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Chapter 4

Flow in Unsaturated Soils and Transport of Herbicides in Agricultural Areas

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Additional information is available at the end of the chapter

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Abstract

Predicting the behavior of pesticides in the environment is necessary to minimize the adverse effects of their application. This means that we have to understand what is happening and how it is applied in the field and predict its fate in the environment to estimate the adverse effects on the subsoil and surface water or on human health. Knowing the level of contamination in soils involves characterizing the movement of water in the transport zone and solutes. The objective of this chapter is to disseminate and highlight the problem of the transport of pollutants in soils and to guide with regard to the available methods to obtain the necessary parameters to achieve their modeling and numerical analysis. To this end, the transport equation applied to the transport of agrochemicals is described and analyzed, and the methods of obtaining the parameters required by the mathematical solution are described. The general characteristics of the different herbicides and the environmental impact that the production of these compounds is producing are also described.

Keywords: unsaturated soils, transport of contaminants, agrochemicals, pollution

1. Introduction

Among the most important global problems affecting the environment are climate change, environmental degradation, loss of biodiversity, water pollution, and the growth of potential conflict due to competition for the use of natural resources. Groundwater does not escape this problem.

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The pollution has dramatically impacted the aquatic habitat in many of the world's most important water bodies. The contamination of the subsoil and the aquifers has the peculiarity of being "silent" and not presenting samples that show the same but until its consequences are observed in the biotic media.

Groundwater is usually more difficult to contaminate than surface water, but when this happens, reversing the situation is a very complex solution. The subsoil waters have a very slow rate of renovation. It is estimated that while the mean time of water stays in the rivers is of days, in an aquifer it is from years to hundreds of years, which makes it very difficult to decontaminate it.

The greatest concern about groundwater contamination has focused on the pollution associated with human activities such as the disposal of waste (liquid and solid waste in landfills of urban waste, waste from the oil industry, waste from the mining industry, radioactive waste, etc.) or not directly related to the emission of waste (agricultural activities, mining, construction and inadequate maintenance of buildings, etc.). On many occasions the situation is aggravated by the late knowledge that the aquifer is deteriorating [1].

Adequate protection of groundwater resources should have as a priority to prevent the entry of harmful elements into groundwater. It is a priority then to carry out geological, hydrological, and hydrogeological studies and potential sources of contamination.

Among the diffuse pollution activities, a very important one is the excessive use of fertilizers and herbicides. This type of pollution can cause situations of concern over time, because it is slow but continuous and in very large areas.

Herbicides are substances, usually of organic origin, which are used mainly for the control of weeds in agriculture. To minimize the environmental impact of the same, its application must be made considering the conditions of the plants, the soil, and the environment and the use of procedures for which they were designed and thus obtain an optimal dosage. However rigorous the conditions of use, there is evidence of the presence of traces of herbicides and other pesticides even in nonagricultural areas, in the atmosphere, and in surface and underground water [2].

The presence of pesticides, and especially herbicides, in groundwater and aquifers represents a frequent situation, especially in those regions that have had or have a high consumption of pesticides [3]. This would rule out the possibility of using water without a purification treatment, given that concentration levels of pesticides have been detected ranging from only traces to high levels of concentration.

When agrochemicals exceed the limits for which they were intended, they constitute both a loss to the agrosystem and a source of contamination for adjacent systems. The level of risk of contamination of soil and water results from the combination of the pollutant load and the natural vulnerability of the environment to the said contamination [4].

In this context, the prediction of the behavior of pesticides released into the environment is necessary to anticipate, and therefore minimize, adverse impacts outside the point of application [5]. This means that we must understand what happens to a pesticide that has been

applied in the field and predict its destiny in the environment. Using this information, the likely adverse impacts on surface or groundwater and/or on human health can be estimated.

To this end, the solute transport equation applied to the transport of agrochemicals is described and analyzed in the following points, and some methods of obtaining the parameters required by the mathematical solution are described. It also describes in a general way the main characteristics of different types of herbicides and the environmental impact that the transport of these compounds is producing.

