

# PESTICIDE BEHAVIOR IN AGRICULTURAL SOILS WITH SPECIAL REFERENCE TO THE TROPICAL REGION

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**ABSTRACT:** Agriculture areas in the tropical region has high occurrence of pests that requires more intense control practices, usually by using pesticides, and soil and water contamination is an increasing problem in the tropics. Once applied in the field, the pesticides undergo several processes of retention (sorption), biotic and abiotic transformation and transport. The behavior of pesticides in tropical soils and climates conditions is differentiated

from other regions. Some specific weather conditions and soil characteristics can be important drivers of distinct pesticide behavior patterns in the tropics. Hence, brief descriptions of the climates and soils in the tropics are presented as a starting point. Considerations on climate change particularly in the tropics and its effects on soils are also presented. Properties and conditions of unsaturated zone of the soil, especially in the top layer, have both direct and indirect effects on the fate of pesticides that are applied to the soil or reach the soil after application and significantly affect the environmental fate of pesticides. Some combinations of predominant soils in the tropics with specific tropical climates, together with distinct agricultural practices, can involve unique sets of characteristics. The warmer climates, more variable rainfall, main soil types, and distinct biota that characterize most tropical locations imply the behavior, fate and effects of pesticides may be different from those in temperate locations. If the onsite behavior and offsite losses of pesticides from an agricultural area is to be understood, soil sorption and degradation, volatilization, surface runoff and leaching data for relevant tropical conditions are required, considering the soil moisture

and temperature, organic matter content and composition, and previous pesticide application practices. This is an important challenge in agricultural and environmental sciences.

**KEYWORDS:** tropics, climate, soil, agriculture, environment, contamination.

## COMPORTAMENTO AMBIENTAL DE PESTICIDAS EM SOLOS AGRÍCOLAS COM REFERÊNCIA ESPECIAL À REGIÃO TROPICAL

**RESUMO:** Áreas agrícolas na região tropical apresentam alta ocorrência de pragas que requerem controle mais intenso, geralmente com uso de pesticidas, e a contaminação do solo e da água é um problema crescente nos trópicos. Uma vez aplicados no campo, os agrotóxicos passam por diversos processos de retenção (sorção), transformação biótica e abiótica e transporte. O comportamento dos agrotóxicos em condições de solos e climas tropicais é diferenciado de outras regiões. Algumas condições climáticas específicas e características do solo podem ser importantes fatores que levam a padrões distintos de comportamento dos pesticidas nos trópicos. Assim, breves descrições dos climas e solos nos trópicos são apresentadas como ponto de partida. Considerações sobre as mudanças climáticas, especialmente nos trópicos, e os seus efeitos nos solos também são apresentadas. As propriedades e condições da zona não saturada do solo, especialmente na camada superior, têm efeitos diretos e indiretos no destino dos pesticidas que são aplicados ao solo ou que chegam ao solo após a aplicação e afetam significativamente o destino ambiental dos pesticidas. Algumas combinações de solos predominantes nos trópicos com climas tropicais específicos, juntamente com práticas agrícolas distintas, podem envolver conjuntos únicos de características. Os climas mais quentes, a maior variabilidade das chuvas, os principais tipos de solos e a biota distinta que caracterizam a maioria dos locais tropicais implicam que o comportamento, o destino e os efeitos dos pesticidas podem ser diferentes daqueles observados em locais de clima temperado. Para compreender o comportamento na área agrícola e as perdas externas de pesticidas, são necessários dados sobre a sorção e a degradação no solo, a volatilização, o escoamento superficial e a lixiviação em condições tropicais relevantes, considerando a umidade e a temperatura do solo, o teor e a composição de matéria orgânica e as práticas anteriores de aplicação de pesticidas. Esse é um importante desafio nas ciências agrícolas e ambientais.

**PALAVRAS-CHAVE:** trópicos, clima, solo, agricultura, meio ambiente, contaminação.

## INTRODUCTION

Agriculture fulfilled in the tropical region of the globe has a greater occurrence of pests that requires more intense control practices, usually by using more pesticides than in temperate regions. Countries in the tropics, most of them developing countries, are great food producers and use pesticides extensively. The Food and Agriculture Organization statistics (FAO, n.d.) reports a world consumption of 4,122,334 t of active ingredients of pesticides in 2018, with Asia as the greatest consumer (2,161,869 t) and South America in second (719,183 t). Brazil is the country with the largest land area in the tropics (Juo & Franzluebbbers, 2003) and used 377,176 t of pesticides in 2018. Despite being the continent with the largest tropical area, Africa consumed much less (82,851 t) in 2018.

Soil and water contamination with pesticides is an increasing problem in the tropics (Carvalho, 2017). Several studies have reported the presence of pesticides in water bodies in the tropics (e.g., Adeyemi et al., 2011; Chowdhury et al., 2012; Kafle et al., 2015; Deknock et al., 2019; Elfikrie et al., 2020; Nag et al., 2020; Bhuiyan et al., 2021). Albuquerque et al. (2016) provided a comprehensive literature review on the occurrence of pesticide residues in Brazilian freshwaters. A review regarding pesticides in groundwater in tropical regions was recently presented by Dores et al. (2023). In the tropics, information on pesticide contamination of soil is often inadequate (Yadav et al., 2015). Tan et al. (2020) reported contamination of agricultural topsoil from tropical riverside basins at detectable levels during several months. As mentioned by Correia et al. (2007), there have been relatively few reports on the behavior of pesticides especially in soils from the humid tropics.

Once applied in the field, the pesticides undergo several processes of retention (sorption), biotic and abiotic transformation and transport. The behavior of pesticides in tropical (soils and climates) conditions is differentiated from other regions, which has been evidenced in sorption, degradation, and transport studies.

## CLIMATES AND SOILS IN THE TROPICAL REGION

The latitudinal definition (geographical delimitation/statement) of the tropical region is inexact at the boundaries because changes in climate conditions and soil types are gradual. Thus, there is no true dividing line between tropical and temperate zones, and intermediate areas are often referred to as subtropical.

