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Chapter

Water Resource Pollution by Herbicide Residues

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Abstract

Herbicides are frequently used in the chemical control of weeds in various crops in Brazil and worldwide, so they are more frequently detected outside the application areas, contributing to the risk of environmental contamination. The importance of knowledge of the physicochemical properties of the environment and the pesticide used in the agricultural area is in order to understand its effects on terrestrial and aquatic ecosystems and the search for the prevention of future bioaccumulation potentials (bioconcentration and/or biomagnification) of molecules of pesticides in living nontarget organisms, minimizing their negative effects on the environment. The understanding of analytical techniques for measuring the quality of water resources as well as techniques for the remediation of contaminated water is essential to minimize the possible impacts caused by the application of pesticides to the environment.

Keywords: contamination, leaching, runoff, volatilization

1. Introduction

The fate of herbicides in the environment contributes to the contamination of water resources and is governed by retention (adsorption, absorption, and precipitation), transformation (decomposition or degradation) and transport (drift, volatilization, leaching, and runoff), and by the interactions of these processes [1]. The problem of contamination is higher mainly with herbicides that are applied directly on the soil in pre-emergence or pre-planting (PPI) in relation to other forms of applications.

Leaching is indicated as the main cause of groundwater contamination by herbicides [2]. This process is the main form of transport in the soil of nonvolatile and water-soluble herbicides [3]. It is of great importance to point out that leaching is essential for the incorporation of herbicides in the soil profile in order to reach the soil seed bank, contributing to the efficiency of the products in weed control [4]. However, negatively, herbicides can be transported to deeper layers of the soil profile until they reach sites less exploited by the roots, contaminating the groundwater table [5].

Water contamination is not only related to the proximity of the water resources of the treated agricultural areas, the physical and chemical characteristics of the products, the climate, the topography, and the management of the area, but also technical application characteristics such as water use, inventory, handling, and packaging [6].

Thus, monitoring practices of water resources and the safe use of herbicides should be applied. According to Santos et al. [6], chromatography is the most used technique for identification and quantification of herbicides and, in general, pesticides and contaminants of the water bodies. However, in addition to the detection of contaminants, adequate control is necessary before and in the moment of application to generate the minimum residues as possible in the environment.

In this chapter, we will discuss the main factors that affect water pollution by herbicides, exemplifying herbicides' potential to contaminate water resources, emphasizing the effects, monitoring, and detection of herbicides in water resources, and finalizing strategies to minimize contamination and herbicide removal techniques in contaminated drinking water.

2. Factors affecting water pollution by herbicides

Several factors affect the pollution of water resources by herbicides, and were listed in the base Safe Drinking Water Foundation (SDWF) [7]. The factors are related with soil, herbicides, and environment.

In soil, drainage affects herbicides because it contributes to leaching. Agricultural soils are often well drained, as are natural soil drainage associated with excess rainwater, and irrigation can increase transport herbicides to groundwater and freshwater. This transport occurs in the water path in the soil profile and rapidly reaching a large geographical area. Thereby, the herbicide mobility in soil is coordinated by the movement of water in different directions, being vertical (leaching) and horizontal (runoff and/or run-in). In soil, temperature also affects the fate of herbicides, for the reason that it interferes in microbiology activity. This fact can promote the less biodegradation of herbicides, a process that results in a product formation, frequently, less toxic for the environment. Besides, the chemical degradation and photochemical degradation also reduce the toxicity of herbicides in soil.

With regard to the herbicides, the physicochemical properties are responsible for their behavior in soil, as well as the risks of contamination. Firstly, the solubility in water (S_w) indicates the possible herbicide leaching with water flux in soil, as also the disponibility of the molecule for other processes of dissipation in soil. The Sw is necessary for many herbicides, because it needs to be applied with water and to be absorbed by the target plant. The higher the solubility of the herbicide, the greater the risk of leaching. When herbicide no leaching, that is, it has your persistence for more time in soil, the sorption is controlling your behavior. The sorption coefficient (K_d) normalized for the organic carbon of soil (K_{oc}) indicates this affinity from molecule to soil sorption. This situation reduces the contamination of groundwater by leaching, but increases surface water contamination by runoff on slopes and high rainfall.