2. Flows in unsaturated soils

Pesticides, fertilizers, and solutes in general get dissolved or dragged with water from the soil through the pores, so the knowledge and measurement of properties such as hydraulic conductivity and effective porosity within the soil are important. These properties depend on the geometry, interconnection, and distribution of pore size within the soil. The presence of interconnected macropores is directly related to the natural aggregation of the soil and can constitute preferential flow paths within the soil [6], which is considered today the main mechanism for the relatively rapid appearance of contaminants in groundwater.

The term preferential flow refers to the fact that the water that infiltrates does not have enough time to get in balance with the water that remains in the soil matrix moving more slowly. These preferential flows can occur, for example, in structured soils, where macropores (cracks, tunnels caused by macroorganisms such as worms and insects, holes in the roots) dominate the hydrogeology of unsaturated to saturated soil, particularly in fine-textured soils, and operate as routes of high flow conductivity through the densest and least permeable matrix of the soil [7].

These preferential flows can also occur in unstructured sandy soils in the form of unstable wetting fronts, which is caused by heterogeneous profiles such as interfaces in the horizons or by water repellency [8].

A consequence of preferential flows is that a heterogeneous front of solute penetration does not occur in the soil; this contradicts the simple (convection-dispersion) equation, which predicts a homogeneous infiltration front.

2.1. Processes of transporting a solute in the soil

The transport process of a solute in the soil will present: volatilization (transport of the solute to the atmosphere); runoff to water surfaces; and leaching into groundwater.

These processes are affected by diffusion, convection, and dispersion. In addition, there are other processes that add to the previous ones such as retention (adsorption or sorption) and chemical transformation.

The processes of chemical transformation can be catalyzed by the constituents of the soil or photochemically induced. Most pesticides are transformed mainly by biochemical processes through soil microorganisms with changes in the molecule toward simpler forms that can be

of equal, less, or greater toxicity than the original, which determines in what form and for how much the solutes will be present on the ground [9].

2.2. Transportation of contaminants

The one-dimensional solute transport equation in an unsaturated medium, which is similar to that of saturated medium, is written as shown in Eq. (1):

$$\frac{\partial C}{\partial t} = -v\frac{\partial C}{\partial z} + D_H\frac{\partial^2 C}{\partial z^2} - \frac{\rho}{n}\frac{\partial S_i}{\partial t} \tag{1}$$

where v is the linear velocity, D_H is the dispersion coefficient, C is the concentration of the pollutant, z is the distance along the direction of the flow, S_i is the concentration of the pollutant adsorbed, ρ is the volumetric density, n is the porosity, where the first, the second, and the third terms of the right hand side refer to advection, dispersion, and adsorption, respectively.

To model the concentration of a pollutant substance subjected to adsorption processes, the advective-diffusive transport equation is used in one dimension expressed by Eq. (2):

$$\frac{\partial C}{\partial t} = \frac{1}{R}\frac{\partial C}{\partial z}\left(-v + D_H\frac{\partial C}{\partial z}\right) \tag{2}$$

D_H: dispersion coefficient

C: concentration of the pollutant

R: delay factor

v: linear velocity

The variation of the solute is difficult to know, so in order to solve the equation, different isotherms can be considered. For the isotherms of variation, linear, second order, or exponential approximations can be considered.

If we assume that the concentration of the solute in the solid and liquid phases is related by a linear adsorption isotherm, the delay factor R takes the following expression Eq. (3):

$$R = \left(1 + \frac{\rho K_D}{\theta}\right) \tag{3}$$

ρ: volumetric density

θ: volumetric moisture content

K_D: distribution or adsorption coefficient that characterizes the linear isotherm.

In order to find the numerical solution of the transport equation, it is necessary to know the form of the concentration of the solute in the solid phase (porous matrix) and liquid phase (water) and how is the variation of the solute and the physical properties of the soils and their moisture content.

2.3. Measurement of solute concentration

The concentration of fertilizers and pesticides in different environmental matrices is estimated based on sampling based on statistical methods. In general, due to the great spatial variability of the concentrations of the different pesticides in the environment, the values obtained in a sample are only an approximation to reality. Therefore, the greater or lesser degree of certainty in obtaining the collected data and their interpretation depends to a large extent on an adequate sampling, on the collection of the sample and on the preservation of these [10].

