





Herbicide Residues in Water Resources: A Scoping Review



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Abstract

Several recent studies have focused on leaching pesticides from agricultural soils into surface and groundwater resources during irrigation. As a result, information about herbicide residues in water was necessary for conserving related resources. This study provided an overview of monitoring herbicides in water resources worldwide. In this scoping review, five databases were searched for publications (1990 to April 2021), including Scopus, PubMed/Medline, Cochrane library, Embase, and Web of Science. Among the 394 identified articles, 17 papers were selected for inclusion. Most of these studies have been conducted in regions with low herbicide concentrations, including Spain, Greece, Canada, Brazil, Hungary, Malawi, Portugal, Lesotho, Germany, Serbia, and the USA. The high-level alachlor, metolachlor, atrazine, metribuzin, and simazine herbicides in groundwater were detected in Portugal (0.4-13 µg/L). An overview of studies demonstrated that herbicides are widely used in water resources, and surface waters are more contaminated than groundwaters.

Keywords: Herbicide, water resources, Surface water, Agriculture activity

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1. Introduction

Humans have used various methods to control pests that threaten food and health throughout history. However, due to the demand for agricultural food products and rapid population growth, toxins and chemical struggles now play a significant role in protecting plants from destructive factors (1). In recent years, the introduction of new herbicide families, which have low consumption per hectare, low toxicity for mammals, and the ability to be absorbed through root and air organs, has quickly been considered by *agricultural producers*. As a result, chemical pesticides are further employed compared to other control methods (2). Herbicides are the most widely applied types of agricultural pesticides, and their use results in environmental pollution that threatens human and ecosystem health. To minimize the adverse effects of herbicides on the environment while optimizing agricultural activities, it is essential to understand their behavior in the environment (3).

As a result, the lack of desired long-term outcomes has adverse effects on the environment, the farmer's health, and the community. Despite various strategies to reduce harmful factors, chemical pesticides have received extensive attention (4). Statistically, there are more than 500 000 cases of acute pesticide poisoning every year, resulting in 20 000 deaths. In developed countries, poisoning cases are generally 13 times higher than in industrialized nations, indicating 85% of global pesticide consumption (5). No pesticide is safe and harmless for humans. The health risks of pesticides can be reduced with proper use and observance of health principles (2,6,7).

Degradation of herbicides in different environments results from biological and chemical processes. Nonetheless, environmental factors such as physical and chemical properties, acidity, temperature, moisture, and soil texture of the herbicides play a more significant role in comparison to other factors. To predict the effects of

herbicides on weed control, damage to future crops, and their durability, it is essential to study the quantitative and qualitative impacts of the environmental fate of herbicides, as well as to determine the potential transfer of these toxins to adjacent environments such as surface and groundwater. Moreover, it is of necessity to determine whether they can adversely affect other organisms and to find cost-effective methods for removing this contaminant. Regarding the environment, different researchers have focused on studying the behavior of agricultural herbicides (2,6,7).

Surface water is contaminated by chemical, physical, and biological agents in most countries. Different requirements and variables exert a role in managing water resources. Water resource monitoring is one of the most critical variables (8), and monitoring water quality is vital for protecting human health and the environment. Generally, water resource quality management can be divided into three main areas including prevention, monitoring, and control. The preventive stage involves using a tool such as an environmental impact assessment for land use planning to ensure that all necessary steps are taken to minimize pollution capacity and water quality degradation (9). During the monitoring phase, plans and activities are implemented to measure and assess water quality at different times. Finally, this control contains enforcement measures to prevent water pollution (10).

2. Methods

2.1. Design

This scoping review followed the Preferred Reporting Items for Systematic Reviews and Meta-analyses (PRISMA) and PRISMA extension for scoping study (PRISMA-ScR) criteria (11,12).

2.2. Objectives

This study aimed at identifying selective herbicides and conducting a systematic scoping review of the literature of herbicides to identify their harmful effects on water resources.

2.3. Herbicides Selection

Part I aimed to identify the applied herbicides, along with their type, and number. Hence, it is based on the nature of agricultural products that lead to pollution in water resources. To this end, several steps were used as follows:

1. Identifying agriculture crops sprayed with herbicides
2. Identifying the main chemicals used for crops by searching for herbicides

Identifying selected herbicides (online search <https://www.corteva.ca/en/label-finder.html>) with the hazard risk for water resources and humans

It should be noted that early herbicide choices were based on their Globally Harmonized System of

Classification (GHS) hazard statement and their toxicity in water resources and humans (Tables 1 and 2).