The more sorbed the herbicide in soil, will more persistence have this molecule in environment. The persistence can be measured by means of the half-life ($t_{1/2}$). In terms of half-life, the longer the degradation takes, the greater is its persistence. The half-life is unique for individual herbicides, but variable depending on application factors and specific environmental conditions, mainly of microbial activity in soil.

Still, about physical chemical properties of herbicides, the same authors indicate the vapor pressure (VP) as interfering in herbicide behavior in the environment. It is directly related to the volatilization of the herbicides, which is the other form of transport of these molecules to the atmosphere and these can be carried by the wind and reach the soil again in the form of precipitation. The formulations are forms for reducing this effect, besides additives used in mixtures (wetting agents, solvents, extenders, adhesives, buffers, preservatives, and emulsifiers) to improve absorption

and decrease losses for the environment. However, much this formulation can contain environmental contaminants also.

Treatment of herbicides in nonagricultural areas can be a cause of environmental pollution. In many areas, such as paved roads, carriers, and sidewalks, among others (rigid surfaces), have nothing to absorb and are particularly vulnerable to transport into watercourses and nontarget areas, especially after precipitation. Thus, herbicides found in water can often be the result of nonagricultural use. In addition, independent of the application area, applying high rates of products can increase the concentration in the environment.

Another factor that affects water pollution by herbicides is precipitation, because high levels of precipitation increase the risk of herbicide contamination. The movement of herbicides in watercourses occurs directly by applying these products to target areas in drains after precipitation. It may also occur within the soil structure by displacement of the herbicides from the absorption sites by the water and the treated soil that has moved into the water by soil erosion. The greater distances of the water resources and the place of application of the herbicides are also crucial to minimize the impacts of the residues in the aquatic system [7].

Persistent herbicides in the environment which have high solubility, mobility, and sorption capacity to soil particles and/or volatilization can present great potential for contamination of water if not used properly. Before carrying out the herbicide application in weed management, checking the risk of each product to the environment is essential. From these data, it is possible to make a decision about the mode of application, season, area, dose, and measures that minimize the impacts.

3. Herbicides with potential for contamination of the environment, ecology, and human health

3.1 Potential for contamination of the environment

For the evaluation of the herbicide runoff, Goss [8] considered the herbicide half-life ($t_{1/2}$) in the soil and the soil sorption potential (K_{oc}) of the herbicide by soil particles when in soil transport as criteria, as presented in **Table 1**. For Leonard [9], the solubility (S_w) of the herbicide is relevant, since it determines the runoff in the soil solution, considering also the intensity and occurrence of rainfall in this process.

In relation to the transport potential associated with sediment, to be will high potential when $t_{1/2} \geq 40$ days and $K_{oc} \geq 1000$ L Kg^{-1}; $t_{1/2} \geq 40$ days, $K_{oc} \geq 500$ L Kg^{-1} and $S_w \leq 0.5$ mg L^{-1}. The potential will low when $t_{1/2} < 1$ day, $t_{1/2} \leq 2$ days and $K_{oc} \leq 500$ L Kg^{-1}, $t1_{/2} \leq 4$ days, $K_{oc} \leq 900$ L Kg^{-1} and $S_w \geq 0.5$ mg L^{-1}, $t_{1/2} \leq 40$ days, $K_{oc} \leq 500$ L Kg^{-1} and $S_w \geq 0,5$ mg L^{-1}; $t_{1/2} \leq 40$ days, $K_{oc} \leq 900$ L Kg^{-1} and $S_w \geq 2$ mg L^{-1} [8].

The transport potential dissolved in water will be high potential when: $t_{1/2} > 35$ days, $K_{oc} < 100,000$ L Kg^{-1} and $S_w \geq 1$ mg L^{-1}; $t_{1/2} < 35$ days, $K_{oc} \leq 700$ L Kg^{-1}, and $S_w \geq 10$ e ≤ 100 mg L^{-1} and low potential when $K_{oc} \geq 100,000$ L Kg^{-1}; $t1_{/2} \leq 1$ day and $K_{oc} \geq 1000$ L Kg^{-1}; $t_{1/2} < 35$ days, and $S_w < 0.5$ mg L^{-1} [8]. The solubility in water will be influenced, when it rains soon after application, $S_w > 30$ mg L^{-1}, and "free" transport in solution (in water) [9].

