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Environmental Risk of Groundwater Pollution by Pesticide Leaching through the Soil Profile

Gabriel Pérez-Lucas, Nuria Vela, Abderrazak El Aatik and Simón Navarro

Abstract

Adsorption, degradation, and movement are the key processes conditioning the behavior and fate of pesticides in the soil. Six processes that can move pesticides are leaching, diffusion, volatilization, erosion and run-off, assimilation by microorganisms, and plant uptake. Leaching is the vertical downward displacement of pesticides through the soil profile and the unsaturated zone, and finally to groundwater, which is vulnerable to pollution. Pesticides are frequently leached through the soil by the effect of rain or irrigation water. Pesticide leaching is highest for weakly sorbing and/or persistent compounds, climates with high precipitation and low temperatures, and soils with low organic matter and sandy texture. On the contrary, for pesticides with a low persistence that disappear quickly, the risk of groundwater pollution considerably decreases. Different and varied factors such as physical-chemical properties of the pesticide, a permeability of the soil, texture and organic matter content of the soil, volatilization, crop-root uptake, and method and dose of pesticide application are responsible for the leaching rate of the pesticides. Soils that are high in clays and organic matter will slow the movement of water, attach easily to many pesticides, and generally have a higher diversity and population of soil organisms that can metabolize the pesticides.

Keywords: aqueous/soil environment, groundwater vulnerability, pesticide leaching, soil pollution

1. Introduction

Agriculture plays an important socioeconomic role in the European Union (EU). The total agricultural area of the EU-28 was 184.6 million hectares in 2015, which supposes 43.5% of its total land area with France and Spain being the countries with greater cultivated land [1]. Therefore, to protect agricultural production and quality, the use of pesticides is widespread.

Pesticides have important benefits in crop protection, food and material preservation, and disease control although unfortunately can pose undesirable effects on human health and environmental ecosystems. The use of pesticides in agriculture is

necessary to combat a variety of pests and diseases that could destroy crops and to improve the quality of the food produced. The main estimated losses in crop yields are due to insect pests (14%), plant pathogens (13% loss), and weeds (13%) [1]. Therefore, pesticides are necessary for agricultural production. Among the different classes of pesticides, the highest percentages of an application are corresponding to herbicides (49%), followed by fungicides and bactericides (27%), and insecticides (19%) [2].

A pesticide also called plant protection product (PPP) is any “substance intended for preventing, destroying, repelling, or mitigating any pest in crops either before or after harvest to prevent deterioration during storage or transport.” A more detailed definition can be found in the document by FAO [3]. The term includes compounds such as antimicrobials, defoliants, disinfectants, fungicides, herbicides, insecticides, insect growth regulators, molluscicides, and other minority groups. Pesticide products include both active ingredients and inert ingredients. Active ingredients are used to control pests, diseases, and weeds, while inert ingredients (stabilizers, dyes, etc.) are important for product performance and usability.

Regulation (EC) No 1107/2009 [4] is the legislation concerning the placing of PPPs on the market in the European Union. EFSA’s Pesticides Unit is responsible for the EU of risk assessments of active substances used in PPPs, in close cooperation with all EU Member States. The risk assessment of active substances evaluates whether, when used correctly, these substances are likely to have any direct or indirect harmful effects on human or animal health, groundwater quality, and nontarget organisms.

Since the 1940s, synthetic pesticides have been widely applied worldwide to protect agricultural crops from pests and diseases, and their use was increased progressively as increased human population and crop production especially from the *Green Revolution*. During 2016, the worldwide consumption of pesticides reached 4.1 millions of tons of active ingredients, which 51.3% was consumed in Asia, 33.3% in Americas (Northern, Central, and South), 11.8% in Europe, 2.2% in Africa, and 1.4% in Oceania. This consumption originated a pesticide trade higher than 60 billion of US \$. **Figure 1** shows the evolution in the use of pesticides during the period 1990–2016 in the world, Europe, the United States of America, and the least developed countries [2].

As can be observed, the consumption was ascending (increasing use) in the worldwide and least developed countries and descending (reduced use) in the most developed areas like EU and USA.

However, many of the pesticides used are chemical compounds that persist in the environment being able to be bioaccumulated through the food web and transported to long distances [5] adversely affecting human health and environment around the world, especially organochlorine pesticides [6]. Toxicity of the compound, amount applied and formulation type, method and time of application and, especially, its mobility and persistence are the main factors involved on the risk when a pesticide is incorporated in the environment. In addition, many of them have been identified as endocrine disruptors (EDs), compounds that alter function (s) of the endocrine system and consequently cause adverse health effects in an intact organism, or its progeny, or subpopulations [7–10]. Humans and wildlife depend on the ability to reproduce and develop normally, which is not possible without a healthy endocrine system. Since the beginning of this century, numerous laboratory studies have added to our understanding of the impact of EDs on human and wildlife health [11, 12] and confirmed the scientific complexity of this issue.

The pollution of soil and water bodies by pesticides used in agriculture can pose an important threat to aquatic ecosystems and drinking water resources. Pesticides can enter in water bodies via point sources or diffuse. Surface waters generally

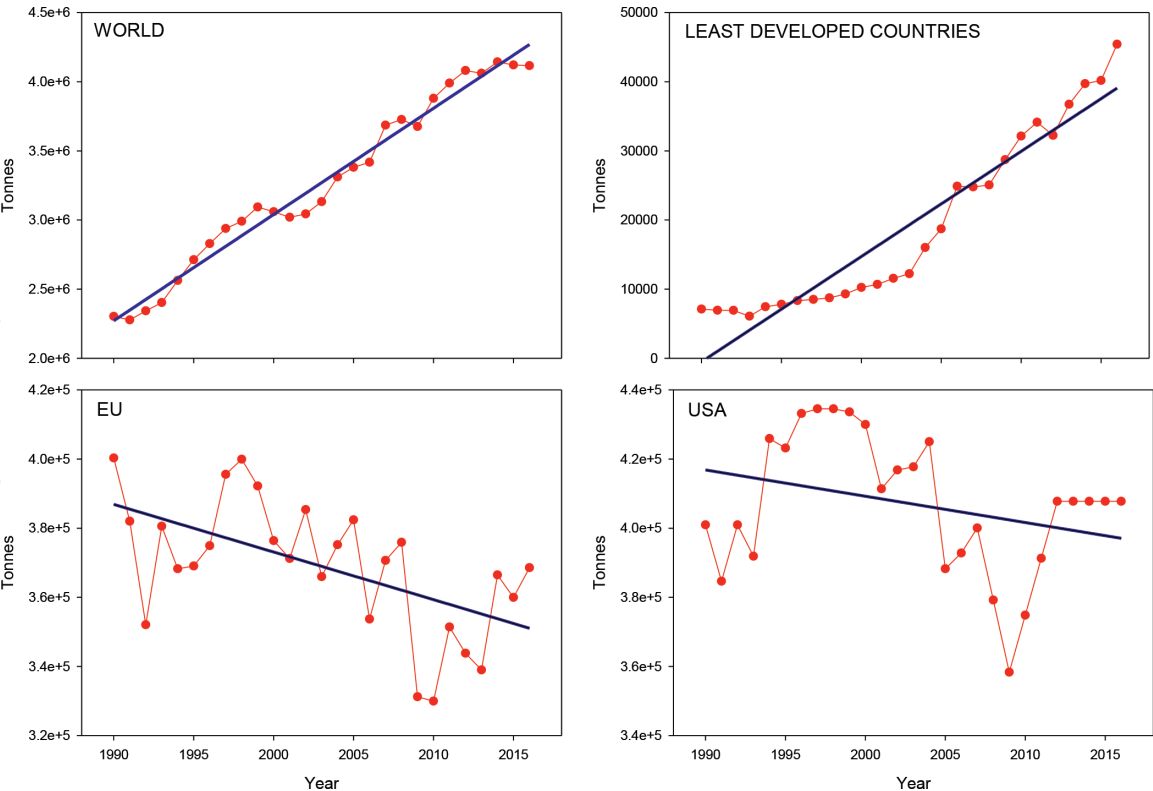


Figure 1.
Evolution of pesticide consumption from 1990 to 2016 (Data obtained from FAOSTAT [2]).

contain a much greater diversity of compounds compared to groundwater although this may be simply a function of the limited amount of groundwater monitoring rather than a surface occurrence. However, according to Directive 2006/118/EC [13], groundwater is the largest body of fresh water in the EU. Concretely, Europe confronts serious episodes of groundwater pollution with agriculture being the biggest polluter. About 60% of European citizens rely on groundwater for drinking water purposes, and its use is threatened by the leaching of pesticides and nitrates due to agricultural practices. In addition, groundwater is used for drinking water by more than 50% of the people in the USA, including almost everyone who lives in rural areas.