Besides the inexact geographical delimitation of the tropical region, according to the purpose of this chapter, descriptions of the climates and soils in the tropics are summarized. Additional information can be found in Spadotto and Mingoti (2023).

**Climate** and natural vegetation in the tropics are closely related and the main classification systems of tropical climates in use employ vegetation names for the different climatic regions. Most of the tropics are not covered by rainforests, as commonly assumed. Savannas are the most extensive type of tropical vegetation.

Most approaches that have been used to classify climates in the tropics are based on the original classification of Köppen (1936), updated by Troll (1965) and Kotteck et al. (2006). Rainy climates (Af, Am), seasonal climates (Aw), dry climates (Bsh), and deserts (BW), are the main tropical climates and are based on the length of the rainy seasons – **Table 1**. Such climates occur at almost all elevations in the tropics.

| Climate (Köppen-Geiger Classification) | Main Characteristics       | Climate Zone     | Proportion of the Tropical Region |
|--|----------------------------|------------------|-----------------------------------|
| Tropical, savanna climate (Aw)         | Seasonal with dry winter   | Subhumid tropics | 49%                               |
| Tropical, rainforest climate (Af)      | Wet without dry season     | Humid tropics    | 24%                               |
| Tropical, monsoon climate (Am)         | Wet with monsoonal changes |                  |                                   |
| Arid, steppe, hot climate (BSh)        | Hot and semiarid           | Semiarid tropics | 16%                               |
| Arid, desert, hot climate (BWh)        | Hot and arid               | Arid tropics     | 11%                               |

Table 1 – Major climates in the tropical region.

According to Köppen (1936), Kottek et al. (2006), Peel et al. (2007), Beck et al. (2018), and Sanchez (2019).

It is worth mentioning that the climate is changing in the tropics, as it is in the rest of the world (IPCC, 2013), despite the less obvious changes, because of the considerable natural variability (Corlett, 2014). According to IPCC (2013), it is estimated that temperature extremes, droughts and floods will increase in much of the tropical region. Climate change is a statistically significant alteration of the climate variables in terms of their distribution both in time (amount and intensity) and in space, as well as in their intrinsic variability in a significantly broad framework of time (Oliveira et al., 2007).

The tropics are projected to warm over the coming 50 to 100 years (IPCC 2013), however most model projections indicate that warming trends over the tropics will be smaller than those for the globe as a whole (Trewin, 2014). Trends in rainfall are less clear than those in temperature and there is low confidence in projected changes in annual rainfall over most of the tropics (Trewin, 2014). Many tropical areas are now significantly wetter or drier than they were a century ago, and others show marked fluctuations (Corlett, 2014).

Studies on climate change have demonstrated impacts in tropical regions which are likely to be disproportionately affected and some regions which currently border the equatorial zone may experience an increase in extreme rainfall (Isaac and Turton, 2014). It is noteworthy that there are evidences from long-term meteorological measurements that the tropical and subtropical zones are expanding poleward in both hemispheres (Seidel et al., 2008; IPCC, 2013; Isaac & Turton, 2014; Lucas et al., 2014).

Major **soils** in the humid and subhumid tropics are mineral soils conditioned by wet climates (Driessen et al., 2001). The most extensive soils in the tropics, classified by the Soil Taxonomy system (Soil Survey Staff, 1999; 2014), are: Oxisols, Ultisols, Inceptisols, Entisols, Alfisols, Aridisols, and Vertisols – **Table 2**. Soils in these orders occupy around 97% of the tropical land area.

| Soil Taxonomy Order | Proportion of the Tropical Land Area |
|---------------------|--------------------------------------|
| Oxisols             | 24.8%                                |
| Ultisols            | 19.6%                                |
| Inceptisols         | 15.7%                                |
| Entisols            | 15.6%                                |
| Alfisols            | 12.4%                                |
| Aridisols           | 4.8%                                 |
| Vertisols           | 3.9%                                 |
| Other soils         | 3.2%                                 |

Table 2 – Main soil orders in the tropical region, classified by the Soil Taxonomy system.

Adapted from Buol et al. (2011) and Sanchez (2019), based on Soil Survey Staff (1999; 2014). Tropical region: 0° – 23°28' of latitude.

In Brazil, the main soils in the humid and subhumid tropical regions (respectively, Amazonia and Cerrado biomes) are Latossolos, according to the Brazilian Soil Classification System (Santos et al., 2018), that are equivalent to the Oxisols (except Aquox) in the Soil Taxonomy (Soil Survey Staff, 1999, 2014).

One limitation of natural soil classification systems is that they quantify only inherent properties, most of them located in the subsoil (Sanchez, 2019). Inherent properties are related to soil formation, resulting from the interaction of parent materials and biotic activities, and are modified by topography and climatic conditions over a long period of time.

Many important soil properties concerning pesticide environmental behavior processes, which occur mostly in the topsoil, are not considered in natural soil classification systems. Relatively short-term weather conditions and soil management practices change the physical, chemical, and biological properties of soils, mainly in the surface layer, as illustrated in **Figure 1**.

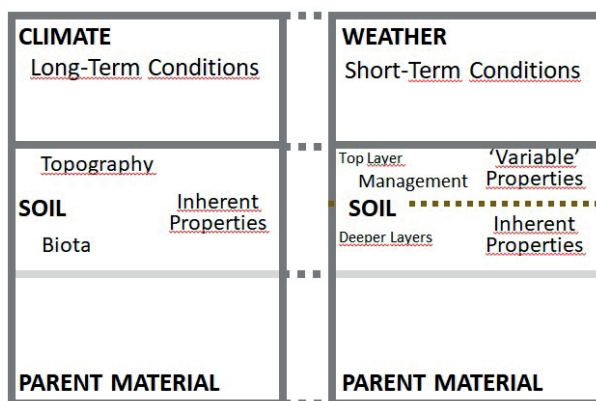


Figure 1 – Determinants of soil properties in the long term (soil formation) and in the relatively short term (agricultural areas).

