

SPATIAL ASSESSMENT OF ENVIRONMENTAL CONTAMINATION BY PESTICIDES IN THE MUNICIPALITY OF PETROLINA-PE - PART I

AVALIAÇÃO ESPACIAL DA CONTAMINAÇÃO AMBIENTAL POR AGROTÓXICOS NO MUNICÍPIO DE PETROLINA-PE - PARTE I

EVALUACIÓN ESPACIAL DE LA CONTAMINACIÓN AMBIENTAL POR PLAGUICIDAS EN EL MUNICIPIO DE PETROLINA-PE – PARTE I

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ABSTRACT

One way to assess the risk of environmental contamination from a pesticide is to consider its physical and chemical properties in terms of soil binding capacity, volatility, leachability, solubility, etc. The GOSS and GUS methods combine this information to create a contaminant profile, serving as a basis for assessing the potential for surface and groundwater contamination by a given pesticide. In this regard, several tools can be used, such as those that consider the combination of these and other models associated with Geographic Information Systems for mapping regions, where soil characteristics and available water resources provide a vulnerability profile for various locations, particularly agricultural producers. The sub-middle São Francisco region is one of Brazil's main fruit producing and exporting hubs, specializing in grape and mango production. The agricultural system implemented in this region requires an assessment of its impacts on the environment, particularly on soil, water, and the atmosphere, through the physical, chemical, and biological characteristics of local natural resources. Controlling pesticide use in this region is a challenge for environmental oversight agencies. This study aims to assess the risk of environmental contamination in the agricultural regions of Petrolina, Pernambuco, based on information generated by a Geographic Information System (GIS). It considers physical aspects of the soil and water compartments, highlighting soil types, hydraulic conductivity potential, and slope, associated with the physicochemical properties of pesticides. These characteristics were found in samples from various crops collected in Petrolina during 2009, 2010, and 2011. Based on the proposed methods (GUS and GOSS), the study revealed high contamination potential for those pesticides that undergo leaching, particularly for azoxystrobin, boscalid, carbendazim, dimethomorph, fenarimol, methomyl, and myclobutanyl thiamethoxam. On the other hand, compounds such as Cyproconazole, Difenoconazole (1,2), Propargite, and Tebuconazole showed a high potential for contaminating surface water. Therefore, leachable pesticides should be avoided in soils with high hydraulic drainage, as well as in soils with relatively steep slopes. The combination of land vulnerability data with pesticide properties showed that it is possible to identify, preliminarily, contamination regions for different pesticides in the municipality of Petrolina. The combination of spatial data with chemical knowledge can point to more rational practices where crop/environment/pesticide should be considered as a whole with interrelationships.

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Keywords: Environmental Contamination. Geographic Information System. Water Resources. Pesticides.

RESUMO

Uma forma de se avaliar o risco de contaminação ambiental por um agrotóxico é considerar suas propriedades físicas e químicas em termos de capacidade de se associar ao solo, volatilidade. lixividade. solubilidade. etc. Os métodos de GOSS e GUS combinam essas informações permitindo criar um perfil do contaminante, servindo como subsidio para avaliar a potencialidade de contaminação dos recursos hídricos superficiais e subterrâneos por um determinado agrotóxicos. Nesse aspecto, várias ferramentas podem ser utilizadas como as que consideram a combinação desses e de outros modelos associados a Sistemas de Informações Geográficas para mapeamento de regiões, em que as características do solo e recursos hídricos disponíveis permitem fornecer um perfil de vulnerabilidade no qual se encontra as diversas localidades, em particular as produtoras agrícolas. A região do submédio São Francisco é um dos principais polos produtores e exportadores de frutas do Brasil, sendo especializada na produção de uva e manga. O sistema agrícola implantado nessa região demanda uma avaliação de seus impactos no meio ambiente, notadamente no solo, na água e na atmosfera, através das características físicas, químicas e biológicas dos recursos naturais locais. Controlar o uso de agrotóxicos nessa região é um desafio para os órgãos de fiscalização ambiental. Este trabalho propõe-se a avaliar o risco de contaminação ambiental das regiões agrícolas de Petrolina-PE, baseado em informações construídas a partir de um Sistema de Informações Geográficas, considerando aspectos físicos dos compartimentos solo e água, destacando-se tipos de solo, potencial de condutividade hidráulica e declividade, associados com as propriedades físico-químicas dos agrotóxicos, recorrentes em amostras de diversas culturas coletadas em Petrolina, durante os anos de 2009, 2010 e 2011. Baseado nos métodos propostos (GUS e GOSS), o estudo revelou alto potencial de contaminação para aqueles agrotóxicos que sofrem lixiviação, com destaque Azoxistrobina. Boscalide. Carbendazim, Dimetomorfe. Fenarimol. Metomil. Miclobutanile Thiamethoxam. Por outro lado, compostos como Cyproconazol, Difenoconazol (1,2), Propargito e Tebuconazol apresentaram alto potencial de contaminação de águas superficiais. Assim sendo os agrotóxicos lixiviáveis devem ser evitados em solos de alta drenagem hidráulica, bem como em solos de relativa declividade. A combinação dos dados de vulnerabilidade das terras com propriedades dos agrotóxicos evidenciou que é possível apontar, de forma preliminar, regiões de contaminação para diferentes agrotóxicos no município de Petrolina. A combinação de dados espaciais com o conhecimento químico pode apontar para práticas mais racionais onde cultura/ambiente/agrotóxico devem ser pensados como um conjunto que estabelece inter-relações.