In the study of the adsorption of a pesticide in a soil, two laboratory techniques are used: batch experiences and experiences in columns. Batch experiences are designed to study the equilibrium of adsorption in a continuously stirred soil suspension. This situation is presented as a physical model of particles of completely dispersed soil, where the entire surface of the particles is exposed and available for interaction with contaminants. Experiences in batches are not representative of the natural conditions that represent the conditions of a closed system and offer adsorption to the greatest possible surface area and, therefore, the maximum possibility of interaction [11].

3. Measurement of moisture in the soil

The infiltration process in the soil can be modeled by the Richards equation whose solution implies knowing the hydraulic functions of the soil. These functions depend on some parameters they need for their calibration of the hydraulic properties, determined by means of measurements. The measurements of the hydraulic properties of the soil present numerous complications due to two important factors: the nonlinearity of the conductivity/ suction function and the nonlinearity of the moisture/suction function [12].

Given the problem of the heterogeneity of the porous medium, the modeling of the water-solute-soil-plant system is more complicated. Therefore, obtaining the parameters that allow adjusting the model as close to reality is what takes most of time and money.

The adequate measurement of the water content in soil plays a critical role for the estimation of water and energy balances, as well as for understanding the biological and chemical processes in the entire soil-plant system [13].

The evaluation of soil moisture content at different suction conditions in the field requires considerable time and effort, as well as equipment. The effort, time, and equipment needed will depend on the range of interest required for the data.

The surface and depth to study must be carefully defined. The surface to study will depend on the variability existing in the place. In certain occasions the characteristics of the soil-water vary more with the depth that with the area.

The moisture in the soil depends mainly on the texture or the particle size distribution. On the other hand, the content of organic matter and the composition of the solution phase can play a determining role in soil moisture function or retention function. Organic matter has a direct

effect on the retention function due to its hydrophilic nature and an indirect effect due to the modification of the soil structure that can be affected by the presence of organic matter [12].

Currently there are different equipment and measurement techniques for moisture content such as capacitance, reflectometry, geo-electric (called dielectrics), and neutrons. Descriptions of them are developed in the following points.

3.1. Neutron probe

A neutron probe is a sophisticated and accurate piece of equipment that measures the moisture content in soil. It requires calibration and operation by a licensed operator.

This technique is based on the theory that fast neutrons are thermalized when they collide with a body of similar mass, such as hydrogen nuclei. The energy of the neutrons is transmitted to the protons which causes the neutron "bounce or shock" to be much lower.

The application of this technique consists of three steps: (1) emission of fast neutrons from a radioactive source, (2) attenuation of the velocity of the neutrons after successive collisions with the atoms at the point of emission, and (3) accounting for neutrons with attenuated velocity by a detector near the source.

By means of electrical impulses the neutrons captured by the detector are translated into a digital reading.

To convert the reading of the neutron probe to volumetric moisture, a calibration model is necessary, where the volumetric moisture of the soil is the main factor. There are some factors that influence measurements such as hydrogen from organic matter, chlorine, iron, and boron present in the soil, capable of attenuating neutrons and absorbing thermally neutron nuclei [14].

3.2. Tensiometers

Tensiometers are widely used to measure the available water content of the soil when the matrix potential is high [15]. These devices are simple, they are not very expensive, and they are very practical in agricultural systems.

They consist of a porous ceramic capsule permeable to water and solutes, connected to a pressure gauge by means of a transparent plastic tube that is filled with water, in such a way that the column of water in its interior forms a continuous with the water of the solution of the floor in the surrounding space, through the porous capsule.

The values obtained reflect the soil tension, are negative values, and their operating range is 0–80 kPa, below this value the water column breaks, penetrating the air and invalidating the following measurements.

The tensiometers are insensitive to the osmotic potential of water in the soil and therefore do not provide an adequate measurement of the water potential in soils with significant salinity.

Tensiometers are often used in combination with the neutron sprayer, resistance blocks, or psychrometers to cover the full range of soil moisture. They require relatively frequent maintenance, which consists of adding water plus a solution for the control of algae [14].