Infiltration through riverbeds and riverbanks and leaching through the soil and unsaturated zone are the main diffuse pesticide input paths into groundwater [14, 15]. Therefore, groundwater resources are vulnerable to pollution [16]. Although no universally accepted definition has been contributed for groundwater vulnerability, the National Research Council of USA [17] defines it as “the likelihood for contaminants to reach a specified position in the groundwater system after introduction at some location above the uppermost aquifer.” In this context, pesticide residues have been detected in groundwater bodies in the EU [18] and USA [19] at higher levels in some cases than the drinking water limit established by the EU (0.1 mg L^{-1} for individual pesticide and 0.5 mg L^{-1} for \sum pesticides). In this way, the Directive 2009/128/EC [20] was named to protect human health and the environment from possible risks associated with the use of pesticides. The aim of this directive is to achieve a sustainable use of pesticides in the EU by reducing the risks and impacts of pesticide use on human health and the environment and promoting the use of Integrated Pest Management (IPM) and alternatives, such as nonchemical techniques. When pesticides are used, appropriate risk management measures should be established and low-risk pesticides, as well as biological control measures, should be considered in the first place. According to FAO, integrated pest management (IPM) is “an ecosystem approach to crop production and protection

that combines different management strategies and practices to grow healthy crops and minimize the use of pesticides” [21]. Other definitions of IPM according to the US EPA [22] involve “an effective and environmentally sensitive approach to pest management that relies on a combination of common-sense practices.” IPM, therefore, utilizes the best mix of control tactics for a given pest problem such as host resistance, chemical, biological, cultural, mechanical, sanitary, and mechanical controls using each technique a different set of mechanisms for suppressing populations [23].

2. Soil: fundamental concepts related to pesticide leaching

Defining soil is always a hard task due to its high heterogeneity, the complex processes involved, and quite often its own use. The soil taxonomy defines the soil as *a natural body comprised of solids (minerals and organic matter), liquid, and gases that occurs on the land surface, occupies space, and is characterized by one or both of the following: horizons, or layers, that are distinguishable from the initial material as a result of additions, losses, transfers, and transformations of energy and matter or the ability to support rooted plants in a natural environment* [24]. Soil structure refers to units composed of primary particles. Seven structural classes are recognized in soils: platy, prismatic, columnar, blocky, granular, wedge, and lenticular.

2.1 Soil profile

A soil profile is a vertical section of a soil, showing horizons (layers running parallel to the surface) and parent material. **Figure 2** shows a drawing of a vertical section of soil.

Soil horizons differ in different easily seen soil properties (color, texture, structure, and thickness) and other less visible (chemical and mineral content, consistency, and reaction). The *O horizon* is the layer containing organic materials such as surface organisms, twigs, and dead leaves. It has different levels of decomposition (minimal, moderately, highly, and completely decomposed organic matter). This horizon is often black or dark brown in color, because of its organic content. The roots of small grass are found in this layer. The *A horizon* (also known as the root zone) constitutes the topsoil. It is typically made of sand, silt, and clay with high levels of organic matter and is highly vulnerable to erosion by wind and water. The *B horizon* contains high concentrations of clay, iron, aluminum, and carbonates. Other specific subhorizons will be mentioned, as needed. For example, a B horizon may have several parts if their characteristics such as texture or color change with depth (denoted as Bt1, Bt2, Btg). The *C horizon* is mainly made up of broken bedrock without organic material. It contains geologic material and cemented sediment and there is little activity. The *R horizon* is bedrock (granite, basalt, and limestone), a compacted and cemented material due to the weight of the overlying horizons.

2.2 Soil composition

Although an infinite variety of substances may be found in soil, four basic components constitute it: minerals (45%), organic matter (5%), air (25%), and water (25%). The voids in the soil are known as pore space, and there are two kinds of pores: matrix and nonmatrix pores. Matrix pores are typically smaller than nonmatrix pores in fine- and medium-textured soils.

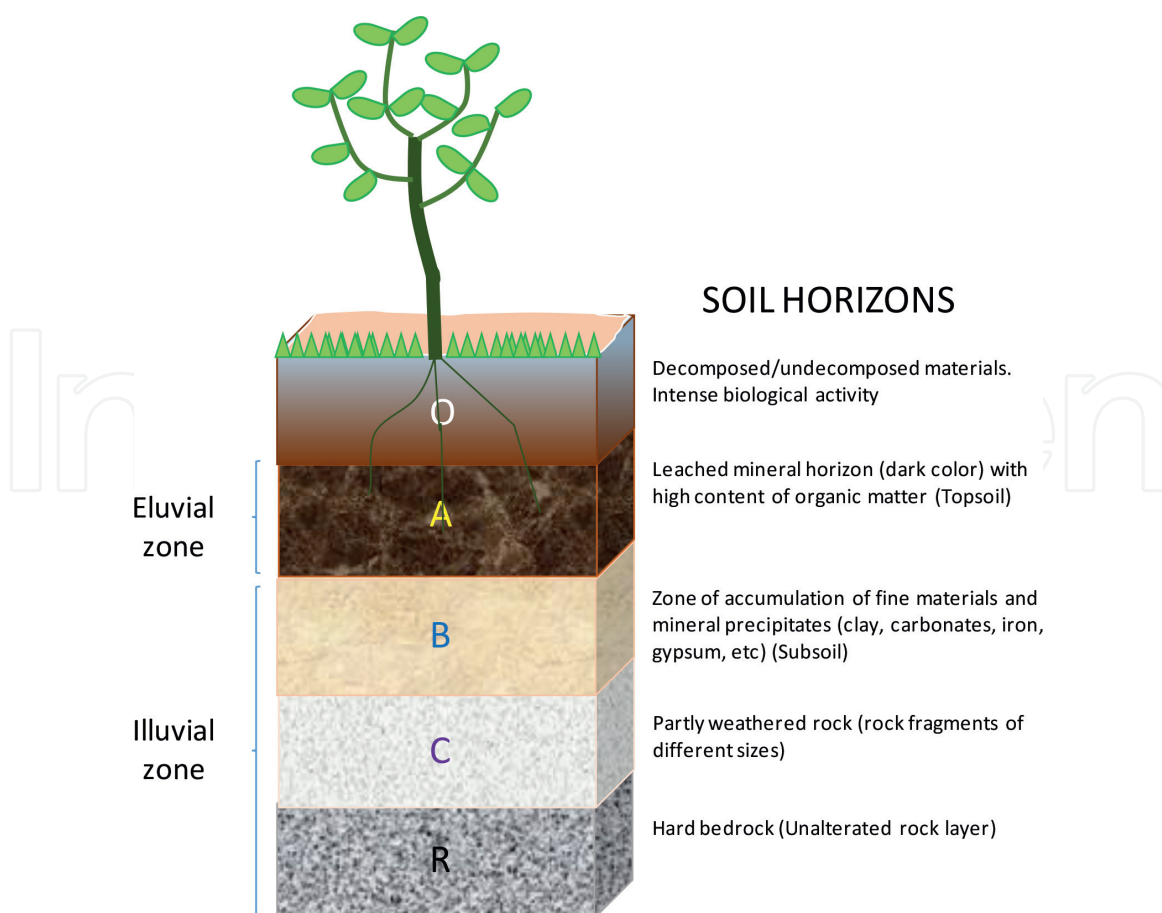


Figure 2.
 Schematic drawing of the soil profile.