Some properties of clayey Oxisols associated with pesticide behavior under natural conditions and in the upper soil layer in rainfed crop areas with conventional tillage in the subhumid tropics are presented in **Table 3**.

| <b>Properties<sup>1</sup> of Clayey Oxisols in the Subhumid Tropics</b> |   |
|---|---|
| <b>Soil under Natural Conditions (fairly uniform in the profile)</b>    | <b>Upper Soil Layer in Rainfed Crop Areas with Conventional Tillage<sup>2</sup></b> |
| Strong granular structure   | Poor structure due to tillage, liming and reduced soil organic matter (SOM)         |
| Moderate to high hydraulic conductivity                                 | Lower hydraulic conductivity caused by loss of structure                            |
| Interconnected macroporosity (for preferential flow)                    | Reduced and non-connected macroporosity because of structure breakdown              |
| Acidity; low pH (< 5.5)   | Adjusted higher (slightly acid) pH by liming  |
| Low cation exchange capacity (CEC)                                      | Higher CEC owing to liming  |
| Some anion exchange capacity (AEC), mainly in subsoil                   | Low AEC due to liming   |
| Moderate to high SOM  | Generally low SOM (depends on fertilizing and organic material addition)            |
| Moderate to small seasonal and daily variation of temperature           | Broader variation at higher temperatures, mainly in bare soil                       |
| High seasonal variation of moisture (3–6 months/year with dry soil)     | High seasonal moisture variation (less in irrigated areas)                          |
| Moderate to low daily variation of moisture                             | Wider daily variation of moisture (less in irrigated areas)                         |

<sup>1</sup>Soil properties associated with pesticide behavior. <sup>2</sup>Properties affected by agricultural practices. Prepared by the authors.

Table 3 – Examples of properties of clayey Oxisols, under natural conditions and in the upper soil layer, in rainfed crop areas with conventional tillage in the subhumid tropics (tropical, savanna climate - Aw).

The effects of climate change on soils are expected mainly through alteration in soil moisture conditions and increase in soil temperature and CO<sub>2</sub> levels and this is projected to have variable effects on soil processes and properties (Pareek, 2017). Soils have diverse biotic and abiotic properties and it is difficult to generalize the impact of climate change on soil conditions.

As highlighted by Brevik (2012), soils are intricately linked to the atmospheric–climate system and altered climate affects soil processes and properties, and soils, in turn, have effects on climate. According to Brevik (2012), study of the effects of climate change on soil processes and properties has shown that climate change will impact soil organic matter dynamics, including soil organisms and multiple soil properties that are tied to organic matter, soil water, and soil erosion.

## PESTICIDE BEHAVIOR IN SOILS IN TROPICAL ENVIRONMENTS

Besides the depth of soil saturated zone (water table depth), properties and conditions of unsaturated zone of the soil, especially in the top layer, at times referred as root zone, are important to mediate the behavior and fate of pesticides.

Environmental pesticide behavior and fate are governed by various processes and differences in pesticide properties and in soil attributes, as well as in weather conditions affect these processes. As commented by Racke et al. (1997), researchers deal with the high variability of these processes, which results from the complex set of interactions involved.

The behavior of pesticides in tropical environments is not as well understood as that for temperate regions, despite considerable increasing in research done on their fate (and effects) in tropical areas over the past decades. Some specific weather conditions, soil characteristics and cropping systems can be important drivers of distinct pesticide behavior patterns in the tropics.

The soil filtration function is an important ecosystem service for the protection of groundwater and surface water (Keesstra et al., 2012). Soils act as a natural filter, where the processes of retention, degradation and movement of pesticides occur – **Figure 2**. Thus, soils have a marked influence on the degree of vulnerability of groundwater bodies to contamination (Racke et al., 1997; Futch & Singh, 1999).

An extensive literature review on pesticide fate in tropical soils was presented by Racke et al. (1997). A year later, Kookana et al. (1998) also provided an important review on pesticide fate and behavior in relation to contamination and management of soil and water in Australia, most of them in tropical weather conditions. This text was prepared based on findings presented in these two reviews, as starting point, along with studies published after them. Only a few works cited in both reviews were directly accessed to prepare this chapter.

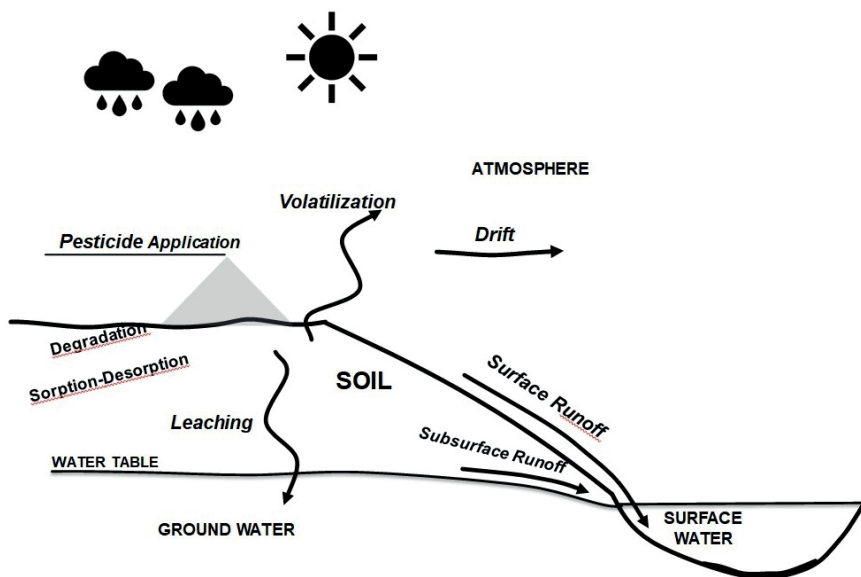


Figure 2 – Representation of the main behavior processes of pesticides in soils.