Table 1 shows the indexes for evaluating the surface runoff of some herbicides, of the relationship between sorption potential and mobility.

To evaluate the potential risk of herbicide leaching, three theoretical indexes (GUS, CDFA, and Cohen) were used according to Inoue et al. [5]. The physico-chemical properties of the herbicides were used to calculate the proposed indexes, compiled from the European database [11], according to **Table 2**.

Herbicide	K_{oc} (L Kg^{-1})	$t_{1/2}$ (days)	S_w (mg L^{-1})	Goss[1]	Goss[2]	Mobility[3]
Cloransulam-methyl	30	11	184	LPC	—	M
Diuron	813	75.5	35.5	PC	PC	LM
Glyphosate	1424	15	10,500	—	—	LM
Sodium hydrogen methyl arsonate (MSMA)	1680[4]	200	580,000	PC	PC	—
Paraquat	10,000,000	3000	620,000	PC	LPC	NM
Trifluralin	15,800	181	0.221	PC	PC	NM

[1]*Transport potential associated with sediment: PC = potential for contamination of surface waters and LPC = low potential for contamination of surface waters.*

[2]*Transport potential dissolved in water: PC = potential for contamination of surface water and LPC = low potential for contamination of surface water.*

[3]*LM = slightly mobile; M = mobile; and NM = not mobile.*

[4]*Kegley et al. [10].*
Source: PPDB [11].

Table 1.
Indexes for evaluating the runoff of herbicides on the potential for surface water contamination (Goss).

Herbicide	K_{oc} (L Kg^{-1})	$t_{1/2}$ (days)	GUS[1]	CDFA	Cohen
Ametryn	316	37	0.52 (LL)	L	L
Aminocyclopyrachlor	24	31	3.19 (HL)	L	L
Atrazine	100	75	3.20 (HL)	L	L
Bentazone	55.3	20	2.89 (HL)	L	L
Comazone	300	83	3.00 (HL)	L	L
Imazaquin	18[1]	60	5.42 (HL)	L	L
Imazethapyr	52	90	6.29 (HL)	L	L
Metolachlor	120	90	2.10 (IN)	L	L
Nicosulfuron	30	26	3.25 (HL)	L	L
Picloram	13	82.8	6.03 (HL)	L	L
Simazine	130	60	2.00 (IN)	L	L
Sulfentrazone	43	541	6.16 (HL)	L	L
Sulfometuron-methyl	85	24	2.86 (HL)	L	L
Tebuthiuron	80	400	5.36 (HL)	L	L

[1]*HL = highly leachable, L = leachable, IN = intermediary, LL = low leaching, and NL = non-leachable. Kegley et al. [10].*
Source: PPDB [11].

Table 2.
Indexes for evaluating herbicide leaching for potential groundwater contamination (GUS, CDFA, and Cohen).

The Groundwater Ubiquity Score (GUS) is like log $t_{1/2}$ (4 - log K_{oc}). GUS < 1.8 is nonleachable, GUS > 2.8 is leachable, and −1.8 < GUS < 2.8 is intermediary [12]. The California Department of Food and Agriculture (CDFA) [13] classifies K_{oc} < 512 L kg^{-1} and $t_{1/2}$ > 11 days as leachable. According to Cohen et al. [14], the criterion of the *Environmental Protection Agency* (EPA) classifies K_{oc} < 300 L kg^{-1} and $t_{1/2}$ > 21 days as leachable and K_{oc} > 500 L kg^{-1} and $t_{1/2}$ < 14 days as nonleachable.

Even the theoretical criteria, taking into account the characteristics of each herbicide molecule, distinguish each other. This can be seen in **Table 2**, where

herbicide properties are directly related to leaching and classification according to the theoretical criteria. On the other hand, these criteria can help in the chemical management with the herbicides, allowing a correct decision-making based on one of the factors that most influence the behavior of the herbicide molecule in the environment.

For the volatilization, estimation proposed by Lyman et al. [15] is considered only the constant of Henry's Law (H), which represents the concentration of the solute in the air in relation to the concentration in the water, being exemplified in **Table 3**. However, the VP is a property that can also contribute to the evaluation of the volatility of the herbicide, as it demonstrates the potential for evaporation of a molecule in relation to temperature.

