEGGQ.

Armas, E.D.; Monteiro, R.T.R.; Antunes, P.M.; Santos, M.A.P.F.; Camargo, P.B.; Abakerli, R.B., 2007. Diagnóstico espaço-temporal da ocorrência de herbicidas nas águas superficiais e sedimentos do rio corumbataí e principais afluentes. Química Nova, v. 30, (5), 1119-1127. https://doi.org/10.1590/s0100-40422007000500013.

Back, A.J.; Deschamps, F.C.; Santos, M.G.S., 2016. Ocorrência de agrotóxicos em águas usadas com irrigação de arroz no sul de Santa Catarina. Brazilian Journal of Environmental Sciences (Online), (39), 47-58. https://doi.org/10.5327/z2176-9478201611014.

Barizon, R.R.M.; Figueiredo, R.O.; Dutra, D.R.C.S.; Reginato, J.B.; Ferracini, V.L., 2020. Pesticides in the surface waters of the camanducaia river watershed, Brazil. Journal of Environmental Science and Health - Part B Pesticides, Food Contaminants, and Agricultural Wastes, v. 55, (3), 283-292. https://doi.org/10.1080/03601234.2019.1693835.

Belchior, D.C.V.; Saraiva, A.S.; Córdova, L.A.M.; Scheidt, G.N., 2014. Impactos de agrotóxicos sobre o meio ambiente e a saúde humana. Cadernos de Ciência & Tecnologia, v. 34, (1), 135-151.

Bhatt, P.; Huang, Y.; Zhang, W.; Sharma, A.; Chen, S., 2020. Enhanced cypermethrin degradation kinetics and metabolic pathway in *Bacillus Thuringiensis* Strain SG4. Microorganisms, v. 8, (2), 223. https://doi.org/10.3390/microorganisms8020223.

Bortoluzzi, E.C.; Rheinheimer, D.S.; Gonçalves, C.S.; Pellegrini, J.B.R.; Maroneze, A.M.; Kurz, M.H.S.; Bacar, N.M.; Zanella, R., 2007. Investigation of the occurrence of pesticide residues in rural wells and surface water following application to tobacco. Quimica Nova, v. 30, (8), 1872-1876. https://doi.org/10.1590/S0100-40422007000800014.

Bortoluzzi, E.C.; Rheinheimer, D.S.; Gonçalves, C.S.; Pellegrini, J.B.R.; Zanella, R.; Copetti, A.C.C., 2006. Contaminação de águas superficiais por agrotóxicos em função do uso do solo numa microbacia hidrográfica de Agudo, RS. Revista Brasileira de Engenharia Agrícola e Ambiental, v. 10, (4), 881-887. https://doi.org/10.1590/s1415-43662006000400015.

Brasil. Ministério da Saúde, 2021. Anexo XX da Portaria de Consolidação nº 5/2017, alterado pela Portaria GM/MS nº 888 de 2021. Diário Oficial da República Federativa do Brasil, Brasília.

Brasil. Presidência da República, Casa Civil, 1989. Lei nº 7.802, de 11 de julho de 1989. Diário Oficial da União, Brasília.

Caldas, S.S.; Bolzan, C.M.; Guilherme, J.R.; Silveira, M.A.K.; Escarrone, A.L.V.; Primel, E.G., 2013. Determination of pharmaceuticals, personal care products, and pesticides in surface and treated waters: method development and survey. Environmental Science and Pollution Research, v. 20, (8), 5855-5863. https://doi.org/10.1007/s11356-013-1650-9.

Carvalho, F.P., 2017. Pesticides, environment, and food safety. Food and Energy Security, v. 6, (2), 48-60. https://doi.org/10.1002/fes3.108.

Chao, H.P.; Lee, J.F.; Chiou, C.T., 2017. Determination of the Henry's Law constants of low-volatility compounds via the measured air-phase transfer coefficients. Water Research, v. 120, 238-244. https://doi.org/10.1016/j.watres.2017.04.074.

Cruz-Alcalde, A.; Sans, C.; Esplugas, S., 2017. Priority pesticides abatement by advanced water technologies: The case of acetamiprid removal by ozonation. Science of the Total Environment, v. 599-600, 1454-1461. https://doi.org/10.1016/j.scitotenv.2017.05.065.