Air and water are in the pores contained between the solid particles of the soil. The pore sizes vary from very fine (<1 mm) to very coarse (≥ 10 mm). The ratio of air-/water-filled pore space vary seasonally, weekly, and even daily, depending on water additions through precipitation, flow, groundwater discharge, and flooding. According to suction and gravimetric water contents as defined by suction, three water state classes can be defined: dry (>1500 kPa), moist (≤ 1500 to >1.0 kPa), and wet (≤ 1.0 kPa). Natural drainage class refers to the frequency and duration of wet periods. Different drainage classes include excessively drained, somewhat excessively drained, well-drained, moderately well-drained, somewhat poorly drained, poorly drained, very poorly drained, and subaqueous [24].

The mineral portion of soil is divided into a fine fraction (<2 mm in diameter) and larger soil particles (>2 mm in diameter) known as rock fragments. Three particle-size classes integrate the fine fraction: sand (2–0.05 mm), silt (0.05–0.002 mm), and clay (<0.002 mm). These particles differ in their effects on soil drainage and their relative capacity to available hold water for uptake by plants. Texture can be defined as the relative combination of sand, silt, and clay in a soil. Thereby, 12 soil textural classes are represented on the USDA soil texture triangle as can be seen in **Figure 3** [24].

On the other hand, soil organic matter (SOM) is a complex mixture of different substances containing fresh deposits of plants and organisms and humus, a fraction of stable organic compounds mainly humic and fulvic acids that are resistant to further rapid decomposition. An important physical property of SOM is its ability to absorb large quantities of water. The mass and volume of water that can be absorbed by SOM often exceed the mass and volume of the SOM itself. In addition, SOM has a much higher CEC than clays and can also form complexes with metals and organic materials like pesticides, sometimes rendering them immobile [25, 26].

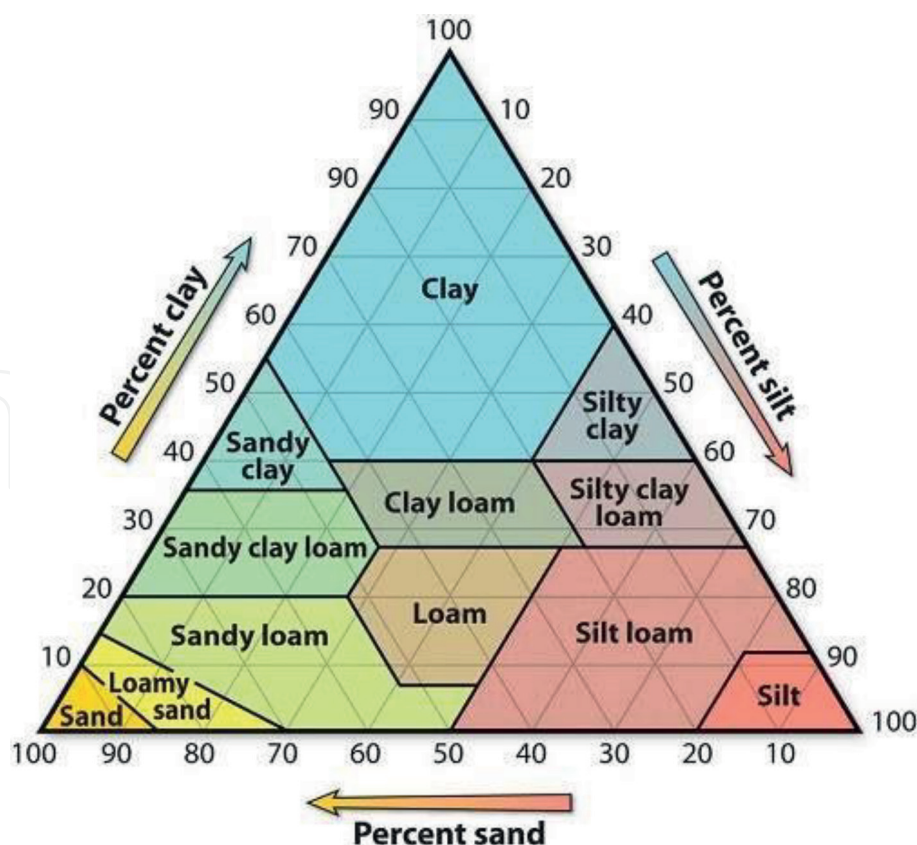


Figure 3.
Possible textural classes of the soil.

3. Behavior and fate of pesticide residues in the soil

In addition to accidental or intentional discharges, the presences of pesticides in agricultural soils mainly have two origins: (i) treatments applied to the aerial part of crops to combat pests, when approximately 50% of the product (insecticides and fungicides, and some herbicides) may reach the soil and (ii) the soil itself is directly treated (insecticides, nematicides, disinfectants, and mainly herbicides), which will obviously lead to a higher concentration in the same [27]. To understand the behavior of a pesticide, it is essential to have the appropriate analytical tools capable of determining residual concentrations in different media (plant, soil, and water) and the main metabolites that can appear. Analytical procedures typically involve a number of equally relevant steps for *sampling, sample preparation, isolation of the target compounds, identification, and quantification* mainly by gas (GC-MS) and liquid chromatography (LC-MS) coupled to mass spectrometry and other minority techniques such as capillary electrophoresis (CE), immunochemical methods (ICMs), electrochemical methods (EMs), chemiluminescence (CL) or ion mobility spectrometry (IMS), and *data processing* [28, 29].

The fate of pesticides in the soil depends on many processes responsible for their mobility and persistence [30, 31]. Persistence may be defined as *the tendency of a pesticide to conserve its molecular integrity and chemical, physical, and functional characteristics for a certain time after being released into the soil*. The half-life time ($t_{1/2}$) is the term commonly used to assess persistence (i.e., the time required for a pesticide to degrade to one-half of its initial amount in the soil). The typical half-life to consider a pesticide as persistent is more than 100 days, while nonpersistent pesticides have less than 30 days. Therefore, moderately persistent pesticides have $t_{1/2}$ ranged from 30 to 100 days [32]. From an environmental point of view, persistent pesticides are undesirable because some of them are intrinsically toxic and

deleteriously affect human, domesticated animals, agricultural crops, wildlife, fish and other aquatic organisms, or microorganisms. Some recalcitrant (i.e., nonbiodegradable) pesticides are not toxic at the levels found in the soil, but they can reach hazardous levels due to biomagnifications through the natural food chains. For this reason, it is very important to know the process by which a pesticide is degraded in order to determine whether it will accumulate in the soil or pass into groundwater and whether it will persist in either.

Once a pesticide is applied to soil, it will most likely follow one of three pathways: (i) adhering to soil particles (mainly organic matter and clays), (ii) degrading by organisms and/or free enzymes, and (iii) moving through the soil with water. From the physical-chemical data of adsorption, mobility, and degradation obtained in the laboratory, it is possible to predict with a high degree of reliability the behavior of pesticides in the soil. For this, different guidelines have been proposed by OECD to study adsorption [33], degradation [34], and leaching [35]. **Figure 4** shows the schematic behavior of pesticides in the soil.

Adsorption that may be chemical (electrostatic interactions) or physical (van der Waals forces) is the result of the electrical attraction between charged particles, pesticide molecules (sorbate), and soil particles (adsorbent). Pesticide molecules that are positively charged are attracted to negatively charged particles on clays and organic matter. Chemical reactions between unaltered pesticides or their metabolites often lead to the formation of strong bonds (chemisorption) resulting in an increase in the persistence of the residues in the soil, while causing it to lose its chemical identity.