Palavras-chave: Contaminação Ambiental. Sistema de Informação Geográfica. Recursos Hídricos. Agrotóxicos.

RESUMEN

Una forma de evaluar el riesgo de contaminación ambiental por un plaguicida es considerar sus propiedades físicas y químicas en términos de capacidad de fijación al suelo, volatilidad, lixiviabilidad, solubilidad, etc. Los métodos GOSS y GUS combinan esta información para crear un perfil de contaminantes, que sirve como base para evaluar el potencial de contaminación de aguas superficiales y subterráneas por un plaguicida determinado. En este sentido, se pueden utilizar diversas herramientas, como las que consideran la combinación de estos y otros modelos asociados con los Sistemas de Información Geográfica para el mapeo de regiones, donde las características del suelo y los recursos hídricos disponibles



proporcionan un perfil de vulnerabilidad para diversas localidades, en particular para los productores agrícolas. La región subcentral de São Francisco es uno de los principales centros frutícolas de Brasil, especializado en la producción de uva y mango. El sistema agrícola implementado en esta región requiere una evaluación de sus impactos sobre el medio ambiente, en particular sobre el suelo, el agua y la atmósfera, a través de las características físicas, químicas y biológicas de los recursos naturales locales. Controlar el uso de plaguicidas en esta región representa un desafío para los organismos de supervisión ambiental. Este estudio tiene como objetivo evaluar el riesgo de contaminación ambiental en las regiones agrícolas de Petrolina, Pernambuco, con base en información generada por un Sistema de Información Geográfica (SIG). Considera aspectos físicos de los compartimentos suelo y agua, destacando tipos de suelo, potencial de conductividad hidráulica y pendiente, asociados con las propiedades fisicoquímicas de los plaquicidas. Estas características se encontraron en muestras de varios cultivos colectados en Petrolina durante 2009, 2010 y 2011. Con base en los métodos propuestos (GUS y GOSS), el estudio reveló un alto potencial de contaminación para aquellos plaguicidas que sufren lixiviación, particularmente para azoxistrobina, boscalida, carbendazim, dimetomorf, fenarimol, metomilo y miclobutanil tiametoxam. Por otro lado, compuestos como ciproconazol, difenoconazol (1,2), propargita y tebuconazol mostraron un alto potencial de contaminación de aguas superficiales. Por lo tanto, se debe evitar el uso de plaguicidas lixiviables en suelos con alto drenaje hidráulico, así como en suelos con pendientes relativamente pronunciadas. La combinación de datos sobre la vulnerabilidad del suelo con las propiedades de los plaguicidas mostró que es posible identificar, de forma preliminar, las zonas de contaminación por diferentes plaquicidas en el municipio de Petrolina. La combinación de datos espaciales con el conocimiento químico puede indicar prácticas más racionales donde la relación cultivo/medio ambiente/plaguicida debe considerarse como un todo, con sus interrelaciones.

Palabras clave: Contaminación Ambiental. Sistema de Información Geográfica. Recursos Hídricos. Plaguicidas.

1 INTRODUCTION

The consumption of thousands of tons of food each year is the result of agricultural practices that have been consolidated throughout human history, ensuring ever-increasing harvests.

Man has learned to explore or even develop natural or synthetic substances that can, in some way, combat and/or control the spread of pests caused by insects, bacteria, fungi or even weeds, agents that cause major impediments to agricultural development, and consequently compromise the agricultural production process.