2.4. Search Strategy

Articles were separately searched for each herbicide. Following the search, screening, and qualitative evaluation of related studies during a scoping review, the final synthesis included 28 articles from different databases, but only 17 of them met the inclusion criteria. The search for herbicides was combined with some key terms including “herbicides”, or “residual pesticides”, and “water resources”, or “water pollution”. The above search was combined with AND, the key search terms for surface water, groundwater, agricultural runoff, or water to focus on water resources. This review was collected from various electronic sources including Scopus, PubMed/Medline, ISI Web of Science, Embase, and Cochrane Library. The inclusion criteria were articles published between 1980 and January 2021. In common studies of pesticides, there are at least three herbicides in water resources.

2.5. Data Handling, Management, and Analysis

The obtained data from the included studies were the year of study, study sites, type of study, herbicide residues, type of water resources, and concentration in different sites. Health studies were removed if they did not simultaneously address several herbicides in water and related diseases.

3. Results and Discussion

3.1. Herbicide Literature

The initial search with 28 articles was investigated in Scopus, PubMed/Medline, ISI Web of Science, Embase, and Cochrane Library. The inclusion criteria were published articles (between 1980 and June 2021) on monitoring and/or herbicide residues. At least three herbicides, agricultural runoff, surface water, and groundwater were selected during the common studies of pesticides. Moreover, the intended data included only English language articles focusing on monitoring and studies with full-texts available online - either free or via an institution's subscription. Articles reporting, monitoring pesticides (fungicides, herbicides, and insecticides) with two herbicides, pesticide monitoring in sediment, soil, and plants, and investigation of the herbicide, along with unpublished data were excluded from the review. A total of 17 studies were reviewed (Figure 1), which were conducted in Spain (n=4), Canada (n=1), Greece (n=1), Brazil (n=3), Malawi (n=1), Hungary (n=1), Serbia (n=1), Germany (n=1), Portugal (n=2), the USA (n=1), and Lesotho (n=1). Water resources worldwide include drinking water, well water, surface water, groundwater, and coastal ecosystems.

Four herbicides with the highest risk to humans and the environment were chosen, including acetochlor,

Table 1. Summary of Studies

Reference	Years	Types of Tested Herbicides	Location	Concentration Range (µg/L)	Frequency (%)	Type Source
(13)	2000	Chlortoluron, atrazine, terbutryn, alachlor, diflufenican, and fluazifop-butyl	Spain	0-2 µg/L, 2-5, and ≥ 5 µg/L	45	Surface and groundwater
(14)	2019	Eptc , Molinate, propachlor, trifluralin, atrazine, terbuthylazine, dimethenamid-P, acetochlor, pirimiphos-methyl, metolachlor, pendimethalin, quinalphos, quizalofop-ethyl, fluometuron, and tebufenpyrad	Greece	0.045-0.255 µg/mL	25.7	Surface water
(15)	2014	Glyphosate	Canada	42	13.2	Ground water
(16)	2007	Clomazone, propanil, and quinclorac	Brazil	0.58-12.9	40	Surface water
(17)	2015	Metribuzin, acetochlor, metolachlor, atrazine, trifluralin, simazine, propachlor, terbuthylazine, and tefluthrin	Hungary	5- 10000	2-51	Surface and groundwater
(18)	2013	Atrazine and metolachlor	Malawi	2-10 µg/mL	15-38	Surface and groundwater
(19)	2003	Alachlor, metolachlor, atrazine, metribuzin, and simazine	Portugal	0.4-13 µg/L	Atrazine (64), simazine (45), and alachlor (25)	Surface and groundwater
(3)	2014	Atrazine and metolachlor-desethylatrazine	Lesotho	25-50	-	-
(20)	2017	Terbuthylazine , metolachlor, atrazine, simazine, deisopropylatrazine, metribuzin, fluometuron, acetochlor, and chlortoluron,	Spain	0.5	65	Surface and groundwater
(21)	2013	Butachlor, propanil, and pretilachlor	Germany	0-1 µg/L	27.5, 68.9,2.8	-
(22)	2007	Pendimethalin, atrazine, metolachlor, and alachlor	Portugal	0.002-18	13, 9	Groundwater
(23)	2007	Atrazine, simazine, and clomazone,	Brazil	0.13-1.88 µg/L	25-50	well
(24)	2013	Metolachlor, terbuthylazine, carbendazim, atrazine, and acetochlor	Serbia	110-200	-	Surface water
(25)	2003	Imazine, metribuzin, metolachlor, trifluralin, atrazine, and two metabolites of atrazine, de-isopropyl atrazine and deethylatrazine	Brazil	0.14-1.7 µg/L	13-48	Groundwater
(26)	2019	Atrazine, alachlor, and trifluralin	USA	80.1-232.1	12-82.5	Agriculture
(27)	2000	Hlortoluron, atrazine, terbutryn, alachlor, diflufenican, and fluazifop-butyl	Spain	0.07-0.71 µg/L	69	-
(28)	2016	Terbuthylazine and oxyfluorfen	Spain	-	0.53	Surface water

metolachlor, atrazine, and terbuthylazine. Herbicide concentration varies depending on environmental variables such as oxygen, soil type, pH, and microbial activity. All herbicides were determined by their strong dependence on soil and water (<https://pubchem.ncbi.nlm.nih.gov>), the details of which are provided in Tables 1 and 2. The general specification of the literature review is presented in Table 1.