Duarte, J.S.; Dores, E.F.G.C.; Villa, R.D., 2016. Microextração líquido-líquido dispersiva assistida por vortex e ultrassom aplicada à determinação de agrotóxicos triazinas, triazinonas e o triazol flutriafol em água. Química Nova, v. 39, (8), 925-931. https://doi.org/10.5935/0100-4042.20160110.

Elfikrie, N.; Ho, Y.B.; Zaidon, S.Z.; Juahir, H.; Tan, E.S.S., 2020. Occurrence of pesticides in surface water, pesticides removal efficiency in drinking water treatment plant and potential health risk to consumers in Tengi river basin, Malaysia. Science of the Total Environment, v. 712, 136540. https://doi.org/10.1016/j.scitotenv.2020.136540.

Elias, D.; Wang, L.; Jacinthe, P.A., 2018. A meta-analysis of pesticide loss in runoff under conventional tillage and no-till management. Environmental Monitoring and Assessment, v. 190, (2), 79. https://doi.org/10.1007/s10661-017-6441-1.

European Parliament, 2020. Directive (EU) 2020/2,184 of the European Parliament and of the Council of 16 December 2020 on the quality of water intended for human consumption (Accessed October 19, 2021) at:. https://eur-lex.europa.eu/eli/dir/2020/2184/oj.

Filizola, H.F.; Ferracini, V.L.; Sans, L.M.A.; Gomes, M.A.F.; Ferreira, C.J.A., 2002. Monitoring and evaluation of the risk of contamination by pesticide in surface water and groundwater in the Guaira region, Sao Paulo, Brazil. Pesquisa Agropecuária Brasileira, v. 37, (5), 659-667. https://doi.org/10.1590/S0100-204X2002000500011.

Fini, N.M.; Madsen, H.; Muff, J., 2019. The effect of water matrix, feed concentration and recovery on the rejection of pesticides using NF/RO membranes in water treatment. Separation and Purification Technology, v. 215, 521-527. https://doi.org/10.1016/j.seppur.2019.01.047.

Gaona, L.; Bedmar, F.; Gianelli, V.R.; Faberi, A.J.; Angelini, H., 2019. Estimating the risk of groundwater contamination and environmental impact of pesticides in an agricultural basin in Argentina. International Journal of Environmental Science and Technology, v. 16, (11), 6657-6670. https://doi.org/10.1007/s13762-019-02267-w.

Goss, D.W., 1992. Screening procedure for soils and pesticides for potential water quality impacts. Weed Technology, v. 6, (3), 701-708. https://doi.org/10.1017/S0890037X00036083.

Guarda, P.M.; Gualberto, L.S.; Mendes, D.B.; Guarda, E.A.; Silva, J.E.C., 2020a. Analysis of triazines, triazoles, and benzimidazoles used as pesticides in different environmental compartments of the Formoso river and their influence on biodiversity in Tocantins. Journal of Environmental Science and Health, Part B, v. 55, (9), 783-793. https://doi.org/10.1080/03601234.2020.1784667.

Guarda, P.M.; Pontes, A.M.S.; Domiciano, R.S.; Gualberto, L.S.; Mendes, D.B.; Guarda, E.A.; Silva, J.E.C., 2020b. Assessment of ecological risk and environmental behavior of pesticides in environmental compartments of the Formoso river in Tocantins, Brazil. Archives of Environmental Contamination and Toxicology, v. 79, (4), 524-536. https://doi.org/10.1007/s00244-020-00770-7.

Guarda, P.M.; Pontes, A.M.S.; Domiciano, R.S.; Gualberto, L.S.; Mendes, D.B.; Guarda, E.A.; Silva, J.E.C., 2020c. Determination of carbamates and thiocarbamates in water, soil and sediment of the Formoso river, TO, Brazil. Chemistry & Biodiversity, v. 17, (4), e1900717. https://doi.org/10.1002/cbdv.201900717.

Guo, F.; Endo, M.; Yamaguchi, T.; Uchino, A.; Sunohara, Y.; Matsumoto, H.; Iwakami, S., 2021. Investigation of clomazone-tolerance mechanism in a long-grain cultivar of rice. Pest Management Science, v. 77, (5), 2454-2461. https://doi.org/10.1002/ps.6274.

Gustafson, D.I., 1989. Groundwater ubiquity score: a simple method for assessing pesticide leachability. Environmental Toxicology and Chemistry, v. 8, (4), 339-357. https://doi.org/10.1002/etc.5620080411.