In this context, pesticides emerged, which, in general, are synthetic or natural substances that have enabled man to triumph in terms of pest control. Throughout history, these compounds have made it possible to realize humanity's dream of harvest records through pest control, however, it has been evidenced that the toxicity of these compounds and consequently their potential to contaminate the environment are problems to be solved (BAIRD, 2011).

Studies have made it possible to correlate various adverse effects caused by pesticides such as deaths and genetic anomalies in animals, diseases in humans such as cancer, neurological anomalies, etc. (WHO, 1990; EPA, 1985; BAIRD, 2011).

Understanding how pesticides spread in the environment allows us to assess the level of contamination of these compounds throughout the biota. Understanding this problem, it is necessary to use conscious practices so that the use of these compounds is not done irresponsibly and randomly, since the diffusion of these substances in the environment can cause several health-related problems.

Environmental monitoring is a powerful set of practices that allows assessing the level of environmental contamination from anthropogenic actions and its relationship with the balance of ecosystems. Through this information, it is possible to measure which guidelines are necessary to maintain the healthiest environment possible. Among the monitoring parameters, we can mention the diagnostic processes, which allow the prediction of several variables that influence the potential for contamination of a given substance in the environment (Andrade, 2011).

The use of a given product cannot only take into account its efficacy as a pesticide, but must be evaluated as a whole, in view of its potential for diffusion and contamination of the environment. One way to assess the risk of environmental contamination by a pesticide is to consider its physical and chemical properties in terms of its ability to associate with the soil, volatility, lixivity, solubility, etc. (GOMES, 1996).

Some theoretical methods allow us to establish the relationship between these properties and the mobility of the pesticide in the environment. A practical example of this is adopted by the United States of America through the criterion for evaluating potential pollutants, the GUS method, which considers the leaching capacity of the pesticide. In this case, the relationship between the lifespan of the pesticide in the soil and its ability to be adsorbed by the organic matter present in it is considered.

Geographic Information Systems can be understood as a set of computational tools formed by equipment and programs that, through techniques, integrates data, people and institutions. This tool enables the collection, storage, processing, analysis and supply of georeferenced information produced through available applications, which aim at greater ease, security and agility in human activities related to monitoring, planning and decision-making related to geographic space (ROSA, 2005).

The combination of this information allows the creation of a profile of the contaminant, and serves as a starting point to assess the probability of contamination of water resources by a given pesticide. In this aspect, several tools can be used with this model and with models associated with Geographic Information Systems for mapping regions. (HAAN et al., 1993; TIM; JOLLY, 1994; JANKOWSKI; HADDOK, 1996; MAIDMENT; DJOKIC, 2000; Montamoros, 2005; LEE, 2008; EKLO, 2009).

In the case of the sub-middle region, São Francisco specializes in the production of grapes and mangoes. The integrated production system implemented favors the correct and safe use of pesticides, which even so requires an assessment of their impacts on the environment, notably on the soil, water and atmosphere.

This work evaluates the risk of environmental contamination in agricultural regions of Petrolina-PE, based on information built from a Geographic Information System, considering physical aspects of the soil and water compartments, highlighting soil types, hydraulic conductivity potential and slope, associated with the physicochemical properties of pesticides, recurrent in samples of various crops collected in Petrolina, Brazil. during the years 2009, 2010 and 2011.

2 OBJECTIVES

2.1 GENERAL OBJECTIVE

To evaluate in a preliminary way the spatio-temporal vulnerability of the contamination of water resources (surface and groundwater) and soils, in the municipality of Petrolina-PE.



2.1.1 Specific objectives

- Survey of soil indicators through hydraulic potential and slope to build a profile of vulnerability of contamination of the soils and groundwater and surface waters;
- Survey the physicochemical properties of recurrent pesticides in crops in the municipality of Petrolina, which will result in the description of the potential contaminating behavior in relation to the soil/water media;
- Construction of thematic maps referring to soil types, slope, drainage potential and hydrography in the municipality of Petrolina, in terms of potential vulnerability and contamination by pesticides;
- Construction of thematic maps resulting from information from 1) and 3) and establish vulnerable regions in relation to pesticide contamination;
- Creation of a database through a Geographic Information System to contribute to new actions to prevent environmental contamination by the use of pesticides.



3 THEORETICAL FRAMEWORK

3.1 PESTICIDES

The great development of agriculture in the last two centuries is associated, among others, with an increasing demand for food, in view of the demographic explosion that has occurred on the planet. The association of technology with standardized agricultural production techniques has made it possible to produce millions of tons per year.