Herbicides are extensively used in most countries for killing weeds. New herbicide families have recently been introduced to agricultural producers due to their numerous advantages, including low utilization per hectare, low toxicity to mammals, and the absorption of water through branches and roots (18,29). Agricultural growth and diversity of pests have increased the number of pesticides, contaminating water resources with herbicides. Pesticides and fertilizers from different soil layers are removed to groundwater by the irrigation of agricultural lands. Thus, groundwater quality monitoring is of great importance in this regard (30). It is known that surface waters have a higher residual pesticide concentration compared to groundwater. Surface waters

were more vulnerable to pollution due to the higher percentage of detectable herbicides during the application period. Pollution in these waters was more persistent due to the slower groundwater dynamics and the decreasing half-life of herbicides below the surface layer (25).

Climatic conditions such as amount, intensity, and durability of rainfall, especially at the time of herbicide application, are the most important factors determining the runoff volume and agricultural operations such as plant, herbicide volume, application time, and soil factors

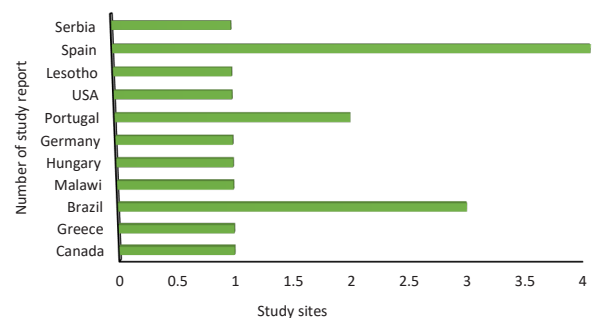


Figure 1. Study Reports on Herbicides Monitoring 18 Study Sites From 1990 to 2021

Table 2. Types of Herbicides and Their Permissible Levels in Water

Types of Tested Herbicides	Permissible Concentration in Water	Herbicide Type	Permissible Concentration in Water
Chlortoluron	0.1 µg/L	Carbendazim	No criteria set
Atrazine	0.003 ppm	Tefluthrin	No criteria set
Terbutryn	0.34 µg/L	Des-ethyl atrazine	
Alachlor	0.002 ppm	Uthylazine	
Diflufenican	No criteria set	Chlorotoluron	
Fuazifop-buty	No criteria set	Diisopropyl	
Eptc	No criteria set	Fluometuron	
Moline	No criteria set	Metribuzin,	The USEPA has set a lifetime health advisory of 175 µg/L. Several states have developed guidelines for metribuzin in drinking water (61), ranging from 1.0 µg/L (Illinois) to 25 µg/L (Wisconsin) to 175 µg/L (Kansas).
Trifluralin,	No criteria set	Deethylerb	
Propachlor	No criteria set	Deisopropylatrazine	
Terbuthylazine	No criteria set	Deethylatrazine	
Dimethenamid	No criteria set	Oxyfluorfen	No criteria set
Acetochlor	Unknown	Hlortoluron	No criteria set
Tebufenpyrad		Terbutryn	
Fluometuron	Accordingly, a long-term health advisory of 5.3 mg/L and a lifetime health advisory of 0.09 mg/L have been calculated	Metolachlor	The USEPA has set a lifetime health advisory of 10 µg/L. Several states have developed guidelines for metolachlor in drinking water ranging from 1.0 µg/L (Illinois) to 17.5 µg/L (Kansas) to 25 µg/mL (Wisconsin).
Quizalofop-ethyl	No criteria set	Fluazifop-butyl	No criteria set
Quinalphos	No criteria set	Diflufenican	No criteria set
Pendimethalin	No criteria set	Clomazone	-
Glyphosate	The USEPA has developed data on glyphosate, including a no-observed adverse effect level of 10 mg/kg/d. This corresponds to a drinking water equivalent level of 3.5 mg/L from which a lifetime health advisory of 0.7 mg/L was derived. California set a guideline of 0.5 mg/L for drinking water	Trifluralin	No-observed adverse effect level of 0.0125 mg/kg/d has been calculated by EPA, and a long-term health advisory of 5.3 mg/L and a lifetime health advisory of 0.09 mg/L have been calculated accordingly.
Pirimiphos-methyl	No criteria set	Metribuzin	The USEPA has set a lifetime health advisory of 175 µg/L. Several states have developed guidelines for metribuzin in drinking water (61) ranging from 1.0 µg/L (Illinois) to 25 µg/L (Wisconsin) to 175 µg/L (Kansas).
Propanil	The former USSRUNEP/IRPTC project has set a MAC in water bodies used for domestic purposes of 0.1 mg/L	Simazine	No criteria set
Quinclorac	No criteria set	Butachlor	
Pretilachlor			
Pendimethalin	No criteria set		