He, D.; Han, G.; Zhang, X.; Sun, J.; Xu, Y.; Jin, Q.; Gao, Q., 2022. Oxidative stress induced by methomyl exposure reduces the quality of early embryo development in mice. Zygote, v. 30, (1), 57-64. https://doi.org/10.1017/S0967199421000277.

Health Canada, 2020. Guidelines for Canadian Drinking Water Quality - Summary Table. Health Canada, Canada. (Accessed October 6, 2021) at:. https://www.canada.ca/en/health-canada/services/environmental-workplace-health/reports-publications/water-quality/guidelines-canadian-drinking-water-quality-summary-table.html.

Instituto Brasileiro do Meio Ambiente e dos Recursos Naturais Renováveis (IBAMA), 2021. Relatórios de comercialização de agrotóxicos. IBAMA (Accessed October 4, 2021) at:. http://www.ibama.gov.br/agrotoxicos/relatorios-de-comercializacao-de-agrotoxicos#historicodecomercializacao.

International Agency for Research on Cancer (IARC), 2020a. Monographs on the identification of carcinogenic hazards to humans. IARC (Accessed October 6, 2021) at:. https://monographs.iarc.fr/monographs-available/.

International Agency for Research on Cancer (IARC), 2020b. Report of the advisory group to recommend priorities for the IARC monographs during 2020–2024. IARC (Accessed October 6, 2021) at:. https://www.iarc.who.int/news-events/report-of-the-advisory-group-to-recommend-priorities-for-the-iarc-monographs-during-2020-2024/.

International Union of Pure and Applied Chemistry (IUPAC), 2020. PPDB A to Z Index. IUPAC, University of Hertfordshire (Accessed October 3, 2021) at:. https://sitem.herts.ac.uk/aeru/iupac/atoz.htm.

Khedr, T.; Hammad, A.A.; Elmarsafy, A.M.; Halawa, E.; Soliman, M., 2019. Degradation of some organophosphorus pesticides in aqueous solution by gamma irradiation. Journal of Hazardous Materials, v. 373, 23-28. https://doi.org/10.1016/j.jhazmat.2019.03.011.

Lei, M.; Zhang, L.; Lei, J.; Zong, L.; Li, J.; Wu, Z.; Wang, Z., 2015. Overview of emerging contaminants and associated human health effects. BioMed Research International, v. 2015, 404796. https://doi.org/10.1155/2015/404796.

López-Doval, J.C.; Montagner, C.C.; Alburquerque, A.F.; Moschini-Carlos, V.; Umbuzeiro, G.A.; Pompêo, M., 2017. Nutrients, emerging pollutants and pesticides in a tropical urban reservoir: Spatial distributions and risk assessment. Science of The Total Environment, v. 575, 1307-1324. https://doi.org/10.1016/j.scitotenv.2016.09.210.

Lorenzatto, L.B.; Silva, M.I.G.; Roman Junior, W.A.; Rodrigues Junior, S.A.; Sá, C.A.; Corralo, V., 2020. Exposição de trabalhadores rurais a organofosforados e carbamatos. Brazilian Journal of Environmental Sciences (Online), v. 55, (1), 19-31. https://doi.org/10.5327/z2176-947820200528.

Malakootian, M.; Shahesmaeili, A.; Faraji, M.; Amiri, H.; Martinez, S.S., 2020. Advanced oxidation processes for the removal of organophosphorus pesticides in aqueous matrices: A systematic review and meta-analysis. Process Safety and Environmental Protection, v. 134, 292-307. https://doi.org/10.1016/j.psep.2019.12.004.

Marchesan, E.; Sartori, G.M.S.; Avila, L.A.; Machado, S.L.O.; Zanella, R.; Primel, E.G.; Macedo, V.R.M.; Marchezan, M.G., 2010. Resíduos de agrotóxicos na água de rios da depressão central do estado do Rio Grande do Sul, Brasil. Ciência Rural, v. 40, (55), 1053-1059. https://doi.org/10.1590/S0103-84782010005000078.

Marchesan, E.; Zanella, R.; Avila, L.A.; Camargo, E.R.; Machado, S.L.O.; Macedo, V.R.M., 2007. Rice herbicide monitoring in two brazilian rivers during the rice growing season. Scientia Agricola, v. 64, (2), 131-137. https://doi.org/10.1590/s0103-90162007000200005.