Degradation generally happens gradually through the formation of one or more metabolites and takes place through photochemical, chemical, and/or microbiological processes. Photodegradation refers to the decomposition induced by radiant energy (ultraviolet/visible light range) on pollutants and is only relevant at the soil

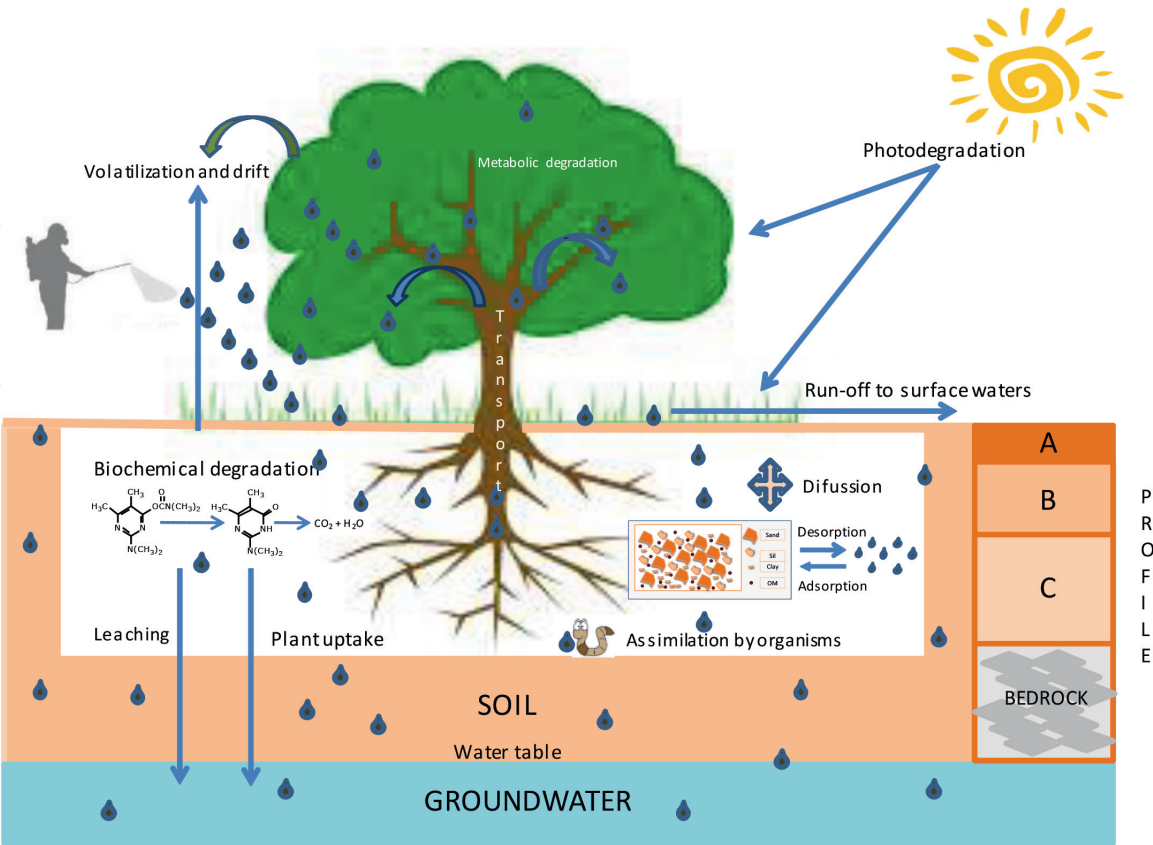


Figure 4.
Behavior and fate of pesticides in the soil.

surface. The solar light may be absorbed by the pollutant, resulting in the formation of by-products, or does not have a direct effect on the pollutant but acts on other substances (photosensitizers) that will promote the degradation of pesticides [36]. Chemical (hydrolysis, oxidation, aromatic hydroxylation, etc.) and biological processes are closely linked and it is difficult to distinguish between them. For this, the process is commonly called biochemical degradation.

The transformations that pesticides may suffer in the soil are many and varied. Besides the characteristics of the pesticide, other factors such as the colloidal composition, texture and moisture content of the soil, the number of microorganisms present (including bacteria and fungi), etc., play a key role. *Biodegradation* can be defined as *a process by which microbial organisms transform or alter, through metabolic or enzymatic action, the structure of pesticides present in the soil* [37]. The metabolic pathways from natural metabolic cycles have enabled the microorganisms to degrade pesticides in the soil although many of them are recalcitrant pesticides. Whereas biodegradable pesticides are broken down within days or weeks by soil microorganisms, recalcitrant pesticides remain for long periods (years or even decades) in the soil.

By a total degradation of a pesticide (mineralization), CO₂, salts, and water are formed, and parts of the chemical are built into new molecular structures in the soil humus or in biomass (bound residues). The terms *free* and *bound* residues were coined to indicate that the former can be readily extracted from soil without altering their chemical structures, whereas the latter are resistant to such extraction [38]. However, the distinction between these two fractions is not always clear, because while they are in the soil, even the extractable residues are not entirely free from any form of binding because they may be adsorbed to the soil solid phases and, therefore, show reduced bioavailability and degradation. According to Roberts [39], bound residues are *chemical species originating from pesticides, used according to good agricultural practice, that is, unextracted by methods which do not significantly change the chemical nature of these residues*. Twelve years later, according to IUPAC, Fuhr et al. [40] proposed a modification to the existing definition of bound residues: *Compounds in soils, plant or animals, which persist in the matrix in the form of the parent substance or its metabolite(s) after extraction*.

Knowledge of the kinetics of biochemical degradation is essential to the evaluation of the persistence of pesticides. Pesticide degradation was described using simple first-order (SFO) kinetics for much time, and it is still the most common mathematical description of pesticide degradation in the scientific literature. However, in some cases, this model is not appropriate. The FOCUS (FORum for the Coordination of pesticide fate models and their USE) degradation kinetic expert group, supported by the European Commission, came up with two alternative equations for pesticide degradation in soil. Both are based on first-order kinetics although composed of several processes [41]. The alternative equations are the First Order Multi-Compartment (FOMC) equation and the Double First Order in Parallel (DFOP) equation.

$$C_t = C_0 e^{-kt} \text{ (SFO)} \quad (1)$$

$$C_t = C_0 \left(1 + \frac{t}{\beta}\right)^{-\alpha} \text{ (FOMC)} \quad (2)$$

$$C_t = C_1 e^{-k_1 t} + C_2 e^{-k_2 t} \text{ (DFOP)} \quad (3)$$

where C_t = amount of pesticide present at time t , k = rate constant for the degradation process, C_0 = amount of pesticide at time 0 (initial amount), β = parameter determined by the variation in k values, α = positional parameter, C_1 = amount of pesticide at time 0 in the first compartment, k_1 = rate constant for degradation in

the first compartment, C_2 = amount of pesticide at time 0 in the second compartment, and k_2 = rate constant for degradation in the second compartment.

Finally, pesticide transfer refers to the movement of pesticides from their site of application. Five processes that can move pesticides are diffusion, volatilization, leaching, erosion and runoff, assimilation by microorganisms, and absorption by plants. Diffusion can be verified in the gaseous and liquid phases, or in the air of the inter-solid phase. The pesticide is transferred through the soil from one zone where it is more concentrated to another where it is less. The volatilization of pesticides from the soil and their subsequent dispersion in the atmosphere is a common occurrence and is perhaps the most important route by which pesticides dissipate. Once volatilized, a pesticide can move in air currents away from the treated surface, a phenomenon known as vapor drift. The soil can be act as a conveyor of the pesticide when its particle is moved from one place to another through the effects of wind or runoff, leading in certain cases to the contamination of surface waters (rivers, seas, and lakes). Runoff determines the movement of water over a sloping surface that occurs when water is applied faster than it enters the soil. Pesticides carried by surface runoff from agricultural areas are a significant portion of the pesticide pollutant loading rates to surface water bodies. Absorption of pesticides by a target and nontarget organisms (bioaccumulation) is quite variable and it is influenced by species characteristics, environmental conditions, and by the chemical-physical properties of both the pesticide and the soil. Pesticide uptake by plants depends on the environmental conditions and the physical-chemical properties of the soil and pesticides and it is influenced by plant species, growth stage, and intended use. Leaching is the vertical downward displacement of pesticides through the soil profile and the unsaturated zone, and finally to groundwater. Pesticide leaching is highest for weakly sorbing and/or persistent compounds, climates with high precipitation and low temperatures (which leads to high groundwater recharge) and sandy-soils with low organic matter.