Note. USEPA: United States Environmental Protection Agency; MAC: Maximum permissible concentration.

such as soil type and land slopes affect the runoff volume. Herbicidal properties including stability, solubility, and vapor pressure can also affect the runoff potential. In general, long-lived herbicides have a more significant potential for runoff (28).

Herbicides are emitted with water flow on the soil surface and can penetrate groundwater, depending on their type. The release of herbicides and the vertical flow of water reduces their effectiveness in combating

target agents (weeds). On the other hand, groundwater infiltration provides the ground for their pollution. The amount of herbicide leaching is determined by the physicochemical properties of herbicides, including adsorption and excretion capacity, physical properties of soil, and water flow rate. Herbicides with wide applications have exhibited the highest frequency among the studies (28). For example, the triazine family (Atrazine, simazine, and cyanazine) and chloroacetamide herbicide family

(alachlor, metolachlor) and 2,4-D are herbicides that can produce groundwater contamination. There are four common ways to move herbicides in the soil as follows:

1. Through insoluble particles
2. Through the soil solution
3. Isolated soil colloids
4. In volatile herbicides through the gas phase of the porous soil (31).

The most common method is the transfer of herbicides through soil solutions in mass flow. The relative contribution of ways, in addition to herbicidal properties, is determined by the rainfall and soil factors. Heavy rainfall shortly after spraying increases leaching, which is especially important for herbicides (e.g., phenoxy), which have a low absorption capacity. Rainfall patterns immediately after application have an essential effect on leaching. Additionally, the herbicide characteristic and structure play a crucial role in its transfer. Herbicides with polar forms have more water solubility and higher leaching potential (32). The soil suspension, surface water flow, soil particles, and water movement remove herbicides from the area. Herbicides can be expelled by evaporation and volatility in case of their use. Physicochemical, biological, and chemical processes determine the fate of herbicides after they are sprayed on target areas. Runoff plays a significant role in the losses of herbicides in soils with high permeability and herbicides with low adsorption capacity and high solubility (greater than 10 mg/L). In soils with low penetration coefficients or hydrophobic herbicides (with a solubility of less than 1 mg/L), most water is lost through surface soil sediments (31,32).

In Spain, six rainfall periods were recorded with the maximum rainfall (55 mm) and 107 days after spraying, indicating the importance of high solubility herbicides in water (28). The percentage of the consumed terbuthylazine and oxyfluorfen in runoff waters during the whole recovery period was 0.46%. Most of these observed rainfall distributions were from the Mediterranean, characterized by low and high precipitation intensity rates. A pesticide with low water solubility and high sorption (e.g., oxyfluorfen) has a lower risk of leaching through the soil. This study showed that these herbicides were exposed to runoff transport. As a result, runoff from these sediments can reach the Guadeloupe River Basin (28).

There was a correlation between herbicides in surface and groundwater and agricultural applications. Pesticide residues have been detected in water, soil, and sediment in the past. As a result of their proximity to suitable locations, these environments were more likely to contain herbicides. Consequently, the pollution may reach larger canals used for drinking, other household purposes, and aquaculture (25). Given that pesticides are applied to topsoil, precipitation can carry their residues to ponds, lakes, creeks, and rivers. In the root

zone, pesticides can spill into porous media and be treated by underground aquifers. According to research, drinking water and agriculture were the most extensive resources (33). Thirteen herbicides were found during the monitoring study of the Louros River. Most of the detected toxins were quizalofop-ethyl, trifluralin, and pendimethalin. Among these toxins, the order of the frequency of falls was as tebufenpyrad > quizalofop ethyl > pendimethalin > propachlor > metolachlor > trifluralin > eptc > dimethenamid-P > acetochlor > terbuthylazine > atrazine > fluometuron. The toxins frequency and mean concentration showed that they were probably most widely applied and easily transferred in the Louros River. These differences can be attributed to the consumption, high polarity, and persistence of herbicides compared to other types of pesticides reported in other recent studies (14, 20). The highest concentration of tebufenpyrad was detected in all stations and seasons with a frequency of 82.85%, indicating that most consumed products were fruits, olives, corn, alfalfa, and cotton. In previous monitoring studies, atrazine, meta chlorines, molybdenum, and trifluoroaniline were detected at mean concentrations ranging from 13.8 to 69.6 ng/L. Considering that herbicides were regularly used in agriculture, they were washed into the Lorus River during rainy seasons. Pesticides were introduced into rivers and groundwater based on the timing and intensity of rainfalls. The increased concentration in the study area is in line with the result of this factor (14).