3.3. Granular matrix sensors

They have been developed recently (they were patented in 1985 and manufactured commercially since 1989). It measures the electrical resistance between two electrodes inserted in a small cylinder composed of a porous material. Each device is covered by a membrane consisting of a stainless steel coupling, externally covered by a rubber that makes the sensor more durable than the plaster block. However, the recorder is calibrated to give the value in water tension, by means of an equation that takes into account the temperature of the soil estimated or measured near the sensor. The size of the pores in the matrix is greater than that of the pores in the gypsum blocks, allowing greater sensitivity in the more humid range of water content in the soil [14].

3.4. Dielectric sensors

The TDR and FDR probes measure the dielectric constant of the medium, which is an intrinsic property of the medium. The FDR system calculates the humidity of a soil by responding to changes in the dielectric constant of the medium using a frequency domain reflectometry technique known as capacitance, while the TDR uses time domain reflectometry [16].

3.4.1. Time domain reflectometry (TDR)

The TDR system consists of an oscilloscope connected to two or three metal rods that are inserted parallel to the ground. If a difference of power is applied to one end of the rods, the energy is transmitted along the ends to the end, where they are reflected to the oscilloscope. In it, the evolution of the potential over time is measured.

Some equipment consists of two main parts: the electronic unit and the waveguides. The electronic unit contains the oscilloscope and the central processor, which controls all measurement, display, and storage functions. The waveguides can be installed horizontally or vertically and remain permanently on the ground to make periodic measurements in the same location or be used in a portable way.

The TDR uses a series of conversion tables to convert the dielectric constant to a percentage of moisture in the soil. There are different conversion tables to be used with the different types of waveguides. It is not necessary to have a different table for the different soil types since the dielectric constant depends more on the amount of water than on the other soil components. The apparatus calculates the average value of the humidity over the total length of the waveguides. The apparatus allows manual measurements or continuous measurements by connecting the fixed sensors to a data logger.

3.4.2. Reflectometry in the frequency domain (FDR)

The FDR method is also known as a capacitance probe. The electrodes and the adjacent floor form a capacitor whose capacity is a function of the dielectric constant of the soil. This is related empirically to the volumetric content of water.

A capacitance sensor requires a probe calibration for each floor and horizon to obtain an optimal measurement of volumetric moisture. The volume of soil measured is not dependent

on the type of soil or water content and approaches a cylinder 10 cm high with a diameter of about 25 cm, assuming there are no spaces with air [17].

All capacitance sensors installed in floors, even with similar characteristics, must be calibrated with the aim of improving their accuracy given the influence on the measurement of other factors independent of the moisture content such as pH variability or electrical conductivity inside of the porous matrix.

Capacitance sensors are the most economical and easy to install. In addition, it allows a continuous recording of the moisture values in the soil, enabling direct information and in real time. They are very useful for the planning of alert monitoring systems. They can be used as substitutes for neutron probes.

4. Herbicides

Herbicides are products intended for the control of weeds of a certain crop that are not desired due to their negative impact on production and yields. These are within the group of phytosanitary products, which of the World Health Organization (WHO) are all those substances or mixture of substances, designed to prevent the action, control, or directly destroy weeds, insects, fungi, mites, molluscs, bacteria, rodents, and other forms of animal or vegetable life that may be harmful to both public health and agriculture.

The growth and development of the food industry have had an effect on the current daily diet, diversifying the foods available in the diet. This progressive increase in production has been accompanied by surveillance and food laws in the countries, regulating and unifying processes and products [18].

In general, all the herbicides belonging to the same generic group act in the same way, for example: once the effect of atrazine on a weed is known, it is also known how simazine, ametryn, and prometryn act, since all these products belong to the same family of triazines [19].

4.1. Mechanisms of action of herbicides

A common feature that may have the herbicides is that they act on physiological processes of plants, being its toxicity very low on other species.

The most useful way of classifying herbicides is according to their mode of action [20]. The mode of action is the sequence of events that occur from the absorption of the herbicide to the death of the plant.

Herbicides with the same mode of action have the same absorption and transport behavior and produce similar symptoms in the treated plants [21].