Lyman et al. [15] classified $H > 10^{-5}$ as highly volatile, $H < 10^{-7}$ as low volatility, and $10^{-7} > H < 10^{-5}$ as moderately volatile.

3.2 Potential for ecological contamination

The ecotoxicology is the science that studies the effects of physical and chemical agents on organisms, populations, and environment of communities, whether terrestrial or aquatic [16–19]. Aquatic ecotoxicology aims to evaluate the effect of toxic chemicals on organisms representative of the aquatic ecosystem. The toxic effects can manifest themselves at different levels of organization, from cellular structures to individuals, populations, and communities [18, 20, 21].

Environmental monitoring through ecotoxicological studies integrates important parameters, since it uses organisms' representative of aquatic environments for the quality of the environment under study. The main advantage of using ecotoxicological studies on the physicochemical approach is that organisms interact with the ambient conditions for a time, while the chemical data are measured instantly in nature, and therefore, require a large number of measurements to obtain greater precision in the results.

Ecotoxicological tests may be classified according to their time available for evaluation of acute and chronic effects. These tests differ in duration and final responses are measured and are a necessary tool for ecotoxicological characterization of environmental samples, both the potential risk assessment as the establishment of maximum permissible limits for the protection of aquatic life [22]. **Table 4** shows definitions of terms commonly used in toxicity tests.

Herbicide	H	Lyman	Volatilization based on constant H	VP	Volatilization based on VP
Atrazine	1.50×10^{-04}	HV	NV	0.039	LV
Clomazone	4.20×10^{-3}	HV	NV	19.2	HV
Dicamba	1.0×10^{-04}	HV	NV	1.67	LV
Linuron	2.00×10^{-04}	HV	NV	0.051	LV
Metsulfuron	2.87×10^{-06}	MV	NV	1.40×10^{-08}	LV
Trifluralin	6.13×10^{-3}	HV	MV	9.5	MV
2.4-D	4.0×10^{-06}	MV	NV	0.009	LV

HV = highly volatile, MV = moderately volatile, LV = low volatility, and NV = nonvolatile.
Source: PPDB [11].

Table 3.
Indexes for evaluating the volatilization of herbicides on the potential for rainwater contamination.

Acute toxicity tests are used to measure the effects of toxic agents on aquatic species over a short period of time over the life span of the organism, while chronic toxicity tests are performed to measure the effects of chemicals on species for a period which may cover part or all of the life cycle of the test organism. The acute toxicity study is important to predict more immediate impacts to ecosystems, while the study of chronic toxicity is important in cases where organisms are continually exposed to toxic substances at lower concentrations.

The toxicological effects of herbicides on aquatic organisms have been studied to determine, mainly, the effect of herbicides on the different trophic levels that surround this environment. Aquatic toxicology contributes to the determination of the maximum concentration of herbicide that can be considered tolerable in an environment without causing significant damage to biota. You also study the quantitative and qualitative effects of these contaminants on aquatic organisms. **Table 5** shows the toxicological effect of herbicides on the major aquatic organisms.

According to FAO [24], herbicides are included in a wide range of organic micro-pollutants that have ecological impacts. Different groups of herbicides have different types of data on the living body, so a generalization is difficult. Water can be contaminated by runoff of herbicides. Contamination can occur directly through pesticide applications in growing areas or indirectly by exposing pesticide residues to the environment. Contamination can occur directly through pesticide applications in growing areas or indirectly by exposing pesticide residues to the environment.

The mechanisms are bioaccumulation, bioconcentration, and biomagnification. The bioaccumulation of substances in organisms, according to their trophic level of the food chain, can be divided into:

- **Bioconcentration**: the direct capture of pollutants present in water, through the gills, skin, and oral route;

- **Biomagnification**: consumption of contaminated prey, associated with different trophic levels.