More than 2000 surface, ground, and raw water samples in Hungary were examined for herbicide residues during 1990-2015. The percentages of these herbicides were 6 (atrazine), 4 (acetochlor), 1.5 (propisochlor), 1.5 (metolachlor), 1 (diazinon), and 1 (2,4-D). Over 100 000 ng/L of atrazine and isoproturon were observed in the above-mentioned study (17). Atrazine was primarily used as an herbicide in corns. Former herbicide producers have been linked to two sources of industrial pollutions. Herbicides can negatively affect surface water resources, mainly when applied to water-soluble materials. In addition, herbicides in raw drinking water have been observed in large surface waters. The low solubility in water and lower concentration of other herbicides resulted in fewer herbicides (17).

Atrazine and acetochlor represented the highest levels in surface water and groundwater at 8240 and 13950 ng/L, as well as 7540 and 10070 ng/L, respectively (17). Glyphosate and aminomethylphosphonic acid (AMPA) were among the herbicides that were found in urban areas, but there was little information on their presence in urban groundwater. In Riparian, the highest concentration of glyphosate was 42 ng/L and 2870 ng/L AMPA. However, APA may also originate from wastewater (15). Riparian areas have short and shallow groundwater flow paths. Considering the above description and the possibility of

adsorption and degradation, glyphosate was primarily found in shallow groundwater pathways (excluding those associated with river inputs). However, some of this material was also found in deep-flow ways (15).

A significant correlation was observed between glyphosate and AMPA, indicating a direct link between the two chemicals. The Burlington groundwater samples had the highest concentrations of glyphosate and AMPA. Research on glyphosate residues in groundwater has mainly focused on agricultural areas. This was the first study to examine glyphosate residues in urban areas, particularly in riparian groundwater. Glyphosate and AMPA were detected in groundwater samples at 4 of 5 locations and in more than 10% of the 281 samples. In some urban streams, riparian groundwater may contain glyphosate and AMPA, contributing to the pesticide load of the flow (15).

In Portuguese agricultural areas, herbicides have been found in surface and groundwater. Alachlor, atrazine, metolachlor, metribuzin, and simazine were detected with maximum concentrations of 13, 30, 56, 1.4, and 0.4 mg/L, respectively. Herbicide levels in forest land areas were below the detection limit. According to reports (19), the global analysis of the Tejo River demonstrated no change during 1983-1993 and was below the maximum permissible concentration (MAC, 0.1 mg/L). Pesticide levels in the water were the highest in the spring after maize and rice had been treated with pesticides. It was observed that atrazine, simazine and chlorfenvinphos residues were higher than maximum acceptable limits in the spring. Although it was not confirmed as a trend for maintaining high values, the annual average concentration of these compounds was well below the MAC (19).

The average concentrations ($\mu\text{g/L}$) of clomazone, propanil, and quinclorac were 1.34, 0.86, 2.79-2.17, 5.66, and not detection (ND). during 2000-2001, 2001-2002, and 2002-2003 in the Vacacaí-Mirim River, respectively. Furthermore, 38, 20, and 40% of samples were contaminated with herbicides at least once during the first, second, and third rice growing seasons, respectively. Rainfall determines the concentration of herbicides during different years (16). The atrazine concentration was higher than 0.1 $\mu\text{g/L}$, twice as high as the alachlor concentration. According to the groundwater ubiquity score (GUS) index, atrazine is a potential leacher, while alachlor is a transient and stable leacher (22). Environmental processes gradually eliminate a herbicide when it enters the environment. Degradation processes determine herbicide fate and are divided into physical (adsorption by the soil and plant, leaching, runoff, and evaporation) and biochemical (biodegradation, hydrolysis, optical degradation, and oxidation-reduction) processes (31). Herbicide uptake is also affected by the molecular structure, soil acidity, and solute concentration. The solubility of herbicides in water increases when

their polarity represents an increase, and they become inaccessible to soil components. Soil acidity affects herbicides with acidic or weakly alkaline properties. For example, when the pH is less than 6, 2,4-D is nonionic, but it is ionic when greater than six. Considering that soil particles have a negative charge, their absorption at pH less than six will be more excellent. Alkaline compounds such as triazines can absorb protons under acidic conditions, thus a decrease in pH affects the amount and strength of adsorption in the soil. Therefore, acidic soil conditions reduce the ability of ionizable herbicides to absorb protons (31).