The introduction of monoculture has led man to develop techniques to get rid of undesirable parasites (insects, bacteria, plants, etc.) that could put the production process at risk. In this context, pesticides emerged, idealized as substances that would combat parasitic pests.

The massive production of organosynthetics, especially after the Second World War, boosted the development of pest control, being celebrated as the "end of all evils", because in addition to pest control, they would be practically indestructible in the environment. In the 1960s, there was a beginning of awareness through Rachel Carlson's warning in her famous book "Silent Spring" which denounced the indiscriminate use of pesticides such as Dichloro-Diphenyl-Trichloroethane (DDT) (CARLSON, 1962).

The current definition of pesticides is well established and has many interpretations. One of them is based on Law No. 7,802 of 07.11.89, which says:

Pesticides are the products and agents of physical, chemical or biological processes, intended for use in the production sectors, in the storage and processing of agricultural products, in pastures, in the protection of forests, native or implanted, and other ecosystems and also in urban, water and industrial environments, whose purpose is to change the composition of flora and fauna, in order to preserve them from the harmful action of living beings considered harmful, as well as the substances and products used as defoliants, desiccants, stimulants and growth inhibitors (BRASIL, 1989).

Another recurring definition is given by the Food and Agriculture Organization (FAO). The entity that is part of the United Nations (UN) structure:

Any substance or mixture of substances intended to prevent, destroy or control pests, including vectors of animal and human diseases that impair or interfere with the production, processing, storage, transport or marketing of food, agricultural products, timber and wood products, or animal feed, or those that can be administered to animals for insect control, arachnids, or other pests internal or external to their bodies. The term includes substances intended for



use as plant growth regulators, defoliants, desiccants, inhibitory agents, or agents intended to prevent premature fruit drop, and substances applied to crops both before and after harvest to prevent spoilage during storage or transport (FAO, 2007).

In general, for both definitions there is a consensus that pesticides are substances used in the preservation of vegetables in terms of their protection against attacks by living beings that cause some damage to their survival or conservation.

3.1.1 Classification

Pesticides can be classified according to several criteria, which may be related to the type of action (Table 1), structure, chemical composition, physical properties, etc.

 Table 1

 Classification of pesticides according to action

Kind	Use/Combat
Insecticides or pesticides	Insects in a generalized way
Fungicide	Different types of fungus
Herbicide	Different invasive plants, weeds etc

Source: Lê Pauder (1994) and Luchini (1995).

It should be noted that there are more specific classifications according to the target organism, so a larvicide is applied in the control of larvae, a molluscide in snails or slugs, nematicides in nematodes, etc. A more general discussion of this division is chosen (BAIRD, 2011).

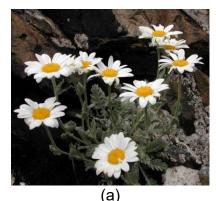
From a chemical point of view, pesticides can be classified as inorganic and organic (natural and synthetic) (BAIRD, 2011). The group of inorganics stands out those based on Arsenic and Copper, such as green paris, a salt widely used as an insecticide in the USA around 1827. The proposed action of these compounds is that they act when in contact with insects, killing them by asphyxiation. The major problem with these compounds is their toxicity to humans, in addition to being extremely persistent, lasting in the environment for several years, contaminating water resources, soil and living beings (BRAIBANTE; ZAPPE, 2012).

The group of organics, of natural origin (animal or vegetable), has as a fundamental characteristic its low persistence and rapid degradability in the environment. Two typical examples of this group are: pyrethroids such as pyrethrin,



which is extracted from pyrethrum, a daisy-like flower used as an insecticide, and the soil bacterium *Bacillusthuriengiensis* (abbrev. Bt) producing protein toxins that are lethal to a wide range of insects (BRAIBANTE; ZAPPE, 2012).

Figure 1
(a) Photo of pyrethrum, and (b) chemical structure of pyrethrin



R 0 0 0

Source: Alemming (2012).

Still on the group of organic pesticides, those of synthetic origin stand out, which, unlike natural ones, have as their main characteristic high persistence in the environment, in addition to being associated with a series of problems related to the health of human beings (ANDREA, 2000). These products penetrate the vector organisms by digestive route and/or by direct contact in the pest integument.

According to Almeida (2002), in terms of chemical structure (characteristic functional groups), pesticides can still be classified into four major groups: organophosphates, organochlorines, carbamates and pyrethroids.