Mekonen, S.; Argaw, R.; Simanesew, A.; Houbraken, M.; Senaeve, D.; Ambelu, A.; Spanoghe, P., 2016. Pesticide residues in drinking water and associated risk to consumers in Ethiopia. Chemosphere, v. 162, 252-260. https://doi.org/10.1016/j.chemosphere.2016.07.096.

Minitab, 2020. Identificação de outliers. Minitab (Accessed October 4, 2021) at:. https://support.minitab.com/pt-br/minitab/18/help-and-how-to/statistics/basic-statistics/supporting-topics/data-concepts/identifying-outliers/.

Moher, D.; Liberati, A.; Tetzlaff, J.; Altman, D.G., 2009. Preferred reporting items for systematic reviews and meta-analyses: The PRISMA statement. PLoS Medicine, v. 6, (7), e1000097. https://doi.org/10.1371/journal.pmed.1000097.

Montagner, C.C.; Sodré, F.F.; Acayaba, R.D.; Vidal, C.; Campestrini, I.; Locatelli, M.A.; Pescara, I.C.; Albuquerque, A.F.; Umbuzeiro, G.A.; Jardim, W.F., 2019. Ten years-snapshot of the occurrence of emerging contaminants in drinking, surface and ground waters and wastewaters from São Paulo state, Brazil. Journal of the Brazilian Chemical Society, v. 30, (3), 614-632. https://doi.org/10.21577/0103-5053.20180232.

Montagner, C.C.; Vidal, C.; Acayaba, R.D.; Jardim, W.F.; Jardim, C.S.F.; Umbuzeiro, G.A., 2014. Trace analysis of pesticides and an assessment of their occurrence in surface and drinking waters from the state of São Paulo (Brazil). Analytical Methods, v. 6, (17), 6668-6677. https://doi.org/10.1039/c4ay00782d.

Monteiro, R.T.R.; Silva, G.H.; Messias, T.G.; Queiroz, S.C.N.; Assalin, M.R.; Cassoli, D.R.; Alves, C.H.R.; Ferreira, A.C.; Blaise, C., 2014. Chemical and ecotoxicological assessments of water samples before and after being processed by a water treatment plant. Ambiente e Água, v. 9, (1), 445-458. https://doi.org/10.4136/ambi-agua.1292.

National Health and Medical Researsch Council (NHMRC), 2021. Australian Drinking Water Guidelines (2011). NHMRC (Accessed October 10, 2021) at:. https://www.nhmrc.gov.au/about-us/publications/australian-drinking-water-guidelines.

National Pesticide Information Center (NPIC), 2020. OSU Extension Pesticide Properties Database. NPIC (Accessed October 8, 2021) at:. http://npic.orst.edu/ingred/ppdmove.htm.

New Zealand, 2020. Guidelines for Drinking-Water Quality Management for New Zealand. New Zealand (Accessed October 10, 2021) at:. https://www.taumataarowai.govt.nz/assets/Uploads/Ministry-of-Health-drinking-water-datasheets/dwg_vol3_datasheets_-_chemical_and_physical_determinands-part_2-3_pesticides.docx.

Olisah, C.; Okoh, O.O.; Okoh, A.I., 2020. Occurrence of organochlorine pesticide residues in biological and environmental matrices in Africa: A two-decade review. Heliyon, v. 6, (3), e03518. https://doi.org/10.1016/j.heliyon.2020.e03518.

Oliveira, T.J.A.; Rodrigues, W., 2019. Spatial analysis of production structures in Brazilian midlands: Agribusiness clusters. Revista Econômica do Nordeste, v. 50, (1), 153-170.

Pérez, D.J.; Okada, E.; Gerónimo, E.; Menone, M.L.; Aparicio, V.C.; Costa, J.L., 2017. Spatial and temporal trends and flow dynamics of glyphosate and other pesticides within an agricultural watershed in Argentina. Environmental Toxicology and Chemistry, v. 36, (12), 3206-3216. https://doi.org/10.1002/etc.3897.

Pérez-Lucas, G.; El Aatik, A.; Vela, N.; Fenoll, J.; Navarro, S., 2021. Exogenous organic matter as strategy to reduce pesticide leaching through the soil. Archives of Agronomy and Soil Science, v. 67, (7), 934-945. https://doi.org/10.1080/03650340.2020.1768531.