In addition, the classification of herbicides according to their mode of action allows us to predict, in general terms, their weed control spectrum, application season, crop selectivity, and persistence in the soil [22].

4.1.1. Inhibitors of photosynthesis

The inhibitors of photosynthesis can be classified into mobile or systemic herbicides and non-mobile or contact herbicides. The inhibitors of photosynthesis include the chemical families of the triazines, triazinones, triazolinones, phenylureas, and uracils and the contact ones to the nitriles, benzothiadiazoles, and amides [23].

It is subdivided into four groups, the first three being those that act on the luminous phase of photosynthesis. Besides, they are not only used in agriculture but also to clean land, railroad tracks, industrial zones, and warehouses [24].

(a) Herbicides that inhibit the transfer of electrons by inhibiting photosynthesis.

Ureas, uracils, and triazines correspond to this group of herbicides. This type of herbicides are applied to the soil and absorbed by the roots, transported via xylem to the aerial part, reach the chloroplasts of the leaves, and there inhibit the light phase. Any plant can be affected by this type of herbicide.

(b) Herbicides that uncouple the electron transport chain.

They have the ability to capture the electrons preventing oxidation and forming free radicals "superoxides." Superoxides are very powerful oxidants, which oxidize the unsaturated lipids of the chloroplast membranes, losing structure, and the chloroplast stops working. These molecules are formulated as bromides and chlorides; they are very soluble and very easily absorbed by the roots.

(c) Herbicides that prevent the formation of adenosine triphosphate (ATP).

Acylanilides, hydroxybenzonitriles, dinitrophenols, pyridazines, N-phenylcarbamates belong to this group. In photosynthesis, ATP is synthesized from the thylakoid membrane (sites of the photochemical reactions of photosynthesis) of chloroplast cells of plants. The photon particles from the sunlight excite the chloroplast thylakoid membrane, which in turn converts this excitation into ATP's chemical energy. Found in all forms of life, ATP is often referred to as the "molecular unit of currency" of intracellular energy transfer. It is used by the plant for metabolic processes. They are applied differently. They can present an important toxicity for animals. Hence, some can be used as herbicides and fungicides.

(d) Herbicides that alter the biosynthesis of carotenoids.

They act at some point in the synthesis of lycopene. The most important is the amino triazole.

The most used inhibitors of photosynthesis are type (a).

4.1.2. Those that alter the biosynthesis of metabolites other than carbohydrates

They are subdivided into three groups:

a. Herbicides that alter the biosynthesis of aromatic amino acids: These amino acids are then part of proteins. The herbicide capable of inhibiting the synthesis of aromatic amino acids

is glyphosate. Glyphosate in animals can be degraded; on the ground it can be inactivated, so that environmentally it has very good behavior.

b. Herbicides that alter the biosynthesis of glutamine.

c. Herbicides that inhibit lipid synthesis: Thiocarbamates that inhibit the conversion of short-chain fatty acids into long-chain AG belong to this group. As a result, they slow down the growth of the vegetable. These molecules can be used in soil treatments for seeds that are germinating; thiocarbamates are easily degraded by enzymes and are poorly absorbed in the soil.

4.1.3. Plant growth regulators

They alter the elongation and cell division. When they are incorporated into a plant, they give rise to an abnormal growth of the plant, and as a consequence it causes deformations, lack of functionality, and the death of the plant.

(a) Herbicides that alter cell elongation

Cell elongation occurs by the action of the auxins in the meristematic cells. The main effect of the auxins is the elongation of the cells, mainly due to the fact that the cell wall becomes more plastic. These at high concentration have herbicidal effects, cause excessive cell elongation with malformations in the apices, and the death of the vegetable. They are not used too much since in their synthesis dioxins are released. They are contact foliar herbicides that act at the point where they fall, they do not translocate. This allows many dicotyledonous weeds to be controlled.

(b) Herbicides that inhibit the synthesis of gibberellins

Gibberellins are phytohormones responsible for the growth of the plant, since they give rise to the internodes having a certain length. If the synthesis of gibberellins is inhibited, the internode distance is shortened, giving rise to the stunting of the plant and loss of functionality, in addition the petioles shorten, and the root system increases. All this causes the plant to lose functionality and die. Chlormequat (is a quaternary ammonium salt) inhibits the synthesis of gibberellins.