According to Racke et al. (1997), tropical soils cannot necessarily be classified as a distinct entity with a unique set of properties, since soils in any single continent, territory, or region may vary significantly. The authors pointed out that the quantity and quality of information on the fate of pesticides in tropical soils and under tropical conditions is somewhat limited and that there are no inherent differences in pesticide fate due to soil properties uniquely possessed by tropical soils. However, as it can be seen in this chapter, some combinations of predominant soils in the tropics, remarkably Oxisols (Ferralsols), with specific tropical climates, that is humid and subhumid weather conditions, together with distinct agricultural practices, can imply unique sets of characteristics.

More recently, Lewis et al. (2016) published an overview of the state of knowledge on pesticide in the tropics. As pointed out in that overview and in other publications, it is well recognized in the literature that the behavior, fate, and effects of pesticides in tropical environments are considerably less understood than for temperate regions and represent a notable research need. According to Kookana and Simpson (2000), while much data is available for temperate region soils, information on pesticide interactions in tropical soils is limited and, given the different soil-weather conditions, directly transferring data from the temperate region may not be appropriate for pesticide management in the tropics.

As pointed out by Langenbach et al. (2001), soil properties (such as, low water-holding capacity and low organic matter content) in the tropics and some tropical climate conditions (e.g., uneven rain distribution and intensity and small seasonal temperature variation) may affect the rates of biodegradation, volatilization, accumulation and transport



of pesticides in soils. The warmer climates, more variable rainfall, predominant soil types, and distinct biota that characterize most tropical locations imply the behavior, fate and effects of pesticides may be different from those in temperate locations (Lewis et al., 2016).

In the Southeastern region of Brazil, as mentioned by Correia et al. (2007), the average temperature variation during the year is small (about 7°C), however rainfall rates change remarkably between 20 mm (in the winter) to 300 mm (in the summer) a month. In that region, pesticides are more intensively applied in the spring season, in the main crop planting period, which occurs at the same time with high rainfall and high temperatures. Application at this period results in increased pesticide transport downward the soil, on the soil and from the soil surface to the atmosphere. In the summer, rains are torrential, resulting in surface runoff when soil infiltration capacity is exceeded, resulting in considerable soil erosion and pesticide transport.

As mentioned by Laabs et al. (2002a), relatively few data were reported on pesticide fate under the specific climatic and pedological conditions in the tropics. Nevertheless, some conclusions can be drawn, as those summarized by Lewis et al. (2016), that is, pesticides are dissipated via volatilization (into atmosphere), surface runoff (overland water flow), soil erosion (terrain soil transport), and leaching (downward the soil), that likely would be influenced by tropical conditions.

As pointed out by Hornsby and Brown (1992), soil properties and conditions significantly affect the environmental fate of pesticides. The authors highlighted that soil properties have both direct and indirect effects on the fate of pesticides that are applied to the soil or reach the soil after application. Retention (sorption) and transformation (degradation) processes may be affected by soil properties and conditions. Amount and intensity of rainfall, terrain slope, and management practices adopted in agricultural areas also affect the behavior of pesticides in the environment. It is noteworthy that the amount of pesticide used is especially important when assessing the environmental risk of pesticides.

Pesticide transport from agricultural soils to surface waters can be via overland runoff, soil erosion, lateral subsurface flow, and drainage. Among these routes, surface runoff and soil erosion generated by rainfall events and irrigation have attracted the most attention.

**Surface runoff** occurs by water flowing on land surface when both soil infiltration and surface storage capacities are exceeded by precipitation and irrigation or when the water table rises to the soil surface and water is unable to infiltrate due to saturation conditions (Campling et al., 2002; Bonell, 2005; Garen & Moore, 2005; Reichenberger et al., 2007; Scherrer et al., 2007; Li & Sivapalan, 2014; Li et al., 2014). Water flowing over the land carries dissolved substances and suspended soil particles.

Depending on soil conservation practices, the fate of surface runoff (flowing water with dissolved substances and suspended particles) is a lake, pond, stream or river, what can lead to the contamination of water and sediment. The primary transport routes

for pesticides, particularly to small surface water bodies in non-irrigation agriculture, are surface runoff and drainage induced by heavy precipitation events (Leu et al., 2004; Lorenz et al., 2017).

Surface runoff is a route that rapidly changes the mass balance of the pesticide in the soil in cases where the application is carried out just before a rain of medium to high intensity. In cases when the initial rainfall infiltrates, this was predicted to lead to reduced offsite movement of pesticides. Conversely, in cases when runoff starts soon after rainfall, as would occur when soil is already wet or crusted, then the washed off pesticides would be present in runoff. This highlights that the timing of pesticide applications away from extreme rainfall events will be important in reducing offsite movement.

Studies have reported contradictory results on the effects of conservation tillage practices reducing surface runoff of pesticides, and this could be due to the combined effects of weather and soil conditions, together with physico-chemical properties of pesticides (Reddy et al., 1995; Holland, 2004; Knowler & Bradshaw, 2007). The effect of tillage practices on sorption of pesticides could play a significant role in determining the effects of land management on their mobility in the environment (Ochsner et al., 2006).

**Soil erosion** by overland water flow starts by detachment of soil particles, caused by raindrop impact and also by the abrasive power of water running off, and then detached particles are transported downslope. Along with surface runoff, soil erosion by water flowing on the land can promptly change the mass of pesticides in upper layers of soils. Erosion by water is larger in fine-sandy and silty soils. Studies had recognized that soil erosion is a function of rainfall intensity rather than of total annual rainfall (e.g., Müller et al., 2004; Douglas & Guyot, 2005; Brown et al., 2009; Payraudeau et al., 2011; Defersha & Melesse, 2012). It is noteworthy that pesticides sorbed on soil particles can also be removed by wind erosion.

During surface runoff and erosion events pesticides are carried off dissolved in water and sorbed to soil particles. The relation between both transport pathways depends amongst others on the physico-chemical and environmental properties of the pesticide (Reichenberger et al., 2007).

Studies have been published on pesticide transport by surface runoff and soil erosion (e.g., Lecomte et al., 2001; Louchart et al., 2001; Silburn, 2003; Syversen, 2005; Berenzen et al., 2005; Vianello et al., 2005; Silburn & Kennedy, 2007; Locke et al., 2008; Lefrancq et al., 2013; Barbosa et al., 2016; Elias et al., 2018; Trovato et al., 2020; Vaz et al., 2021; Silburn, 2023). Heavy and frequent rainfalls in tropical regions enhance pesticides losses by surface water runoff and soil erosion and consequent contamination in surface water bodies (water and sediment contamination).