Herbicides such as methoxychlor, terbuthylazine, carbendazim, atrazine, and acetochlor have been discovered in the basin of the Danube River of Serbia. In this study, five sampling sites were used, including the Danube (S3-S7) and its tributaries Tisa, Sava, and Morava (S13-S15) to analyze the annual variation herbicides. Herbicide application rates were expected to be the highest in May and June 2010 and June 2011, and herbicide application coincided with agricultural use. However, concentrations decreased in other months. Changing rainfall and runoff patterns can explain periodic changes in annual concentration (24). The precipitation rate was extremely higher than usual (compared to the average rainfall year) in May and June 2010, resulting in severe runoff and increased concentrations in surface waters. Rainfall returned to normal and a low concentration of herbicides was detected in June 2009. Additionally, rainfall participation in October 2009 was higher than normal for the same month in 2010. Herbicides in the Danube basin are terbuthylazine (130-200 ng/L), atrazine (188 ng/L), metolachlor (150 ng/L), and acetochlor (110 ng/L). In Serbia, atrazine was banned in 2008, but it was in the range of 20-188 ng/L. In other countries including Spain, France, Hungary, Portugal, and Switzerland, this range was 10-630, 30-40, 200-10 000, 80-630, and 30 ng/L, respectively [23].

According to pesticide detections in European surface waters, concentration templates were dynamically influenced by point sources (28). These pesticides are assumed to be applied in the recommended amounts. Given that herbicides were part of the natural agronomic methods for eliminating weeds, water pollution may be related to their regular use. Certain herbicides (e.g., terbuthylazine) have been banned in the European Union since 2004 (20). The herbicides were washed away during rainy months and seasonal runoff and entered the river. Pesticides can enter waterways and groundwater depending on the duration and intensity of rainfalls, which may explain the concentration of herbicides in different areas (14, 16).

4. Limitations

Articles reporting, monitoring pesticides (fungicides,

herbicides, and insecticides) with two herbicides, pesticide monitoring in the sediment, soil, and plants, and investigation of the herbicide, along with unpublished data were excluded from this review.

5. Conclusion

This scoping review provided information about the residual herbicides of water resources worldwide. The accessible scientific documents on herbicide concentrations were collected from different water resources such as drinking water, well water, surface water, groundwater, and coastal ecosystems in various countries (e.g., Spain, Canada, Greece, Brazil, Malawi, Hungary, Serbia, Portugal, USA, and Lesotho). The findings of this work indicated evidence of the harmful effects of herbicides on water resources when used in the entire field. Specifically, highly water-soluble herbicides should be widely used in the dry season to minimize their impact on water resources. Moreover, it is complicated to establish regulatory restrictions on the maximum number of herbicides remaining in water worldwide. First, data on the type of source water and the proposed limit should be reported, including drinking water, lakes, streams, groundwater, and irrigation water. In terms of water resource protection, small steps can be taken to prevent contamination, including the proper use of herbicides packaging and crop-managing practices that prevent crop wastage, whether using the required escape, runoff, and/or washing. Preventing herbicides from entering the water reduces the need for corrective actions that are often costly and ineffective for a wide range of herbicides.

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Conflict of Interests Disclosures

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the reported work in this paper.

Ethical Statement

Not applicable.