The bioaccumulation process refers to the entry of xenobiotic molecules into organs of living organisms, over the time of exposure. Now the rate of excretion of

Parameter	Definition	Exposure time
LD_{50}	Average lethal dose: dose of sample causing mortality of 50% of organisms at the time of exposure and test conditions.	24 to 96 h
LC_{50}	Medium lethal concentration: concentration of sample that causes an acute effect (death, for example) to 50% of organisms at the time of exposure and under test conditions.	24 to 96 h
EC_{50}	Average effective concentration: concentration of sample causing an acute effect (immobility, for example) to 50% of organisms at the time of exposure and under test conditions.	24 or 48 h
CENO	Unobserved effect concentration: higher concentration of toxic agent that does not cause statistically significant deleterious effect on organisms at the time of exposure and test conditions.	7 days
CEO	Observed effect concentration: lower concentration of toxic agent causing statistically significant deleterious effect on organisms at time of exposure and test conditions.	7 days

Source: Espíndola et al. [23].

Table 4.
Definition of some terms used in toxicity tests.

Herbicide	Toxicological test	Value (mg L^{-1})	Water agencies	Classification
2.4-D	Fish—Sharp 96 h LC50	100.00	*Pimephales promelas*	Moderate
	Fish—Chronic 21 days CENO	27.20	*Oncorhynchus mykiss*	Low
	Aquatic invertebrates—Acute 48 h EC50	134.20	*Daphnia magna*	Low
	Aquatic invertebrates—Chronic 21 days CENO	46.20	*Daphnia magna*	Low
	Aquatic plants (biomass)—Acute 7 days EC50	2.70	*Lemna perpusilla*	Moderate
	Algae—Acute 72 h EC50	24.20	*Raphidocelis subcapitata*	Low
	Algae—Chromatic 96 h CENO	100.00	*Chlorella vulgaris*	Low
Ametryn	Fish—Sharp 96 h LC50	5.00	*Oncorhynchus mykiss*	Moderate
	Aquatic invertebrates—Acute 48 h EC50	28.00	*Daphnia magna*	Moderate
	Aquatic invertebrates—Chronic 21 days CENO	0.32	*Daphnia magna*	Moderate
	Aquatic crustaceans—Acute 96 h EC50	1.70	*Americamysis bahia*	Moderate
	Aquatic plants (biomass)—Acute 7 days EC50	0.10	*Lemna perpusilla*	Moderate
	Algae—Acute 72 h EC50	0.0036	*Raphidocelis subcapitata*	High
Atrazine	Fish—Sharp 96 h LC50	4.50	*Oncorhynchus mykiss*	Moderate
	Fish—Chronic 21 days CENO	2.00	*Oncorhynchus mykiss*	Low
	Aquatic invertebrates—Acute 48 h EC50	8.50	*Daphnia magna*	Moderate
	Aquatic invertebrates—Chronic 21 days CENO	1.00	*Daphnia magna*	Moderate
	Aquatic crustaceans—Acute 96 h EC50	1.00	*Americamysis bahia*	Moderate
	Sediment Organisms—96 h acute LC50	1.00	*Chironomus riparius*	Moderate
	Aquatic plants (biomass)—Acute 7 days EC50	0.10	*Lemna perpusilla*	Moderate
	Algae—Acute 72 h EC50	0.0036	*Raphidocelis subcapitata*	Moderate
Diuron	Fish—Sharp 96 h LC50	6.70	*Cyprinodon variegatus*	Moderate
	Fish—Chronic 21 days CENO	0.41	*Oncorhynchus mykiss*	Low
	Aquatic invertebrates—Acute 48 h EC50	5.70	*Daphnia magna*	Moderate
	Aquatic invertebrates—Chronic 21 days CENO	0.096	*Daphnia magna*	Moderate
	Crustáceos aquáticos—Agudo 96 h CE$_{50}$	1.10	*Americamysis bahia*	Moderate
	Aquatic plants (biomass)—Acute 7 days EC50	0.0183	*Lemna perpusilla*	Moderate
	Algae—Acute 72 h EC50	0.0027	*Scenedesmus agricauda*	High