Pérez-Lucas, G.; Vela, N.; El Aatik, A.; Navarro, S., 2019. Environmental risk of groundwater pollution by pesticide leaching through the soil profile. In: Larramendy, M.L.; Soloneski, S. (Eds.), Pesticides: use and misuse and their impact in the environment. IntenchOpen, London, p. 1-27.

Pignati, W.A.; Souza e Lima, F.A.N.; Lara, S.S.; Correa, M.L.M.; Barbosa, J.R.; Leão, L.H.C.; Pignatti, M.G., 2017. Distribuição espacial do uso de agrotóxicos no Brasil: Uma ferramenta para a vigilância em saúde. Ciência e Saúde Coletiva, v. 22, (10), 3281-3293. https://doi.org/10.1590/1413-812320172210.17742017.

Pinheiro, A.S.; Andrade, J.B., 2009. Development, validation and application of a sdme/gc-fid methodology for the multiresidue determination of organophosphate and pyrethroid pesticides in water. Talanta, v. 79, (5), 1354-1359. https://doi.org/10.1016/j.talanta.2009.06.002.

Porter, S.N.; Humphries, M.S.; Buah-Kwofie, A.; Schleyer, M.H., 2018. Accumulation of organochlorine pesticides in reef organisms from marginal coral reefs in South Africa and links with coastal groundwater. Marine Pollution Bulletin, v. 137, 295-305. https://doi.org/10.1016/j.marpolbul.2018.10.028.

Primel, E.G.; Milani, M.R.; Demoliner, A.; Niencheski, L.F.H.; Escarrone, A.L.V., 2010. Development and application of methods using SPE, HPLC-DAD, LC-ESI-MS/MS and GFAAS for the determination of herbicides and metals in surface and drinking water. International Journal of Environmental Analytical Chemistry, v. 90, (14-15), 1048-1062. https://doi.org/10.1080/03067310902962791.

Rashtbari, Y.; Américo-Pinheiro, J.H.P.; Bahrami, S.; Fazlzadeh, M.; Arfaeinia, H.; Poureshgh, Y., 2020. Efficiency of zeolite coated with zero-valent iron nanoparticles for removal of humic acid from aqueous solutions. Water, Air, and Soil Pollution, v. 231, (10), 514. https://doi.org/10.1007/s11270-020-04872-9.

Rodrigues, A.A.Z.; Neves, A.A.; Queiroz, M.E.L.R.; Oliveira, A.F.; Prates, L.H.F.; Morais, E.H.C., 2018. Optimization and validation of the salting-out assisted liquid-liquid extraction method and analysis by gas chromatography to determine pesticides in water. Eclética Química Journal, v. 43, (1), 11-21. https://doi.org/10.26850/1678-4618eqj.v43.1SI.2018.p11-21.

Rodriguez-Narvaez, O.M.; Peralta-Hernandez, J.M.; Goonetilleke, A.; Bandala, E.R., 2017. Treatment technologies for emerging contaminants in water: a review. Chemical Engineering Journal, v. 323, 361-380. https://doi.org/10.1016/j.cej.2017.04.106.

Sabarwal, A.; Kumar, K.; Singh, R.P., 2018. Hazardous effects of chemical pesticides on human health–cancer and other associated disorders. Environmental Toxicology and Pharmacology, v. 63, 103-114. https://doi.org/10.1016/j.etap.2018.08.018.

Salomão, G.R.; Américo-Pinheiro, J.H.P.; Isique, W.D.; Torres, N.H.; Cruz, I.A.; Ferreira, L.F.R., 2021. Diclofenac removal in water supply by adsorption on composite low-cost material. Environmental Technology (United Kingdom), v. 42, (13), 2095-2111. https://doi.org/10.1080/09593330.2019.1692078.

Sanford, R.F.; Pierson, C.T.; Crovelli, R.A., 1993. An objective replacement method for censored geochemical data. Mathematical Geology, v. 25, (1), 59-80. https://doi.org/10.1007/BF00890676.

Severo, E.S.; Marins, A.T.; Cerezer, C.; Costa, D.; Nunes, M.; Prestes, O.D.; Zanella, R.; Loro, V.L., 2020. Ecological risk of pesticide contamination in a brazilian river located near a rural area: a study of biomarkers using zebrafish embryos. Ecotoxicology and Environmental Safety, v. 190, 110071. https://doi.org/10.1016/j.ecoenv.2019.110071.