Figure 5 summarizes major factors (pesticide and soil properties, site conditions, and management practices) affecting the fate of pesticides in the soil [32].

3.1 Leaching process

Nowadays, the study of pesticide leaching represents an important field of research concerning environmental pollution. A large number of papers published

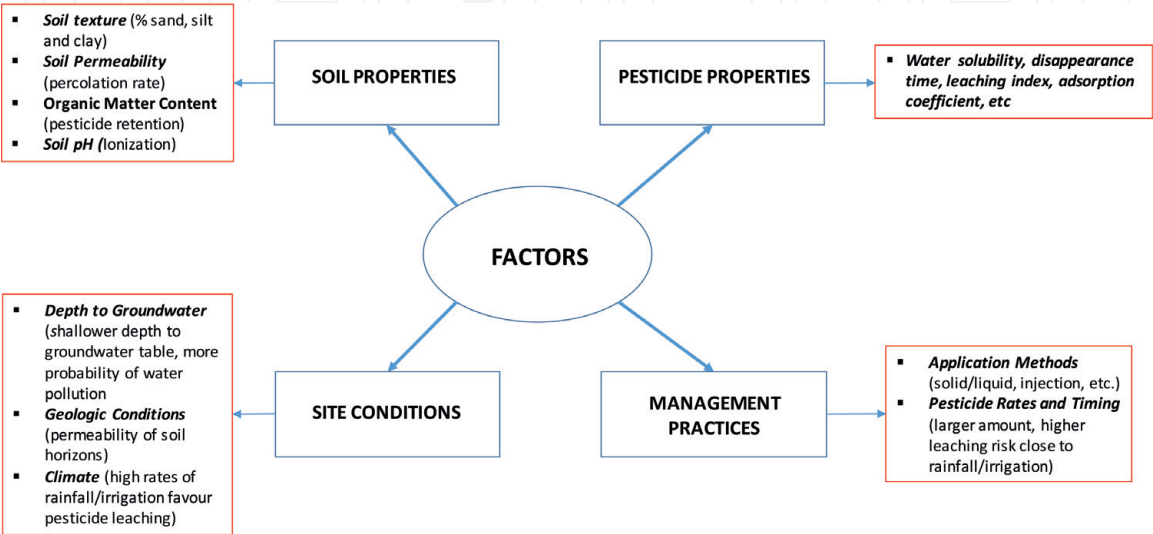


Figure 5.
Factors affecting the fate of pesticides in the soil.

from the beginning of this century to the current moment confirm this interest. A review to the literature extracted from The Web of Science™ (www.isiknowledge.com) managed by Thomson Reuters (Philadelphia, USA) using the keywords *pesticides* AND *leaching* AND *soil* shows about 2500 papers in the period considered.

Leaching constitutes an environmental risk because they can reach the water table and contaminate shallow groundwater and deeper aquifers. However, for pesticides with a low persistence that disappear quickly, the risk of groundwater pollution considerably decreases.

Two different types of flow are associated with pesticide leaching: (i) preferential flow, related to water that flows rapidly through large voids, root channels, and cracks and (ii) matrix flow, due to the slow movement of pesticide/water through the small pores of the soil having in this case more time to contact soil particles [42].

Pesticides are frequently leached through the soil by the effect of rain or irrigation water but for this to happen, the product must be sufficiently soluble in water. The pesticide may be displaced, dissolved, suspended, or simply emulsified in water. Water movement concerns rates of flow into and within the soil and the related amount of water that runs off and does not enter the soil. Infiltration is the process of downward water entry into the soil. Three infiltration stages may be differentiated: (i) steady ponded, (ii) preponded, and (iii) transient ponded. Water that is moving at a high velocity can better carry pesticides of high molecular weight and has the potential to move them farther.

3.1.1 Influential factors

The factors (chemical, physical, and biological) influencing the leaching rate of the pesticides are varied including among others, physical-chemical properties of the pesticide, permeability of the soil, texture and organic matter content of the soil, volatilization, crop-root uptake, and method/dose of pesticide application. Also important is climate change. Pesticide leaching can be affected directly by climate change due to variations in temperature and precipitation patterns or indirectly by any change in the agroecosystem caused by changes in land use, modified application timings, or the use of different pesticides against new invasive pests, diseases, or weeds [43]. Regarding direct effects, increased temperatures should in principle increase pesticide degradation rates, which will, in turn, reduce the risk of leaching although also increase desorption (endothermic process) favoring the liberation of pesticides from soil colloids. On the other hand, an increase in rainfall leads to an increased risk of pesticide leaching.

Different soil adsorption models have been developed for different pesticide classes in order to identify the properties governing retention class-specific quantitative structure-property relationship [44]. **Table 1** summarizes the main physical-chemical properties of a pesticide that can affect its leaching rates and the suggested thresholds according to PPDB [45].

The relation between the concentrations of the compound in the solid and liquid phases is known as the distribution coefficient and is directly proportional to the solubility of the pesticide in water and inversely proportional to the organic matter (OM) and clay content of the soil.

$$K_d = \frac{C_a}{C_d} \quad (4)$$

where K_d = coefficient of partition between soil and water (V/M); C_a = amount of pesticide adsorbed per unit of adsorbent mass (M/M); and C_d = concentration of pesticide dissolved (M/V).

Parameter	Thresholds
WS (mg L ⁻¹)	<50 = low; 50–500 = moderate; >500 = high
Log K _{OW}	<2.7 = low bioaccumulation; 2.7–3 = moderate; > 3.0 = high
DT _{50SD} (days)	<30 = nonpersistent; 30–100 = moderately persistent; 100–365 = persistent; > 365 = very persistent
DT _{50AP} (days)	<1 = fast; 1–14 = moderately fast; 14–30 = slow; >30 = stable
DT _{50AH} (days)	<30 = nonpersistent; 30–100 = moderately persistent; 100–365 = persistent; > 365 = very persistent
GUS index	>2.8 = high leachability; 2.8–1.8 = transition state; <1.8 = low leachability
VP (mPa)	<5 = low volatility; 5–10 = moderately volatile; >10 = highly volatile
H (Pa m ³ mol ⁻¹)	>100 = volatile; 0.1–100 = moderately volatile; <0.1 = nonvolatile
Log K _{OC}	<1.2 = very mobile; 1.2–1.9 = mobile; 1.9–2.7 = moderately mobile; 2.7–3.6 = slightly mobile; >3.6 = nonmobile
pK _a	pH < pK _a neutral state; pH > pK _a negative charge

WS: water solubility; K_{OW}: octanol-water partition coefficient; DT: disappearance time; SD: soil degradation; AP: aqueous photolysis; AH: aqueous hydrolysis; GUS: groundwater ubiquity score index; VP: vapor pressure; H: Henry's law constant; K_{OC}: organic carbon normalized sorption coefficient; K_a: acid dissociation constant.

Table 1.
Main physical-chemical properties influencing the leaching of pesticides.

Karickhoff et al. [46] demonstrated the existence of a linear correlation between the coefficient of partition and the soil's organic carbon content:

$$K_{OC} = \left(\frac{K_d}{OC} \right) \times 100 \tag{5}$$

where K_{oc} = soil organic partition coefficient and OC is the organic carbon content (%).

For polar molecules and soils with low OM content and high clay content, Hermosín and Cornejo [47] found a similar correlation:

$$K_{OC} = \left(\frac{K_d}{CC} \right) \times 100 \tag{6}$$

where K_{cc} = clay content partition coefficient and CC = clay content (%). Both K_{oc} and K_{cc} are linearly correlated with the coefficient of partition between octanol and water (K_{ow}), which indicates the affinity degree of the pesticide for water (low value) or for soil (high value).

Sorption and degradation processes, both influenced by chemical-physical properties of the soils and compounds involved, and weather conditions, mainly affect the movement of water and dissolved pesticides through the soil. According to some authors, adsorption and desorption are the processes that regulate the magnitude and speed of leaching, and a pesticide should not be affected by other processes while it is adsorbed to the humic-argillic complex [48]. The use of clay barriers modified with cationic surfactants has been demonstrated as an effective method to increase the retention of pesticides in soil [49, 50]. The content of organic carbon (OC) is considered as the single largest factor having maximum influence on pesticide degradation, adsorption, and mobility in soil [51]. Therefore, the soil organic adsorption coefficient (K_{OC}) is generally used as a measure of the

relative potential mobility of pesticides in soils to describe the partitioning of them in the water/soil/air compartments.