(c) Herbicides capable of inhibiting cell division

There are many types, but the most important ones are the N-phenyl carbamates and maleica hydrazida.

They are used in the soil and have little mobility and alter cell division as they prevent the correct organization of proteins that are part of the microtubules of achromatic use; this causes cells with giant nuclei without functionality. These herbicides affect meristematic cells, preventing them from thickening, there is no cell differentiation, and the plant stops growing and dies.

4.1.4. Herbicides with other mechanisms of action

(a) Herbicides that cause disruption of the cell membrane

These are the so-called herbicidal mineral oils. They are complex mixtures of long-chain CH that come from the fractional distillation of oil + dry fraction of coal. They are substances with very soluble lipids. They are used as total herbicides; they are also used as selective herbicides

in some crops when the crops resist these oils and only the weeds will be eliminated. They were the first substances used as herbicides.

(b) Herbicides that act on pigments

These are the inhibitors of carotenoid biosynthesis (PDS). They interfere in the formation of chlorophyll, either by inhibiting the synthesis of typhoid, of carotenoids, or of the amino acid histidine.

They are applicable to soil or foliage. The characteristic symptom is foliar albinism after application. They are important herbicides when plants are exposed to full sun and depend on the light intensity; its effect begins to be close to 2 hours when the amount of carotenoids has decreased enough [24].

(c) Herbicides with hormonal activity

These are the disruptors of cell growth. Synthetic Auxins belong to this class with probable action towards indoleacetic acid. These herbicides interfere in the synthesis of nucleic acids, controlling the protein synthesis in different stages; affecting the regulation of DNA during the formation of RNA, an effect that can be achieved by the depression of a gene or activation of RNA polymerase; or simply affecting the RNA message to proteins. They are characterized by having a greater phytotoxicity toward dicotyledons and Cyperaceae than toward grasses; they act as growth regulators; transport occurs via symplast with the assimilated from the source of production to the organs in consumption or storage. They generally exhibit a short residual effect. The grasses are tolerant because they do not have cambium, besides the knots and internodes hinder the arrival of the herbicide to the site of action [24].

5. Conclusions

Pesticides, fertilizers, herbicides, and animal waste are sources of contamination of groundwater of agricultural origin. These sources of agricultural pollution are very varied and numerous: spillage of fertilizers and pesticides during handling, runoff by loading and washing spray pesticides or other application equipment, and the use of chemicals up the slope and a few 100 meters of wells or well-feeding waters. Contamination can also occur when chemicals are stored in uncovered areas, which are not protected from wind and rain, or stored in places where groundwater flows from chemical storage to wells.

The movement of water in the soil is the main mechanism for the transfer of pollutants to surface and groundwater [25]. The physics of water in the soil and the movement of solutes can be used to determine the behavior of these materials.

The movement of solutes through the unsaturated, vadose zone is particularly important in relation to environmental and agronomic contamination [26].

The limited availability of data obtained from field studies represents the main limitation to assess the degree of contamination of groundwater against the effects of herbicide applications, especially in agricultural areas.

On the other hand, the scarcity of measurements makes it difficult to validate the mathematical models for determining the content of herbicides and fertilizers in groundwater and in the vadose zone. However, isolated data from groundwater in agricultural areas under the application of herbicides and fertilizers in recent years show that the waters of unconfined aquifers are contaminated by herbicides. In the medium and long term, this pollution will affect the environment in agricultural areas.

To minimize the environmental damage caused by the application of herbicides, its application must be carried out taking into account, strictly, the conditions of the plants, the soil and the environment, as well as the doses and proper procedures for use, but this is not enough.

The current challenge is to advance in the knowledge of solute transport processes and determine the contamination that can be submitted if continued or continued with the current application methodologies and their concentrations.

But what is more important is that we must not forget that the purification possibilities of an aquifer are limited and that the best method of protection is, therefore, prevention. Do not contaminate; control sources of contamination to know the effects well and avoid contaminants.

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