Sharma, A.; Kumar, V.; Shahzad, B.; Tanveer, M.; Sidhu, G.P.S.; Handa, N.; Kohli, S.K.; Yadav, P.; Bali, A.S.; Parihar, R.D.; Dar, O.I.; Singh, K.; Jasrotia, S.; Bakshi, P.; Ramakrishnan, M.; Kumar, S.; Bhardwaj, R.; Thukral, A.K., 2019. Worldwide pesticide usage and its impacts on ecosystem. SN Applied Sciences, v. 1, 1446. https://doi.org/10.1007/s42452-019-1485-1.

Sharma, K.K.; Tripathy, V.; Mohapatra, S.; Matadha, N.Y.; Pathan, A.R.K.; Sharma, B.N.; Dubey, J.K.; Katna, S.; George, T.; Tayade, A.; Sharma, K.; Gupta, R.; Walia, S., 2021. Dissipation kinetics and consumer risk assessment of novaluron + lambda-cyhalothrin co-formulation in cabbage. Ecotoxicology and Environmental Safety, v. 208, 111494. https://doi.org/10.1016/j.ecoenv.2020.111494.

Silva, D.R.O.; Avila, L.A.; Agostinetto, D.; Bundt, A.C.; Primel, E.G.; Caldas, S.S., 2011. Ocorrência de agrotóxicos em águas subterrâneas de áreas adjacentes a lavouras de arroz irrigado. Química Nova, v. 34, (5), 748-752. https://doi.org/10.1590/S0100-40422011000500004.

Silva, D.R.O.; Avila, L.A.; Agostinetto, D.; dal Magro, T.; Oliveira, E.; Zanella, R.; Noldin, J.A., 2009. Pesticides monitoring in surface water of rice production areas in southern Brazil. Ciência Rural, v. 39, (9), 2383-2389. https://doi.org/10.1590/s0103-84782009000900001.

Singh, N.S.; Sharma, R.; Parween, T.; Patanjali, P.K., 2018. Pesticide contamination and human health risk factor. In: Oves, M.; Khan, M.Z.; Ismail, I.M.I. (Eds.), Modern age environmental problems and their remediation. Springer International Publishing, Cham, pp. 49-68.

Souza, L.F.C.B.; Montagner, C.C.; Almeida, M.B.; Kuroda, E.K.; Vidal, C.; Freire, R.L., 2019. Determination of pesticides in the source and drinking waters in Londrina, Paraná, Brazil. Semina: Ciências Agrárias, v. 40, (3), 1153-1164. https://doi.org/10.5433/1679-0359.2019v40n3p1153.

Souza, R.M.; Seibert, D.; Quesada, H.B.; Bassetti, F.J.; Fagundes-Klen, M.R.; Bergamasco, R., 2020. Occurrence, impacts and general aspects of pesticides in surface water: A review. Process Safety and Environmental Protection, v. 135, 22-37. https://doi.org/10.1016/j.psep.2019.12.035.

Sposito, J.C.V.; Montagner, C.C.; Casado, M.; Navarro-Martín, L.; Solórzano, J.C.J.; Piña, B.; Grisolia, A.B., 2018. Emerging contaminants in brazilian rivers: Occurrence and effects on gene expression in zebrafish (Danio rerio) embryos. Chemosphere, v. 209, 696-704. https://doi.org/10.1016/j.chemosphere.2018.06.046.

Teixeira, M.F.F.; Silva, A.A.; Nascimento, M.A.; Vieira, L.S.; Teixeira, T.P.M.; Souza, M.F., 2018. Effects of adding organic matter to a red-yellow latosol in the sorption and desorption of tebuthiuron. Planta Daninha, v. 36, 1-8. https://doi.org/10.1590/S0100-83582018360100095.

Tuelher, E.S.; Silva, E.H.; Rodrigues, H.S.; Hirose, E.; Guedes, R.N.C.; Oliveira, E.E., 2018. Area-wide spatial survey of the likelihood of insecticide control failure in the neotropical brown stink bug euschistus heros. Journal of Pest Science, v. 91, (2), 849-859. https://doi.org/10.1007/s10340-017-0949-6.

Uçkun, A.A.; Öz, O.B., 2021. Evaluation of the acute toxic effect of azoxystrobin on non-target crayfish (Astacus leptodactylus eschscholtz, 1823) by using oxidative stress enzymes, atpases and cholinesterase as biomarkers. Drug and Chemical Toxicology, v. 44, (5), 550-557. https://doi.org/10.1080/01480545.2020.1774604.