Thus, a possible mitigation measure to reduce pesticide leaching through the soil could be the increase of the OM content of the soil by agronomic practices like the incorporation of crop residues or animal manures to increase sorption of nonionic pesticides [52]. Another option to reduce leaching by matrix flow would be the use of compounds with high/fast sorption. Addition of OC in the form of crop residues, manure, or sludge is a common soil management practice followed in some areas of the Mediterranean Basin. In this zone, high temperature and evapotranspiration, adverse climatic conditions, and soil degradation are responsible for the decrease in plant growth and consequent lack of organic compounds that would improve the soil nutrient status since its addition contributes to enhancement of active humified components (humic and fulvic acids) [53]. Soils of low OC content have a low capacity to avoid pesticide mobility because humic substances are the primary adsorbent materials for pesticides. Nowadays, the addition of organic amendment (OA) to soils is being intensely studied to know its effect on pesticide sorption and its movement through the soil profile in order to minimize the risk of water pollution associated with rapid runoff and leaching. Soil amended with sludge, urban waste compost, composted straw, fly ash, olive oil mill wastes, spent mushroom substrates, or wood residues has been shown to increase pesticide [54–64]. In addition, recent studies have demonstrated the ability of biochar to decrease pesticide leaching to groundwater. The concept to use biochar as a soil amendment is recent but it really comes from the study of very ancient soils in the Basin of Amazon. Biochar can be defined as a carbon-rich solid material produced by heating biomass in an oxygen-limited environment [65]. Biochar is distinguished from charcoal by its use as a soil amendment. Many and varied properties are attributed to biochar such as C sequestration, reduction of N_2O emissions from soil, bioenergy generation, stimulation of soil microorganisms, sorption of pesticides and nutrients, improvement of soil structure and retention of water, and control of soil-borne pathogens [66–68].

The main benefit concerning the sorption of pesticides to OM is that it generally decreases leaching, where it is due to the presence of additional OM in the amended soil but also to the structural changes in the porosity induced by the presence of new OC content [69]. As a part of the OA added, dissolved organic matter (DOM) is incorporated to the soil, which affects movement and sorption of pesticides [70, 71]. Pesticide leaching may be enhanced by pesticide-DOM interactions and competition for sorption sites between pesticides/DOM molecules [72]. Polarity and molecular weight of the pesticides are key factors on the extent and nature of this behavior [73]. Moreover, the microbiological activity is increased by addition of OA to soil, which enhances the biodegradation of pesticides in polluted soils. Therefore, pesticide behavior in amended soil has reported different results because diverse effects have been pointed [74].

3.1.2 Methodology for leaching studies

In addition to thin-layer chromatography (TLC) and reverse-phase LC, other methods are commonly used to assess the potential leaching of pesticides through the soil. These methods include soil columns, outdoor lysimeters, and field studies [75].

The use of the packed column is a valuable tool to analyze pesticide displacement through the soil. OECD [35] and USEPA [76] have standardized methods to study the leaching process. These studies are generally carried out using disturbed soil columns filled with sieved soil (<2 mm). The use of disturbed soil columns

has the advantage of obtaining more reproducible results than other methods. Pesticides are applied on the top of the column followed by percolation with a pesticide-free solution after 24–48 h with distilled or deionized water, and preferably with electrolytes as 0.01 M CaCl₂ to minimize colloidal dispersion [77].

Outdoor lysimeters were developed to avoid or at least decrease the differences obtained between laboratory and field conditions [78]. In addition, lysimeters having a large surface area can be used to plant crops to assess pesticide behavior under simulated natural conditions and being the water easily collected from the bottom of them. An additional advantage of the lysimeters over laboratory columns is that the seasonal effect of an application on leaching can be evaluated. For contrast, outdoor lysimeter studies may require many replicates to obtain accurate results on pesticide transport due to the variability of profiles. At field scale, groundwater monitoring and terrestrial field dissipation studies can be considered methods that are more realistic to assess the potential risk of the leaching process.

3.1.3 Indexes for pesticide leaching

Many authors have proposed various indices to predict the mobility of pesticides in the soil. The *K_{oc}* value, obtained by using the batch equilibrium method, is simple and one of the most useful indexes for nonionic pesticides for which the leaching potential is indicated by a mobility classification of immobile to very mobile. They are simple index-based screening tools, which use both the physical-chemical properties of pesticides and soil to make a quick evaluation of pesticide leaching potential considering setting threshold values. **Table 2** summarizes some of the main indices published during the last four decades.

Index/ reference	Parameters/equation/interpretation criteria
Hamaker's RF [79]	$R_F = \frac{1}{\{1 + (K_{OC} * f_{OC} * \rho_b * (\theta^{-0.67} - 1))\}}$ $R_F = 0.64\text{--}1$: high; $R_F = 0.35\text{--}0.64$: moderate; $R_F = 0.1\text{--}0.35$: low; $R_F < 0.1$: very low
McCall's [80]	K_{OC} 0–50, very high; 50–150, high; 150–500, medium; 500–2000, low; 2000–5000, slight; > 5000, immobile
Briggs's RF [81]	$\text{Log}(1/R_F - 1) = \text{Log}(K_{OW}) + \text{Log}(OM) - 1.33$ $R_F = 0.90\text{--}1.0$: class 5 (very high); $R_F = 0.89\text{--}0.65$: class 4 (high); $R_F = 0.64\text{--}0.35$: class 3 (moderate); $R_F = 0.34\text{--}0.10$: class 2 (low); $R_F = 0\text{--}0.09$: class 1 (very low)
LEACH [82]	$LEACH = \frac{S_w * t_{1/2}}{V_p * K_{OC}}$ Comparison (lower values; lower leaching potential)
Cohen's [83]	Soil DT ₅₀ > 2–3 weeks; hydrolysis DT ₅₀ > 25 weeks; aqueous photolysis DT ₅₀ > 1 week; soil <i>K_{oc}</i> < 300; soil <i>K_d</i> < 5; <i>K_H</i> < 10 ^{–2} ; WS > 30 mg L ^{–1} or field leaching at >75–90 cm High leaching potential
Hornsby index [84]	$HI = \left(\frac{K_{OC}}{t_{1/2}}\right) * 10$ $HI \leq 10$: high; $HI \geq 2000$: low
AF [85]	$RF = \left[1 + \frac{\rho_b * f_{OC} * K_{OC}}{\theta_{FC}} + \frac{\theta_s * K_H}{\theta_{FC}}\right] AF = \exp\left[\frac{-0.693 * d * RF * \theta_{FC}}{q * t_{1/2}}\right]$ $AF = 0$ to -1 : high; $AF = -1$ to -2 : moderate; $AF = -2$ to -3 : low; $AF = -3$ to -4 : very low; $AF < -4$: nonleachable
GUS [86]	$GUS = [4 - \text{log}(K_{OC})] * \text{log}(t_{1/2})$ $GUS > 2.8$: leachable; $GUS = 1.8\text{--}2.8$: intermediate; $GUS < 1.8$: nonleachable