Herbicide	Toxicological test	Value (mg L^{-1})	Water agencies	Classification
Glyphosate	Fish—Sharp 96 h LC50	38.00	*Oncorhynchus mykiss*	Moderate
	Fish—Chronic 21 days CENO	25.00	*Oncorhynchus mykiss*	Low
	Aquatic invertebrates—Acute 48 h EC50	40.00	*Daphnia magnmagnaa*	Moderate
	Aquatic invertebrates—Chronic 21 days CENO	30.00	*Daphnia magna*	Low
	Aquatic crustaceans—Acute 96 h EC50	40.,00	*Americamysis bahia*	Moderate
	Aquatic plants (biomass)—Acute 7 days EC50	12.00	*Lemma perpusilla*	Low
	Algae—Acute 72 h EC50	4.40	*Scenedesmus agricauda*	Moderate
	Algae—Chromatic 96 h CENO	2.00	—	Low
Simazine	Fish—Sharp 96 h LC50	90.00	*Lepomis macrochirus*	Moderate
	Fish—Chronic 21 days CENO	0.70	—	Moderate
	Aquatic invertebrates—Acute 48 h EC50	1.10	*Daphnia magna*	Moderate
	Aquatic invertebrates—Chronic 21 days CENO	25.00	*Daphnia magma*	Moderate
	Aquatic plants (biomass)—Acute 7 days EC50	3.00	*Lemma perpusilla*	Moderate
	Algae—Acute 72 h EC50	0.04	*Scenedesmus agricauda*	Moderate
	Algae—Chromatic 96 h CENO	0.60	—	Moderate
Trifluralin	Fish—Sharp 96 h LC50	0,088	*Oncorhynchus mykiss*	High
	Fish—Chronic 21 days CENO	10.00	*Pimephales promelas*	Moderate
	Aquatic invertebrates—Acute 48 h EC50	0.245	*Daphnia magna*	Moderate
	Aquatic invertebrates—Chronic 21 days CENO	0.051	*Daphnia magna*	Moderate
	Aquatic crustaceans—Acute 96 h EC50	0.074	*Americamysis bahia*	High
	Sediment Organisms—96 h acute LC50	1.00	*Chironomus riparius*	Moderate
	Sediment Organisms—Chronic 21 days CENO—water	0.25	*Chironomus riparius*	Moderate
	Sediment Organisms—Chronic 21 days CENO—sediment	810.00	*Chironomus riparius*	Low
	Aquatic plants (biomass)—Acute 7 days EC50	0.0122	*Lemma perpusilla*	Moderate
	Algae—Acute 72 h EC50	0.0036	*Raphidocelis subcapitata*	Moderate
	Algae—Chromatic 96 h CENO	0.60	—	Moderate

Source: PPDB [11].

Table 5.
Toxicological effects of herbicides detected in different water resources in Brazil on the main aquatic organisms.

the substances present in the organism and/or their metabolism is low; besides the sorption of the molecules of the substances to the constituents of the body, there will be an increase of the concentration in the organisms, exceeding the values of the medium. The mechanism of bioconcentration is the direct transfer of a molecule of xenobiotic into the body, in its tissues and/or organs [25].

The environment is formed by different phases, such as terrestrial, aquatic, atmospheric, and biota, and the xenobiotic when introduced in this system is distributed according to its physicochemical properties. The sediment has particles and colloids from the soil, serving as a reservoir of xenobiotic molecules, being a source of accumulation of pollutants. Thus, there may be higher concentrations of persistent toxic pollutants in the sediments relative to water, and aquatic biota may metabolize significant amounts of pollutants over time, but these concentrations may be below the detection limits of traditional analytical techniques.

The indicator used to measure the bioaccumulation potential of pollutants in living organisms is the octanol/water partition coefficient (K_{ow}). Thus, K_{ow} (**Table 6**) is the measure of the affinity of the molecule for the apolar phase (1-octanol = lipophilicity) and polar (water = hydrophilicity). Therefore, the higher the K_{ow} value, the greater the lipophilicity (**Table 7**), that is, the higher the bioaccumulation potential [26].

Some herbicides such as diclofop-methyl, fluazifop-P-butyl, atrazine, and oxyfluorfen are lipophilic, which means that they are soluble and accumulated in adipose tissue, such as edible fish tissue and human adipose tissue. Other herbicides with low K_{ow}, such as glyphosate, are metabolized and excreted.

The term biomagnification refers to the increasing concentration of a chemical as food energy is transformed within the food chain. As larger organisms consume smaller organisms, the concentration of herbicides and other pesticides is increasing in tissues and other organs. Very high concentrations can be observed in higher predators, including man.