Research findings on overland flow and soil erosion, comparing no-tillage with conventional tillage, are inconsistent. Results from a global literature review, carried out by Mhazo et al. (2016), using meta-analysis, indicated that no-tillage has greater potential

to reduce runoff and soil losses in temperate regions where soils are relatively young, moderately weathered and fragile compared to the heavily weathered clayey tropical soils that are well aggregated and less erodible.

**Leaching**, as the straight pathway for ground water contamination, is a function of water flow as well as pesticide sorption and degradation mechanisms. However, ground water and surface water are a fully connected resource responding to changes in hydrologic conditions and exchange of them occurs at multiple scales, rates and time frames, what is clearly supported by scientific literature, as pointed out by Woessner (2020). Understanding the transport of pesticides through soils is essential in assessing water quality impacts of pesticide use (Hornsby & Brown, 1992).

Pesticide leaching downward the soil occurs mainly driven by the mass flow of water. Thus, in the leaching process, chemicals are mainly taken in solution together with the water that percolates in soil and feeds aquifers. Sorption of pesticides delays their movement through the soil, whereas abiotic and biotic degradation processes in the soil biomass reduce the mass of pesticides in the leachate (Hornsby & Brown, 1992). Leaching is a function of many factors including pesticide properties, soil attributes (e.g., organic carbon content, hydraulic conductivity), weather conditions (e.g., temperature regime, rainfall and groundwater recharge rate), as well as terrain slope, depth to groundwater.

Leaching can be classified as matrix or preferential transport, depending on the water flow type. Matrix transport of pesticides occurs in soils with uniform water flow conditions. In soils with large pores and well-drained it can be assumed that pesticide transport occurs mainly by advection, where the mass of solute (pesticide) is concentrated at a specific point in the water column and not dispersed in the soil profile ('piston flow' type). This transport process is predominantly vertical, with some retardation in relation to water that percolates in soil. In cases where soil does not have good porosity and it is excessively compacted or even unstructured, transport of the solute by diffusion and dispersion becomes important.

In the nonuniform water vertical flow condition, the solute (pesticide) movement is referred to as preferential transport. The preferential (or rapid) transport of pesticides in soil has been observed and its importance has been highlighted in several works (e.g., Flury et al., 1994; Lennartz et al., 1999; McGarry et al., 2000; Laabs et al., 2002a; Reichenberger et al., 2002; Scorza Jr. & Boesten, 2005; Dores et al., 2009; 2016).

In some soil and weather combinations in the tropics, leaching of pesticides can be enhanced by preferential transport and consequent contamination in ground water can occur. As highlighted by Laabs et al. (2002a) and Sanchez-Bayo and Hyne (2011), greater leaching under conditions of high rainfall plays an important role in the overall behavior of pesticides in tropical agricultural areas. However, Sanchez-Bayo and Hyne (2011) noted that data on medium to long-term leaching of pesticides in representative soils of the tropics are lacking in the literature for most compounds.

Macropores in structured soils, as well as cracks and biopores (such as termite burrows), can lead to preferential flow and facilitate leaching of pesticides to ground water and studies has suggested that is especially relevant in tropical soils (e.g., McGarry et al., 2000; Reichenberger et al., 2002). According to Chai (2008), the presence of macropores, which occur amply in humid tropical soils, may induce preferential flows and this may cause leaching of most pesticides without regard for their sorption properties.

Correia et al. (2010) presented results that showed no correlation between tropical soil permeability and herbicide leaching. According to the authors, higher permeability in no-tillage and natural soils than in the conventional tillage indicated that leaching occurs predominantly by preferential flow through macropores, which are destroyed in the top soil by tilling in the conventional tillage. The leaching under continuous flow, representing intense rainfall, was higher under no-tillage than in the conventional tillage, opposite to reports in literature of field experiments with intermittent rain. Thus, pesticide leaching is not only determined by the soil management practices but also by the intensive rainfall conditions in the tropics.

Pesticide behavior and fate in the environment are influenced by rainfall distribution and intensity, especially in some tropical conditions, where extreme rainfall events and/or very dry seasons occur frequently (Gentil et al., 2020). As mentioned by Sanchez-Bayo and Hyne (2011), extreme rainfall can cause high leaching, resulting in more pesticide moving toward ground water. Episodes of torrential rainfall in some tropical areas and intensive irrigation practices have often been associated with increased transport of soil contaminants to ground water by leaching (Daam et al., 2019).

Langenbach et al. (2001) studied the behavior of an herbicide in Brazilian soils in closed aerated laboratory microcosms, under standardized conditions (air temperature, relative air humidity, precipitation) and under natural tropical climatic conditions. As reported, leaching was higher in sandy soil than in clay soil and in organic soil. Under natural Brazilian summer conditions, leaching was enhanced as compared to standardized conditions comprising lower rainfall rates.

The most important mechanism affecting the matrix transport of pesticides through the soil profile is sorption-desorption balance because it controls the amount of pesticide available for degradation and transport (Koskinen et al., 2002; Rice et al., 2007). Partition between solid and liquid phases determines the proportion of pesticide in solution and sorbed to soil particles, and together with degradation determine the persistence and leaching of the pesticide in soil profile.

Sorption is, in fact, very important in the overall behavior of pesticides in the environment. Retention in solid phase tends to limit bioavailability and biodegradation of pesticides and volatilization can also be influenced by sorption. Thus, interactions of pesticides with soil components determine their mobility and persistence, with agronomic and environmental implications.

As summarized by Hornsby and Brown (1992), retention of pesticides in soils has been described by sorption into organic matter and on mineral fraction of soils, by means of partitioning processes as such hydrophobic interactions, ion exchange, and physical adsorption. Studies have highlighted the influence of dissolved organic matter on sorption and leaching [mobility] of pesticides (Li et al., 2005; Cox et al., 2007; Jiang et al., 2008; Song et al., 2008).