References

1. WHO Expert Committee on Insecticides, World Health Organization. Safe Use of Pesticides: Twentieth Report of the WHO Expert Committee on Insecticides [Meeting Held in Geneva from 10 to 16 October 1972]. World Health Organization; 1973.
2. Davies JE, Enos HF, Barquet A, Morgade C, Danauskas JX, Freed VH. Minimizing occupational exposure to pesticides: epidemiological overview. In: Gunther FA, Gunther JD, eds. Residue Reviews. New York, NY: Springer; 1980. p. 7-20. doi: [10.1007/978-1-4612-6104-9_2](https://doi.org/10.1007/978-1-4612-6104-9_2).
3. George MJ. Monitoring of herbicides in aquatic environments using the bubble-in-drop single drop micro-extraction (BID-SDME) method. *S Afr J Chem*. 2014;67(1):56-60.
4. Ramezani MK. Soil persistence of herbicides and their carryover effects on rotational crops-a review. *Weed Research Journal*. 2010;2(1):95-118. [Persian].
5. World Health Organization (WHO). Multilevel Course on the Safe Use of Pesticides and on the Diagnosis and Treatment of Pesticide Poisoning. Geneva: WHO; 1992.
6. Edwards CA. Environmental Pollution by Pesticides. Springer Science & Business Media; 2013.
7. Harris TH, Cummings JG. Enforcement of the federal insecticide, fungicide and rodenticide act in the United States. In: Gunther FA, eds. Residue Reviews/Rückstands-Berichte. New York, NY: Springer; 1964. p. 104-35. doi: [10.1007/978-1-4615-8386-8_8](https://doi.org/10.1007/978-1-4615-8386-8_8).
8. Zhang Y, Guo F, Meng W, Wang XQ. Water quality assessment and source identification of Daliao River Basin using multivariate statistical methods. *Environ Monit Assess*. 2009;152(1-4):105-21. doi: [10.1007/s10661-008-0300-z](https://doi.org/10.1007/s10661-008-0300-z).
9. Soncini-Sessa R, Castelletti A, Weber E. A DSS for planning and managing water reservoir systems. *Environ Model Softw*. 2003;18(5):395-404. doi: [10.1016/s1364-8152\(03\)00035-5](https://doi.org/10.1016/s1364-8152(03)00035-5).
10. Hino M. Water Quality and its Control. AA Balkema; 1994.
11. Moher D, Liberati A, Tetzlaff J, Altman DG. Preferred reporting items for systematic reviews and meta-analyses: the PRISMA statement. *Int J Surg*. 2010;8(5):336-41. doi: [10.1016/j.ijso.2010.02.007](https://doi.org/10.1016/j.ijso.2010.02.007).
12. Tricco AC, Lillie E, Zarin W, O'Brien KK, Colquhoun H, Levac D, et al. PRISMA extension for scoping reviews (PRISMA-ScR): checklist and explanation. *Ann Intern Med*. 2018;169(7):467-73. doi: [10.7326/m18-0850](https://doi.org/10.7326/m18-0850).
13. Carabias Martínez R, Rodríguez Gonzalo E, Fernández Laespada M, Sánchez San Román F. Evaluation of surface- and ground-water pollution due to herbicides in agricultural areas of Zamora and Salamanca (Spain). *J Chromatogr A*. 2000;869(1-2):471-80. doi: [10.1016/s0021-9673\(99\)01188-7](https://doi.org/10.1016/s0021-9673(99)01188-7).
14. Kapsi M, Tsoutsis C, Paschalidou A, Albanis T. Environmental monitoring and risk assessment of pesticide residues in surface waters of the Louros River (N.W. Greece). *Sci Total Environ*. 2019;650(Pt 2):2188-98. doi: [10.1016/j.scitotenv.2018.09.185](https://doi.org/10.1016/j.scitotenv.2018.09.185).
15. Van Stempvoort DR, Roy JW, Brown SJ, Bickerton G. Residues of the herbicide glyphosate in riparian groundwater in urban catchments. *Chemosphere*. 2014;95:455-63. doi: [10.1016/j.chemosphere.2013.09.095](https://doi.org/10.1016/j.chemosphere.2013.09.095).
16. Marchesan E, Zanella R, de Avila LA, Camargo ER, de Oliveira Machado SL, Macedo VR. Rice herbicide monitoring in two Brazilian rivers during the rice growing season. *Sci Agríc*. 2007;64(2):131-7. doi: [10.1590/s0103-90162007000200005](https://doi.org/10.1590/s0103-90162007000200005).
17. Székács A, Mörtl M, Darvas B. Monitoring pesticide residues in surface and ground water in Hungary: surveys in 1990–2015. *J Chem*. 2015;2015:717948. doi: [10.1155/2015/717948](https://doi.org/10.1155/2015/717948).
18. Lakudzala DD. Atrazine and metolachlor contamination in surface and ground water in the Zomba/Bvumbwe region in Malawi. *Int Lett Chem Phys Astron*. 2013;6:33-45. doi: [10.18052/www.scipress.com/ILCPA.6.33](https://doi.org/10.18052/www.scipress.com/ILCPA.6.33).
19. Cerejeira MJ, Viana P, Batista S, Pereira T, Silva E, Valério MJ, et al. Pesticides in Portuguese surface and ground waters. *Water Res*. 2003;37(5):1055-63. doi: [10.1016/s0043-1354\(01\)00462-6](https://doi.org/10.1016/s0043-1354(01)00462-6).
20. Herrero-Hernández E, Rodríguez-Cruz MS, Pose-Juan E, Sánchez-González S, Andrades MS, Sánchez-Martín MJ. Seasonal distribution of herbicide and insecticide residues in the water resources of the vineyard region of La Rioja (Spain). *Sci Total Environ*. 2017;609:161-71. doi: [10.1016/j.scitotenv.2017.07.113](https://doi.org/10.1016/j.scitotenv.2017.07.113).
21. Van Toan P, Sebesvari Z, Bläsing M, Rosendahl I, Renaud FG. Pesticide management and their residues in sediments and