The ecological effects of herbicides are varied and are often interrelated. The effects on the organism or the ecological level are generally considered as an indicator of early warning of possible impacts on human health. The main types of effects are listed below and vary depending on the organism studied and the type of herbicide. The important point is that many of these effects are chronic (nonfatal) and often not observed by casual observers, but have consequences for the entire food chain, as described below, according to FAO [24]:

- Death of the organism;

- Cancers, tumors, and lesions in fish and animals;

- Inhibition or reproduction failure;

- Suppression of the immune system;

- Endocrine (hormonal) disturbance;

- Cell and DNA damage;

- Teratogenic effects (physical deformities such as curved beaks in birds);

- Weakened health of fish marked by a low proportion of red to white blood cells, excessive slime in fish scales, and gills, among others;

- Inter inter-generational effects (effects are not evident until subsequent generations of the organism); and

- Other physiological effects, such as the thinning of eggshell.

LogK$_{ow}$	K$_{ow}$	Lipophilicity
<0.1	<1	Hydrophilic
0.1–1	1–10	Moderately liposoluble
1–2	10–100	Lipophilic
2–3	100–1000	Very lipophilic
3	>1000	Extremely lipophilic

Source: Christoffoleti and López-Ovejero [26].

Table 6.
Classification of lipophilicity of herbicides.

Herbicide	Log K$_{ow}$	Potential to bioaccumulate
Alachlor	3.09	High
Atrazine	2.70	Moderate
Glyphosate	−3.2	Low
Imazapyr	1.34	Low
Mesotrione	0.11	Low
Paraquat	−4.5	Low
Pendimethalin	5.4	High
Tebuthiuron	1.79	Low

Source: PPDB [11].

Table 7.
Bioaccumulation potential of herbicides.

Herbicide	Effects on human health
2.4-D	Effects on the kidney (pigmentation of tubular cells)
Atrazine	Developmental effects (reduction of children's body weight) Other: increased potential risk of ovarian cancer or lymphomas (classified as possible carcinogen)
Dicamba	Liver effects (vacuolation, necrosis, fatty deposits, and changes in liver weight)
Diclofop-methyl	Liver effects (enlargements and enzymatic changes)
Diquat	Cataract formation
Diuron	Weight loss, increased liver weight, and blood effects
Glyphosate	Reduced body weight gain
MCPA	Effects on the kidney (increase of absolute and relative weight, urinary bilirubin, crystals, and pH) Others: systemic, hepatic, testicular, reproductive, and developmental effects, and effect on the nervous system
Metolac3hlor	Liver lesions and tumors in the nasal cavity
Metribuzin	Liver effects (increased incidence and severity of mucopolysaccharide droplets)
Paraquat	Various effects on body weight, spleen, testis, liver, lung, kidney, thyroid, heart, and adrenal gland
Picloram	Changes in body and liver weights and clinical chemistry parameters Others: effects on kidney (ratio of liver weight and body weight, and histopathology)
Simazine	Changes in body weight and effects on serum and thyroid gland
Trifluralin	Changes in liver and spleen weights and serum chemistry

Source: Health Canada [27].

Table 8.
Effects on human health from exposure to herbicides based on the acceptable maximum residue limit (MRL).

These effects are not necessarily caused solely by exposure to herbicides or other organic contaminants, but may be associated with a combination of environmental stresses such as eutrophication and pathogens. These associated stresses need not be large to have a synergistic effect with organic micro pollutants. The ecological effects of herbicides extend beyond individual organisms and can extend to ecosystems, affecting biodiversity.

3.3 Potential for contamination to human health

The effects of herbicides on human health generally affect the rural worker who, in some way, has exposure to these compounds. Problems are often associated with factors such as inappropriate substance use, high toxicity of certain products, lack of health and safety information, and lack of vigilance. In addition to occupational exposure, food and environmental contamination places other groups of people at risk, including families of farmers, the surrounding population of the production unit, and the general population, through the consumption of contaminated food or water. The effects of some herbicides on human health are reported in **Table 8**.

4. Some of the techniques for removal from water resources

To remove herbicides from drinking water, various strategies involving, for example, adsorption, photocatalysis, and/or advanced oxidation processes were used. Regarding adsorption, adsorbents of natural origin (for example, plant biomass) have become attractive in view of the availability of abundant supplies, high adsorption capacity, and low cost. This is a remarkable aspect, especially if the regional biomass is used. The use of agricultural residues follows well the strategies of treatment of effluents with high efficiency and economic viability; for example, Silva et al. [28] reported that dry banana peel was efficient in removing atrazine and ametryn in drinking water and rivers.