Pesticides belong to different classes of chemicals and several soil properties affect the mechanism and degree of sorption. The various types of interactions with soil colloids are complex; however the predominance of sorption of organic nonionic compounds into soil organic matter has been extensively documented. However, there are pesticides that are ionizable, thus a factor that has an important influence on sorption and, consequently, on leaching of these compounds is soil pH, as mentioned more recently by Kah and Brown (2006), van der Linden et al. (2009), Klein (2011), van den Berg et al. (2016), and Spadotto et al (2020).

Some evidence has been gathered that in addition to affecting rates of degradation, temperature can also modulate leaching behavior (Racke et al., 1997). Soil temperature changes with depth and there are variation differences between tilled and untilled soils. Soil temperatures in the tropics, as defined in the Soil Taxonomy system (Soil Survey Staff, 1999; 2014), fall in the 'iso' temperature regimes, that is, those with "less than 6°C difference between the average soil temperature of June–August and the average soil temperature of December–February at 50 cm depth or to a dense, lithic or paralithic contact". Thus, this definition does not take into consideration the topsoil temperature variation. As pointed out by Sanchez (2019), very high soil temperatures have been registered on the surface of bare soils during dry periods.

Based on Hornsby and Brown (1992), following are some considerations regarding soil parameters affecting pesticide retention and consequently transport, particularly leaching:

- Organic matter content of soil is a factor in determining the amount of pesticide sorbed, the greater the organic matter content the greater the amount of pesticide that can be sorbed.
- Soil mineral surfaces are also responsible for pesticide sorption, i.e., adsorption (high-energy bonding: ion exchange and ligand exchange; and low-energy bonding: hydrogen bonding, charge transfer, charge-dipole and dipole-dipole bonding, and London-van der Waals forces). In soils with chelated transition metals on clays and humic acids, some pesticides may be bound by ligand exchange, a high-energy bonding mechanism.
- Soils with high specific surface areas exhibit greater physical adsorption than those with low specific surface areas. The specific surface area of soil colloids is related to the degree to which adsorption by low-energy bonding mechanisms contribute to pesticide retention.

- Soil colloids, including both clays and organic matter, with charged surface sites interact with ionic pesticides. Most soils contain clay minerals with net negative surface charges providing exchange sites for cationic pesticide (e.g., herbicides paraquat and diquat). Some soils such as Oxisols contain metal oxides that exhibit positive charge, thus providing exchange sites for anionic pesticides. Ion exchange capacity of the soil is an important soil parameter affecting the fate of ionic or ionizable pesticides in soil
- Soil reaction (pH) might have a dual role. The amount of ionizable pesticide sorbed would depend on soil pH and chemical dissociation tendency (expressed as pKa or pKb). Ionizable pesticides may be in molecular form in certain soil pH ranges and ionic form in other soil pH ranges.
- In some soils, during biodegradation some fraction of the pesticide becomes “bound residue” that cannot be extracted by conventional extraction methods. The form and bioactivity of the bound residues are not widely known.
- Soil water content affects sorption at certain relative humidity levels of water-unsaturated soils.
- Temperature mediates the rate of the sorptive processes in soils and limits the amount of sorption.

Besides leaching, surface runoff, soil erosion, and plant uptake, a main dissipation process of pesticides from the top soil (root zone, for example) in the application site is volatilization into the atmosphere.

**Volatilization** as used here refers to the evaporation of pesticide from soil and its subsequent loss to the atmosphere. Pesticides can also volatilize during application or afterward from plant canopy and from surface water bodies.

Vapor drift is the movement of pesticides as gaseous vapor from the application site. Thus, the volatilized pesticide is transported into the atmosphere and sometimes is deposited in long distances from the treated site. Pesticide may volatilize again and may be transported further via the atmosphere (van Jaarsveld & van Pul, 1999). Several factors are cited in the literature as important in the emission and transport of pesticides into the atmosphere and deposition in adjacent areas of application sites.

Racke et al. (1997) reported the following summarized results from several studies on pesticide loss through volatilization:

- Volatilization from the surface of soil is influenced by physico-chemical properties of the chemical, method of application, properties of the soil (e.g., temperature, moisture), and weather conditions.
- A major physical parameter influencing loss through volatilization is the vapor pressure of the chemical, which is temperature dependent.
- The rate of volatilization increased with air flow and temperature, as well as, with the inherent vapor pressure and concentration of the chemical.

- Volatilization from the soil increases with increasing temperature and relative humidity, with humidity having greater impact on volatilization at higher temperatures.
- The major influence on volatilization is due to weather (meteorological) variables, such as temperature, soil moisture, relative humidity (insofar as it influences soil moisture), and wind turbulence.

Gentil et al. (2020) noted that, even if vapor pressure is an intrinsic chemical characteristic, higher temperature enhances the ability of a pesticide to turn into vapor and volatilize into the air. Shunthirasingham et al. (2010), for example, estimated an increase in volatilization rates of pesticides by a factor of 3–4 for a 10°C increase in soil temperature.

The high air temperature associated with the high soil moisture levels can enhance volatilization of pesticides (Rice et al., 2002). Shunthirasingham et al. (2010) also stated that higher soil humidity has been associated with faster pesticide volatilization and that, when soils become wet after a period of drought, pesticides are lost from the soils through rapid volatilization due to the replacement of the sorbed pesticides with water molecules.

Pesticide **transformation** occurs through degradation by physico-chemical and biological processes, such as photolysis, hydrolysis, oxidation-reduction and biological degradation. The rates of degradation of some pesticides are relatively high and their residues remain in the environment for a short time. Some molecules degrade completely in the environment reaching the mineralization. Although part of this process is caused by chemical or physico-chemical reactions, such as hydrolysis and photolysis, microbiological catabolism and metabolism are generally the main mineralization processes. Degradation rates of pesticides and their metabolites are among the most essential parameters in evaluating their environmental fate.