Index/ reference	Parameters/equation/interpretation criteria
LPI [87]	$RF = \left[1 + \frac{\rho_b * f_{OC} * K_{OC}}{\theta_{FC}} + \frac{\theta_g * K_H}{\theta_{FC}} \right] LPI = \frac{1000 * t_{1/2} * q}{0.693 * RF * Z}$ <p>$LPI > 90$: very high; $LPI = 75-89$: high; $LPI = 50-74$: moderate; $LPI = 25-49$: low; $LPI = 0-24$: very low</p>
SNV [88]	1. Water solubility greater than 3 ppm; 2. Organic carbon normalized soil sorption coefficient (K_{OC}) < 1900 mL g ⁻¹ ; 3. Hydrolysis DT ₅₀ > 14 days; 4. Aerobic soil metabolism DT ₅₀ > 610 days; 5. Anaerobic soil metabolism DT ₅₀ > 9 days. If the Boolean expression “(1 or 2) and (3 or 4 or 5)” is TRUE = potential leacher
PLP index [89]	$PLP_{value} = \frac{R * F * t_{1/2}}{K_{OC}} PLP_{index} = (\log PLP_{value})(14.3) + 57$ <p>$PLP_{index} = 90-100$: very high; $PLP_{index} = 70-89$: high; $PLP_{index} = 50-69$: moderate; $PLP_{index} = 30-49$: low; $PLP_{index} = 0-29$: very low</p>
GWCP [90]	$GWCP = \frac{PLP + SLP}{2}$ <p>$GWCP > 150$: high; $GWCP = 75-150$: moderate; $GWCP < 75$: low</p>
AFT & AFR [91]	$AFT = \ln AF / (-0.693) AFR = \ln AFT + k$ <p>Comparison (lower values; lower leaching potential)</p>
LIX [92]	$LIX = \exp(-k * K_{OC}) \text{ or } LIX = \exp\left(-\frac{0.693}{t_{1/2}} * K_{OC}\right)$ <p>$LIX = 1$: high leachable; $LIX = 0.1-1$: leachable; $LIX = 0-0.1$: transition; $LIX = 0$: nonleachable</p>
LIN [93]	$LIN = -0.531 \log K_{OW} + 0.518 \log S_w - 0.495 \log K_{OC} - 0.023 \log V_p - 0.452 \log K_H$ <p>Comparison (lower values; lower leaching potential)</p>
M. LEACH [94]	$M.LEACH = \frac{S_w * t_{1/2}}{K_{OC}}$ <p>Comparison (lower values; lower leaching potential)</p>
GLI [94]	$GLI = 0.579 LIN + 0.558 GUS + 0.595 M.LEACH$ <p>$GLI > 1$: high; $GLI = -0.5$ to 1: medium; $GLI < -0.5$: low</p>
DTK [95]	$DTK = e^{-depth} (a \ln t_{1/2} - b \ln K_{OC})$ <p>Leaching value > 0 = potential leacher; leaching value = 0 = nonleacher</p>
VI [16]	$VI = \frac{200 * k * \theta_{FC}}{d * \rho_b * (\%OM)} * \left(\frac{t_{1/2}}{K_{OC}} \right) * F_{DGW}$ <p>Comparison (lower values; lower leaching potential)</p>

$t_{1/2}$: half-life (days); θ : volumetric soil water content; Z or d : depth to groundwater (m); q : net groundwater recharge rate (m/day); ρ_b : soil bulk density (kg/m³); OM: organic matter; S_w : water solubility (mg/L); V_p : vapor pressure (mm Hg); θ_{FC} : volumetric water content at field capacity; F : fraction of pesticide reaching the soil during application; K_H : Henry constant; K_{ow} : octanol/water partition coefficient; K_{oc} : organic carbon normalized soil sorption coefficient (mL/g organic carbon); θ_g : gas content; RF : retardation factor; V : volatility (bar); f_{oc} : organic carbon fraction; R : rate of pesticide application (kg/ha).

Table 2.
Main indices published during the last four decades about the risk potential of pesticide leaching for groundwater pollution.

Thus, a pesticide screening can be estimated with relatively few input data need, and therefore, these index-based methods are easy to apply, unlike other models that require very intensive field-based data that are very difficult to obtain in many cases as summarized in the next section.

4. Vulnerability risk of groundwater to pesticide pollution

Groundwater can be defined as the water located beneath the earth’s surface in soil pore spaces and in the fractures of rock formations [96]. The alteration of the chemical

equilibrium established between groundwater and the surface through which it circulates, reflected in the appearance of foreign substances or compounds to which they constitute natural quality, serves as an indicator of human activity. When this alteration constitutes a negative impact on the water bodies or affects the potential of the resource for its subsequent use, it can be called pollution. Unlike what happens in surface waters, the detection of pollution and the evaluation of its effects on groundwater resources present serious difficulties. In the groundwater, degradation of quality is often noticed when the polluting process has affected large areas of the aquifer. The adoption of corrective measures, which are expensive and not always effective, is difficult due to the evolution of the contaminant in the medium and the consequent difficulty in establishing a diagnosis of the cause-effect relationships. Therefore, the vulnerability of an aquifer to pollution indicates the sensitivity of groundwater to an alteration in its quality caused by human activities. In addition to the influence exerted by the unsaturated zone, the vulnerability of groundwater as a consequence of a pollution episode is also conditioned by climatological factors (rainfall and temperature), and others related to the polluting load such as method and place of penetration, mobility, and persistence of the pesticide (**Figure 6**).

In 1996, the EPA developed SCI-GROW (Screening Concentration in Groundwater) as a screening-level tool to estimate drinking water exposure concentrations in groundwater resulting from pesticide use [97]. As a screening tool, SCI-GROW provides conservative estimates of pesticides in groundwater, but it does not have the capability to consider variability in leaching potential of different soils, weather (including rainfall), cumulative yearly applications, or depth to aquifer. In 2004, concurrently, the EPA Office of Pesticide Programs (OPP) and Canada's Pesticide Management Regulatory Authority (PMRA) initiated a project to develop a harmonized approach to modeling pesticide concentrations in groundwater called the Pesticide Root Zone Model (PRZM). After this project was completed, the two agencies recommended PRZM-GW as the harmonized tool for assessing pesticide concentrations in groundwater, which was implemented as an exposure model in 2012 [98].

In addition to these models, there are three traditional methods for assessing groundwater vulnerability to pollution with pesticides and other pollutants: (i) process-based, involving numerical modeling, (ii) statistical, involving correlating

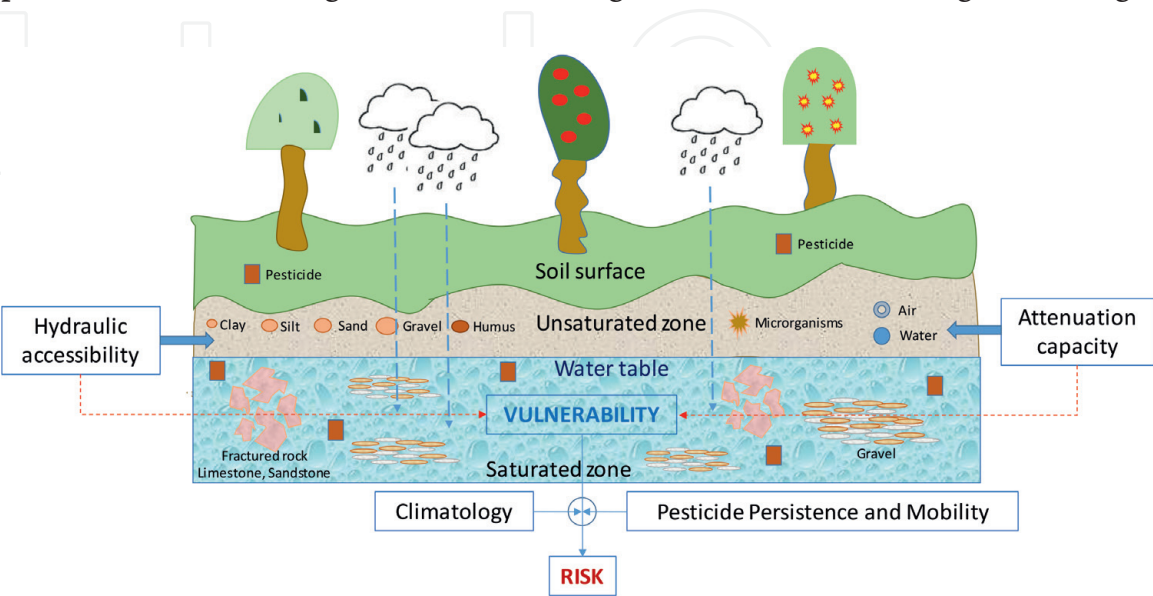


Figure 6.
Schematic drawing of the properties and factors affecting groundwater vulnerability.

water quality data to spatial variables, and (iii) overlay and index, involving obtaining and combining maps of the parameters that affect the transport of contaminants from the surface to groundwater.