In order to mitigate pesticide leaching contamination in surface and groundwater with practices within agricultural properties, the biobed system, created in 1993 in Sweden, has been developed and studied [29]. This system consists of a tank excavated at 60 cm depth covered with impermeable material or not, containing a straw, soil, and peat biomass (50:25:25% volume), covered by a layer of grass. It is used to deposit water from the washes of the containers and sprayers, in order to retain the pesticides, promoting the sorption and biodegradation of the product by the microbial stimulus that occurs with the use of the organic materials in the soil. The substrate is used for 12 months without the need of renewal, and at the end of the use, this material should be stored in the form of composting for 6 months and later distributed in the agricultural areas. Sannino et al. [30] verified in a sorption cycle the total removal of paraquat and partial 2.4-D with the use of a polymeric substance, a polymer of humic acid recovered from the waste water of olive oil mill, presenting potential for use in biomechanics of biobeds, as well as in biofilters. However, there is a need for further research into the efficacy of other biosorbents that may assist in this system.

The use of bovine bone char (bone charcoal) is an alternative for the removal of hexazinone, diuron, ametryn, and sulfometuron methyl in drinking water [31]. In general, the authors stated that herbicide removal in contaminated drinking water samples was in the following descending order: diuron > ametryn > sulfometuron methyl > hexazinone. After 7 days of the application of the bone char treatment, no herbicide desorbed the material, remaining strongly retained. For all herbicides, the removal of about 100% was obtained with the highest dose of bone char (1 g) added

to the water samples. The bovine bone char presented a great herbicide removal potential for use in contaminated drinking water. Depending on each geographical region, the water samples are contaminated with different herbicides. Thus, this bone char can be tested more specifically for each region and potentially can represent a low-cost method to be used in water treatment plants or household filters.

Hexazinone and diuron are often found as micro-contaminants of soil and water resources located near agricultural sites where they are constantly applied [32–35]. In addition, the concentrations of both herbicides found in water resources ranged from 15.0 ng L^{-1} to 408.0 μg L^{-1}.

Conventional techniques applied in water treatment systems do not exhibit great efficiency in the removal of organic micro contaminants, such as herbicides, and it is necessary to add suitable pre- or post-treatments for the removal of these undesirable compounds [36]. Due to this, currently, we are looking for technologies that are environmentally and economically feasible in the removal of these micro contaminants.

In order to obtain high quality water, membrane technologies that include reverse osmosis [37] are used. This technique is used in water desalination and demineralization [38] whose principle is to apply a force higher than the osmotic pressure in the concentrated solution compartment, causing the inversion of flow, forcing the passage of solvent, and retaining the solvent and solute [39]. Reverse osmosis has been widely applied as an important option for wastewater recovery because it can achieve high efficiency of removal of microorganisms, colloidal matter, dissolved solids, and organic and inorganic materials present in water [40].

Several technologies have been studied and developed with the aim of minimizing the impacts generated by the use of herbicides and pesticides in general in the environment. Many of the techniques are extremely costly; however, it is up to the organs and professionals of the different regions to adapt and implement them, in order to serve the population with regard to the supply of drinking water.

5. Final considerations

Highly water-soluble herbicides should be applied exclusively during the dry season so that impacts on water resources are minimized. In addition, establishing regulatory limits for the maximum amount of herbicide residues in the water is complex worldwide. First, the type of water is relevant to the proposed limit, for example, drinking water, reservoir water, lakes and streams, groundwater, aquaculture water, irrigation water, and drinking water for farm animals. A limit based on a risk to human health or the environment could allow much higher levels of herbicide residues in waters than would ever occur in practice.

Also, regarding the preservation of water resources, small actions that contribute to the noncontamination of the water, such as the proper handling of herbicide packaging and agronomic management techniques that avoid the loss of products, be it by volatilization, runoff and/or leaching, are essential. Preventing the arrival of herbicide residues from water sources reduces the need for remediation practices, which are often extremely costly and ineffective for a range of herbicides.

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