In soil, biological degradation (or biodegradation) – oxidation, reduction, hydrolysis and their conjugations, mediated by microorganisms – is the most efficient in degrading pesticide residues. Therefore, soil microorganisms play an important role in the intermediate degradation and subsequent mineralization of many pesticides (Racke et al., 1997).

According to Hornsby and Brown (1992), soils serve as the environment in which water, heat, oxygen, and nutrients are provided to soil microorganisms and all these factors interact to determine the microbiological degradation of pesticides in soils. As mentioned by the authors, organic matter and associated nutrients provide energy and presence of oxygen affects the mechanism and rate of microbial degradation.

Racke et al. (1997) highlighted that an important consideration is the quite different microbially-mediated reactions which can be associated with aerobic or anaerobic conditions. The authors mentioned that most preceding investigations of soil microbial pesticide degradation in tropical soils have been associated with flooded, rice paddy conditions and that, under anaerobic conditions, reductive reactions represent an important route of pesticide degradation.

Racke et al. (1997), referring to a review of microbial pesticide degradation in tropical soils, concluded that improved microbial activities due to high temperatures was the main factor responsible for increasing degradation of pesticides under tropical rice paddy soil conditions. However, other environmental factors were also cited as potentially important variables governing microbial activities. In many tropical areas characterized by intermittent heavy rain and dry seasons, soils are subjected to alternate periods of flooding and drying with concomitant increases in the activities of anaerobic and aerobic microorganisms, respectively. The authors mentioned that such alternate reduction and oxidation cycles in soil could provide favorable conditions for more extensive decomposition of organic compounds than in either system alone.

Laabs et al. (2002a) suggested that in tropical regions, the high temperatures can enhance biological degradation, besides increasing volatilization of pesticides. Daam et al. (2019), citing previous studies, mentioned an increase in estimated degradation rates of pesticides by a factor of 2, for a 10°C increase in soil temperature (Shunthirasingham et al., 2010) and faster pesticide degradation associated with higher soil humidity (Klein, 1989; Shelton & Parkin, 1991).

Biodegradation is more active in unsaturated root zone of the soil, mainly due to the presence of aerobic bacteria, which are more efficient in degrading pesticides, higher content of organic matter and better soil-water-air relationships for this biota. In acid soils, as some soils in the tropics, there is predominance of fungi, which are less efficient in degrading organic chemicals. In close to neutral or slightly alkaline conditions there is a predominance of bacteria and actinomycetes. Other factor has a great weight, which is the adaptability of soil populations to the substrate.

Depending on soil moisture content, hydrolysis may be important, especially when combined with other processes, such as biodegradation. In water saturated conditions, the hydronium ion ( $H_3O^+$ ) availability of the medium interferes in hydrolysis, due to the interaction with physical and chemical characteristics inherent to the molecule. Another interfering factor is temperature, which has also great influence on hydrolysis rates.

According to Racke et al. (1997), degradation of pesticides by hydrolysis in soil may occur due to reactions occurring in the soil pore water (base-catalyzed or acid-catalyzed reactions) or on the surfaces of clay minerals (heterogenous surface catalysis), and soil pH has also been implicated as an important factor influencing hydrolytic reactions.

Hornsby and Brown (1992) highlighted that soil pH can affect hydrolysis rate in several ways, because the rate of the acid-promoted process is a function of hydrogen ion concentration. The authors also mentioned that components of soil organic matter are known to catalyze the hydrolysis of some pesticides, as organophosphate compounds (chlorpyrifos, fenitrothion, malathion, parathion, as examples).

As reported by Racke et al. (1997), data in the literature support the conclusion that chemical degradation through hydrolytic reactions is dependent on the nature of the



pesticide and the characteristics of the soil. As the authors stated, these factors cannot be directly correlated to the region from which soils originate, however, the climate in which a soil is found can directly influence the rate of hydrolysis through modulation of the temperature and moisture of the soil.

In photolysis, light causes the breakdown of chemical bonds, at first by means of photochemical reactions. Indirect photolysis can also occur, where light acts as a catalyst for other physico-chemical processes, especially in water. Photolysis is considered as the process of transformation with the greatest spectrum of action, because it reaches any pesticide that is on surface of plants, soil and water.

Evidence suggests that photoinduced transformations can, in some instances, be significant and more rapid photodegradation of pesticides on moist soil surfaces versus dry soil surfaces has been reported. Although a pesticide may not be directly transformed by solar radiation, due to low absorbance between 290 and 400 nm wavelengths, indirect photodegradation may still be an important factor (Racke et al., 1997).

It is noteworthy that the level of solar radiation reaching tropical areas is approximately twice that of temperate areas (Reading et al., 1995). However, as pointed by Sanchez (2019), there is much less seasonal variability in sunlight in the tropical zone and daily averages during summer can be higher in some of the temperate zones. Sanchez (2019) also mentioned that the annual solar radiation is lowest in the humid tropics due to high cloud cover, and highest in tropical deserts, and in areas with even rainfall distribution, such as rainforests or deserts, there is little seasonality in solar radiation, whereas in areas with distinct rainy and dry seasons, cloudiness causes considerable seasonality.

Oxidation-reduction process mainly acts on chemical changes that the pesticide undergoes in photodegradation or biodegradation reactions, catalyzed, respectively, by light or microorganisms. However, in some very special situations, these reactions can occur alone, and are related to environments without light and in absence of microorganisms, in deep layers of soil or in ground water. As mentioned by Racke et al. (1997), some pesticides are susceptible to oxidation or reduction reactions which most occur in soils, respectively, under aerobic and anaerobic conditions.

Soil organic matter contains both potential oxidizing and potential reducing agents and the presence of organic matter may affect soil oxygen concentration through increased microbial activity, which, in turn affect indirectly the rate of oxidation or reduction (Hornsby & Brown, 1992).