United Nations Environment Programme (UNEP), 1999. Chemical risk assessment: human risk assessment, environmental risk assessment and ecological risk assessment. UNEP (Accessed October 7, 2021) at:. https://apps.who.int/iris/handle/10665/66398.

United States Environmental Protection Agency (USEPA), 2016a. Contaminant Information Sheets (CISs) for the Final Fourth Contaminant Candidate List (CCL4). USEPA (Accessed October 7, 2021) at:. https://www.epa.gov/ccl/contaminant-candidate-list-4-ccl-4-0.

United States Environmental Protection Agency (USEPA), 2016b. Cypermethrin. USEPA (Accessed October 16, 2021) at:. https://iris.epa.gov/static/pdfs/0380_summary.pdf.

United States Environmental Protection Agency (USEPA), 2017. Regulations. USEPA (Accessed 10 October, 2021) at:. https://www.regulations.gov/document/EPA-HQ-OPP-2010-0480-0299.

United States Environmental Protection Agency (USEPA), 2020a. IRIS Assessments. USEPA (Accessed October 8, 2021) at:. https://iris.epa.gov/AtoZ/?list_type=alpha.

United States Environmental Protection Agency (USEPA), 2020b. IRIS Advanced Search. USEPA (Accessed October 8, 2021) at:. https://cfpub.epa.gov/ncea/iris/search/index.cfm.

United States Environmental Protection Agency (USEPA), 2021. National Primary Drinking Water Regulations. USEPA (Accessed October 15, 2021) at:. https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations.

Vieira, C.E.D.; Costa, P.G.; Lunardelli, B.; Oliveira, L.F.; Cabrera, L.C.; Risso, W.E.; Primel, E.G.; Meletti, P.C.; Fillmann, G.; Martinez, C.B.R., 2016. Multiple biomarker responses in Prochilodus lineatus subjected to short-term in situ exposure to streams from agricultural areas in southern Brazil. Science of the Total Environment, v. 542, part A, 44-56. https://doi.org/10.1016/j.scitotenv.2015.10.071.

Vieira, M.G.; Steinke, G.; Arias, J.L.O.; Primel, E.G.; Cabrera, L.C., 2017. Avaliação da contaminação por agrotóxicos em mananciais de municípios da região sudoeste do Paraná. Revista Virtual de Química, v. 9, (5), 1800-1812. https://doi.org/10.21577/1984-6835.20170105.

Vigiagua, 2020. Revisão da norma de potabilidade da água para consumo humano. Vigiagua (Accessed 16 October, 2021) at:. https://jornalismosocioambiental.files.wordpress.com/2020/04/documento-de-contextualizac3a7c3a3o.pdf.

Von Ameln Lovison, O.; Jank, L.; Souza, W.M.; Guerra, R.R.; Lamas, A.E.; Ballestrin, R.A.C.; Hein, C.S.M.; Silva, T.C.B.; Corção, G.; Martins, A.F., 2021. Identification of pesticides in water samples by solid-phase extraction and liquid chromatography-electrospray ionization mass spectrometry. Water Environment Research, v. 93, (11), 2670-2680. https://doi.org/10.1002/wer.1621.

Wahlbrinck, M.G.; Bica, J.B.; Rempel, C., 2017. Percepção dos agricultores do município de imigrante (RS) sobre os riscos da exposição a agrotóxicos. Brazilian Journal of Environmental Sciences (Online), (44), 72-84. https://doi.org/10.5327/z2176-947820170128.

World Health Organization (WHO), 2017. Guidelines for Drinking-Water Quality: Fourth Edition Incorporating the First Addendum, WHO, Geneva (Accessed 14 October, 2021) at:. https://www.who.int/publications/i/item/9789241549950.

Yang, D.; Donovan, S.; Black, B.C.; Cheng, L.; Taylor, A.G., 2018. Relationships between compound lipophilicity on seed coat permeability and embryo uptake by soybean and corn. Seed Science Research, v. 28, (3), 229-235. https://doi.org/10.1017/S096025851800017X.

Zanella, R.; Primel, E.G.; Machado, S.L.O.; Gonçalves, F.F.; Marchesan, E., 2002. Monitoring of the herbicide clomazone in environmental water samples by solid-phase extraction and high-performance liquid chromatography with ultraviolet detection. Chromatographia, v. 55, (9-10), 573-577. https://doi.org/10.1007/BF02492903.