- surface and drinking water in the Mekong Delta, Vietnam. *Sci Total Environ.* 2013;452-453:28-39. doi: [10.1016/j.scitotenv.2013.02.026](https://doi.org/10.1016/j.scitotenv.2013.02.026).
22. Gonçalves CM, Esteves da Silva JCG, Alpendurada MF. Evaluation of the pesticide contamination of groundwater sampled over two years from a vulnerable zone in Portugal. *J Agric Food Chem.* 2007;55(15):6227-35. doi: [10.1021/jf063663u](https://doi.org/10.1021/jf063663u).
23. Bortoluzzi EC, Rheinheimer DS, Gonçalves CS, Pellegrini JB, Maroneze AM, Kurz MH, et al. Investigation of the occurrence of pesticide residues in rural wells and surface water following application to tobacco. *Quím Nova.* 2007;30(8):1872-6. doi: [10.1590/s0100-40422007000800014](https://doi.org/10.1590/s0100-40422007000800014).
24. Antić N, Radišić M, Radović T, Vasiljević T, Grujić S, Petković A, et al. Pesticide Residues in the Danube River Basin in Serbia – a Survey during 2009–2011. *Clean (Weinh).* 2015;43(2):197-204. doi: [10.1002/clen.201200360](https://doi.org/10.1002/clen.201200360).
25. Dores EF, Carbo L, Ribeiro ML, De-Lamonica-Freire EM. Pesticide levels in ground and surface waters of Primavera do Leste Region, Mato Grosso, Brazil. *J Chromatogr Sci.* 2008;46(7):585-90. doi: [10.1093/chromsci/46.7.585](https://doi.org/10.1093/chromsci/46.7.585).
26. Panthi S, Sapkota AR, Raspanti G, Allard SM, Bui A, Craddock HA, et al. Pharmaceuticals, herbicides, and disinfectants in agricultural water sources. *Environ Res.* 2019;174:1-8. doi: [10.1016/j.envres.2019.04.011](https://doi.org/10.1016/j.envres.2019.04.011).
27. Tadeo JL, Sanchez-Brunete C, García-Valcarcel AI, Martínez L, Pérez RA. Determination of cereal herbicide residues in environmental samples by gas chromatography. *J Chromatogr A.* 1996;754(1-2):347-65. doi: [10.1016/s0021-9673\(96\)00279-8](https://doi.org/10.1016/s0021-9673(96)00279-8).
28. Calderon MJ, De Luna E, Gomez JA, Hermosin MC. Herbicide monitoring in soil, runoff waters and sediments in an olive orchard. *Sci Total Environ.* 2016;569-570:416-22. doi: [10.1016/j.scitotenv.2016.06.126](https://doi.org/10.1016/j.scitotenv.2016.06.126).
29. Almasi H, Takdastan A, Jaafarzadeh N, Babaei AA, Tahmasebi Birgani Y, Cheraghian B, et al. Spatial distribution, ecological and health risk assessment and source identification of atrazine in Shadegan international wetland, Iran. *Mar Pollut Bull.* 2020;160:111569. doi: [10.1016/j.marpolbul.2020.111569](https://doi.org/10.1016/j.marpolbul.2020.111569).
30. Khalijian A, Sobhanardakani S, Cheraghi M. Investigation of diazinon residue in groundwater resources of Hamedan-Bahar Plain in 2014. *J Res Environ Health.* 2016;2(3):203-11. doi: [10.22038/jreh.2016.8075](https://doi.org/10.22038/jreh.2016.8075).
31. Müller K, Magesan GN, Bolan NS. A critical review of the influence of effluent irrigation on the fate of pesticides in soil. *Agric Ecosyst Environ.* 2007;120(2):93-116. doi: [10.1016/j.agee.2006.08.016](https://doi.org/10.1016/j.agee.2006.08.016).
32. Leili M, Pirmoghani A, Samadi MT, Shokoohi R, Roshanaei G, Poormohammadi A. Determination of pesticides residues in cucumbers grown in greenhouse and the effect of some procedures on their residues. *Iran J Public Health.* 2016;45(11):1481-90.
33. Sullivan P, Clark JJ, Agardy FJ, Rosenfeld PE. *Toxic Legacy: Synthetic Toxins in the Food, Water and Air of American Cities.* Elsevier; 2010.