Different groundwater models such as MODFLOW (1984), DRASTIC (1987), GOD (1987), AVI (1993), SINTACS (1994), SEEPAGE (1996), EPIK (1999), HAZARD-PATHWAY-TARGET (2002), INDICATOR KRIGING (2002), GLA & PI (2005), ISIS (2007) GSFLOW (2008), GWM-2005 (2009), or VULPES (2015) among others have been used to evaluate groundwater vulnerability, although these models require significant input data to run, and for most users, it is not easy to use them [99–103]. The most commonly used model is DRASTIC in the framework of GIS environment (GIS-based DRASTIC model), an overlay and index method developed by US EPA [104]. GIS is a system of hardware and software used for storage, retrieval, mapping, and analysis of geographic data showing one of the leading tools in the field of hydrogeological science that helps in assessing, monitoring, and conserving groundwater resources, while DRASTIC provides a basis for evaluating the vulnerability to pollution of groundwater resources based on hydrogeological parameters. The DRASTIC model uses seven environmental parameters (Depth to water, net Recharge, Aquifer media, Soil media, Topography, Impact of the vadose zone, and hydraulic Conductivity) to characterize the hydrogeological setting and evaluate aquifer vulnerability, which helps prioritize areas with respect to groundwater contamination vulnerability. Each parameter has assigned a rate and a weight (**Table 3**).

$$\text{DRASTIC index} = (\text{Dr} \times \text{Dw}) + (\text{Rr} \times \text{Rw}) + (\text{Ar} \times \text{Aw}) + (\text{Sr} \times \text{Sw}) + (\text{Tr} \times \text{Tw}) + (\text{Ir} \times \text{Iw}) + (\text{Cr} \times \text{Cw}) \tag{7}$$

Ratings				Weights	
Topography (% slope)		Impact of the vadose zone media			
Range	Rating	Media type	Rating	Parameter	Weight
0–2	10	Confining layer	1	Depth to water	5
2–6	9	Silt/clay	3	Net recharge	4
6–12	5	Shale	3	Aquifer media	3
12–18	3	Limestone	6	Soil media	2
>18	1	Sandstone	6	Topography	1
		Bedded limestone/sandstone/shale	6	Impact of the vadose zone media	5
		Sand and gravel with clay/silt	6	Hydraulic conductivity of the aquifer	3
		Metamorphic/igneous	4	Net recharge	4
		Sand and gravel	8		
		Basalt	9		
		Karst limestone	10		

Table 3
Ratings and weights of each parameter in DRASTIC index.

where r is the rating for the parameter and w is an assigned weight for each parameter.

Thus, according to them, the governing equation becomes:

$$\text{DRASTIC index} = 5Dr + 4Rr + 3Ar + 2Sr + Tr + 5Ir + 3Cr \quad (8)$$

Depending on this model, five categories for groundwater vulnerability are established: very low, low, moderate, high, and very high. Two DRASTIC models (Pesticide DRASTIC GIS-based models) have been developed to predict generic groundwater vulnerability and pesticide groundwater vulnerability. They differ in weights, which are used as key factors to determine the DRASTIC vulnerability index. In the last decade, several authors have used this model to study the effect of different pesticides to groundwater vulnerability [105–107]. In other cases, a Bayesian methodology has been used to calculate the vulnerability of groundwater to pesticide contamination directly from monitoring data [108]. In this regard, passive samplers like polar organic chemical integrative samplers (POCIS) have shown to be suitable for the monitoring of pesticides with a wide range of physical-chemical properties in groundwater [109]. Many monitoring studies carried out worldwide in different countries of all continents have demonstrated the occurrence of pesticide residues in groundwater since the beginning of the actual century [18, 19, 110–112]. Among others, herbicides such as triazines (atrazine, simazine, terbuthylazine, propazine, cyanazine, terbutryn, prometryn), phenylureas (diuron, linuron, isoproturon, chlortoluron) and anilides (alachlor, acetochlor, metolachlor) and insecticides such as organophosphorus (malathion, chlorfenvinphos, dimethoate, parathion-methyl, azinphos-ethyl, chlorpyrifos, fenitrothion) and organochlorine (lindane and DDTs) and some of its transformation products (metabolites) are the most common pesticides found in groundwater.

5. Conclusions

Pesticides have important benefits in crop protection because they combat a variety of pests and diseases that could destroy crops increasing the quality of the harvested products. However, due to the heavy use of phytosanitary products (the worldwide consumption of pesticides reached 4.1 millions of tons of active ingredients in 2016), the occurrence of pesticide residues in the groundwater resources (water located beneath the soil's surface) constitutes a global problem worldwide, especially in the least developed countries where the use of plant protection products is very high. Herbicides, mainly triazine and urea compounds, have been the most detected pesticides since the beginning of this century. The pollution of soil and water bodies by pesticides used in agriculture can pose an important threat to aquatic ecosystems and drinking water resources because groundwater is the largest body of fresh water in many areas of the world. Diffuse pesticide input paths into groundwater are caused by leaching through the soil and unsaturated zone and infiltration through riverbanks and riverbeds. Therefore, the groundwater resources are vulnerable to pollution, which indicates the sensitivity of groundwater to an alteration in its quality caused by human activities. Adsorption, degradation, and movement processes are key processes to know the persistence of a pesticide and its ability to contaminate groundwater bodies. The main factors affecting the fate of pesticides are their physicochemical properties (water solubility, vapor pressure, adsorption coefficient, etc.), soil characteristics (texture, organic matter content, etc.), site (hydrogeological conditions), and management practices (method of application and dosage).

Abbreviations

CE	capillary electrophoresis
CEC	cation exchange capacity
DFOP	double first order in parallel equation
DOM	dissolved organic matter
DRASTIC	D epth to Water, N et R echarge, A quifer M edia, S oil M edia, T opography, I mpact of V adose Z one, and H ydraulic C onductivity
DTK	depth, half-life ($t_{1/2}$), and organic carbon normalized sorption coefficient (K_{OC})
EDs	endocrine disruptors
EFSA	European Food Safety Agency
EM	electrochemical method
EPA	Environmental Protection Agency
EPIK	development of the E pikarst, E ffectiveness of the P rotective C over, C onditions of I nfiltration, D evelopment of the K arst N etwork
EU	European Union
FAO	Food Agriculture Organization
FOCUS	F orum for the C oordination of P esticide F ate M odels and their U se
FOMC	First-Order Multi-Compartment
GC	gas chromatography
GIS	Geographic Information System
GLA&PI	G eologische L andesamter, P rotection C over, I nfiltration C onditions
GOD	G roundwater O ccurrence, O verlying L ithology and D epth to the A quifer
GSFLOW	C oupled G round-Water and S urface-Water F LOW M odel
GWM-2005	G round W ater M anagement process for MODFLOW-2005
ICMs	immunochemical methods
IMS	ion mobility spectrometry
IPM	Integrated Pest Management
LC	liquid chromatography
MODFLOW	M ODular three-dimensional finite-difference groundwater F LOW M odel
MS	mass spectrometry
OA	organic amendment
OC	organic carbon
OECE	Organization for Economic Co-operation and Development
OPP	Office of Pesticide Programs
OM	organic matter
PMRA	Pesticide Management Regulatory Authority
POCIS	Polar Organic Chemical Integrative Samplers
PPDB	Pesticide Properties Database
PPP	plant protection product
PRZM-GW	pesticide root zone model-groundwater
SCI-GROW	screening concentration in groundwater
SEEPAGE	S ystem for E arly E valuation of P ollution P otential of A gricultural G roundwater E nvironments
SFO	simple first order

SINTACS	depth to water (S), net infiltration (I), unsaturated zone (N), soil media (T), aquifer media (A), hydraulic conductivity (C), slope (S)
SNV	specific numerical value
SOM	soil organic matter
US EPA	United States Environmental Protection Agency
USA	United States of America
USDA	United States Department of Agriculture
VULPES	VUL nerability to PEST icides

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