According to Racke et al. (1997), unless a sufficient diversity of soils is compared, it is not possible to establish whether the differences in pesticide degradation rate are due to soil types, in general, or reflect the variability across soils from a given region, whether temperate or tropical. In their report, Racke et al. (1997) summarized that:

- Since soil microbial activities are affected by temperature, pesticide degradation is expected to be greater in soils in the tropics, with higher year-round temperatures than in the temperate region.
- In soil at higher average year-round temperatures (tropical and subtropical regions), the rate of hydrolytic degradation would be greater than in soil at lower temperatures; however, the increase in rate is dependent on the activation energy of the reaction.
- Given that sunlight intensity affects rates of pesticide photolysis, variations due to geographical location and season is expected. Estimation of half-lives of photosensitive pesticides indicates that due to more uniform light intensities throughout the year in the tropics, photolytic reactions would be likely to occur uniformly more rapidly.

Degradation and sorption data for locally relevant soils are required together with an understanding of soil moisture status, organic carbon content and composition, soil temperature, and previous application history (Lewis et al., 2016).

It is worth noting that when degradation, by any mechanism, is not complete, degradation products or metabolites may also be of importance to the environment and human health because some of them have the same or higher ecological and human toxicity than the original molecules.

Reviews, such as those presented by Racke et al. (1997) and Kookana et al. (1998), have called for further research to identify the key dissipation pathways, especially in soils of the tropical region. According to Daam and van den Brink (2010), although laboratory degradation and field dissipation of pesticides has often been indicated to be faster under tropical than temperate conditions, special care must be taken in extending such circumstantial evidence for a specific ecosystem in any region.

Pesticide leaching in soils is a function of water flow, sorption, and degradation, as seen, and it is influenced by other field dissipation processes, since the amount of pesticide available to leach also depends on surface runoff, volatilization and plant uptake (**Figure 2**). Thus, leaching, and consequent ground water contamination potential, can be approached as resultant from the mass balance with other dissipation mechanisms in soils over time.

The overall dissipation of a pesticide from soil results from a combination of loss mechanisms (Racke et al., 1997). When measured in the field, dissipation from soil is affected by the processes of retention, transformation and transport, as a result of prevailing soil and weather conditions (Lewis et al., 2016).

Thus, it is needed clearly to distinguish between field dissipation and laboratory degradation studies, because, as mentioned by Racke (1993), field investigations of pesticide fate are conducted under natural environmental conditions, which are characterized by variation, unpredictability, and extremes, due to the multiple forces of dissipation working simultaneously.

Field investigations of pesticide fate in the tropical region indicate that dissipation often occurs more rapidly than under temperate conditions. Based on a few instances

in literature, Racke et al. (1997) noted that, researchers reported increased dissipation under tropical field conditions as compared with published results from temperate regions. Besides increased volatility, enhanced chemical (hydrolysis) and microbial degradation account to the rapid field dissipation in the tropical region (Laabs et al. 2002a; Racke, 2003; Dores et al., 2009; Sanchez-Bayo & Hyne, 2011). Chai (2008) noted that the fast initial dissipation can be attributed to surface losses (runoff, volatilization, and photodegradation) and leaching, whereas subsequent slower dissipation is related to abiotic and microbial degradation processes inside the soil.

The most prominent mechanisms for the increase in pesticide field dissipation appear to be related to the tropical climates (Racke et al., 1997; Laabs et al. 2002a; Racke, 2003; Dores et al., 2009; Sanchez-Bayo & Hyne, 2011, Lewis et al, 2016). Lewis et al. (2016) stated that the available data suggest that field dissipation of most pesticides in soils is generally faster in tropical environments that are characterized by warmer and wetter climates (that is, in tropical rainy and seasonal climates). Corroborating with this statement, studies have demonstrated that pesticide tend to dissipate faster in humid and subhumid tropical conditions (Helling, 1997; Laabs et al., 2000; Laabs et al., 2002a; 2002b; Dores et al., 2009; 2016). As previously seen, humid and subhumid tropics are, respectively, related to rainy and seasonal climates (**Table 1**).

Chai (2008) mentioned that the higher rainfall and soil moisture accelerate the dissipation of pesticides in humid tropical soils. Dores et al. (2016) highlighted that several factors may contribute to the reduction of field half-life in subhumid tropics, such as high temperatures and soil humidity, increasing soil microbial activities, as well as intense rainfall, which contribute to runoff.

In a review, Daam and van den Brink (2010) summarized that there are four basic elements of climate that are important for pesticide dissipation especially when one compares temperate and tropical agroecosystems: rainfall, temperature, sunlight and microorganisms. The authors mentioned that rainfall is primarily responsible for surface runoff of pesticides from their treatment sites, transported in solution and with soil through erosion, and for leaching and hydrolytic degradation.

As previously cited, the various soils in the tropics cannot be classified as a distinct entity with a unique set of properties, however, Kookana and Simpson (2000) noted that, besides climate-related factors (high temperature, high humidity, and intense rainfall), highly weathered soil types in the tropical regions have the potential to markedly influence pesticide behavior.

Supported by the modeling work performed by Sanchez-Bayo and Hyne (2011), Lewis et al. (2016) stated that the lower organic carbon contents in tilled tropical soils, largely due to enhanced microbial activity, suggest that greater losses of most pesticides can occur in the water phase.

Studies on pesticide behavior and ground water contamination potential in the various tropical environments are still insufficient to draw solid conclusions. As pointed out by Chai (2008), there is a need to conduct more research, including leaching of pesticides from single profile to whole catchment, microbial degradation pathways and kinetics, identification of microorganisms responsible for pesticide degradation, enhanced degradation in soils and transport modelling using the local climatic data.

As early stated by Racke (2003), although the published literature contains several reports on behavior of pesticides in tropical ecosystems, further experimental and modeling research targeted at developing a more complete understanding and better predictive capability of the behavior of these organic chemicals under tropical environmental conditions should be encouraged.

In summary, if the onsite behavior and offsite losses of pesticides from an agricultural area is to be understood, soil sorption and degradation, volatilization into the atmosphere, surface runoff (in water solution and sorbed to soil particles) and leaching in soil profile (matrix and preferential-flow transport) data for locally relevant tropical conditions are required, considering the soil moisture and temperature, organic carbon content and composition, and previous pesticide application practices; what is an important challenge in agricultural and environmental sciences.

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