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Chapter

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

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:

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

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:

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

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

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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