(a) Organochlorines

They are characterized by the presence of the element chlorine attached to an organic molecule. Of low volatility (low vapor pressure), they are very fat-soluble compounds (being hydrophobic), which characterizes the tendency of animal bioaccumulation in fat, and thus in the food chain, or in soils with a large presence of organic matter (such as clay soils). They are stable to the action of light, heat, air and strong acids. They are able to remain in the soil, without fully decomposing, for up to five years. Some examples of organochlorines are Aldrin, Chlordane, Mirex, Dihredrin, DDT, Endrin, Heptachlor, BHC and Toxafene (FLORES, 2004).

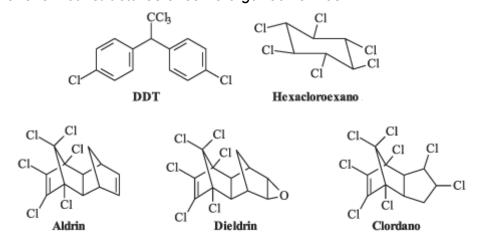
They are compounds that have acute toxicity. They act at the level of



cholinesterase (an enzyme that acts in the transmission of impulses in the nervous system) causing immediate death (SANTOS, 2009).

Figure 2

Example of chemical structures of some organochlorines



Source: Santos et al. (2007).

b) Organophosphates

Also considered fat-soluble, organophosphate pesticides are extremely unstable compounds in alkaline environments and some even in acidic environments. Because they are less stable than organochlorines, they decompose in a matter of days, and are hardly found in the food chain. Its toxicity is achieved via direct contact by inhalation, ingestion or direct absorption. Examples of organophosphates are: Phorate, Parathion Methyl, Ditalinfós, Diazinon, Fenitrothion, Mevinfós, Triazofós and Monocrotofós (SANTOS, 2009; WHO, 1986).

Figure 3

Example of chemical structures of some organophosphate

$$C_2H_5O$$
 OC_2H_5

Paraoxon

Paration $X = p-NO_2$

Fensulfotion $X = p-SOCH_3$
 C_2H_5O
 OC_2H_5

Paraoxon

Paration $X = p-SOCH_3$
 C_2H_5O
 OC_3H_7

Profenofos



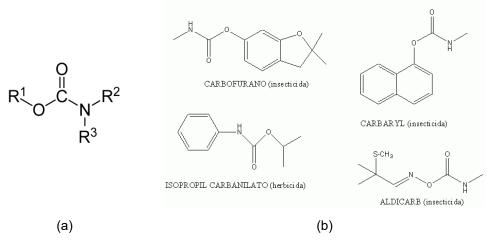
Source: Federal University of Santa Catarina (2012).

(c) Carbamates

They are esters derived from carbamic acid. They are obtained by replacing the hydrogen of hydroxyl (-OH) with an alkyl or aryl radical. In its molecule, nitrogen-bound hydrogens can also be replaced by organic radicals (R2 and R3) (figure 4). They are considered of medium toxicity, since they are unstable in the face of light and can be quickly decomposed, and therefore do not appear in the trophic chain (SANTOS, 2009).

Figure 4

Example of chemical structure of carbamates



Source: Universidad de Granada (2012).

d) Pyrethroids

They are synthetic, biodegradable compounds that have structures similar to pyrethrin, a substance found in the flowers of *Chrysanthemum* (*pyrethrum*) *cinerariacfodium*. The mode of action of these compounds is similar to that of organochlorines, as they act on the membrane of neurons, altering it (SANTOS, 2009).



Figure 5 - Example of the chemical structure of pyrethroids

Piretróides	R ₁	R ₂	R ₃
λ-cialotrina	CI	CF ₃	CN
cipermetrina	CI	CI	CN
deltametrina	Br	Br	CN
permetrina	CI	CI	Н

Source: Vieira et al. (2007).

3.2 ROUTES OF ENVIRONMENTAL CONTAMINATION BY PESTICIDES

Studies on the diffusion of pesticides in the environment reveal a relationship between some diseases and exposure to these compounds (MAPA, 2009). Contact with pesticides can occur through the air (volatility), water ingestion (solubility) or even through the consumption of contaminated food of plant or animal origin (bioaccumulation) (MARICONE, 1985).

3.2.1 Air pollution

Atmospheric contamination by pesticides can be associated with two important aspects:

- 1) its spraying in the open air, in which pesticide molecules would diffuse by the action of the winds;
- 2) By the very nature of the pesticide, that is, its higher or lower vapor pressure would be associated with greater or lesser volatilization.

Batista (1988) suggests that the diffusion of pesticides in the atmosphere is also an important factor for environmental contamination, since rainfall can drag them from the atmosphere to the soil and surface water resources.

3.2.2 Water contamination

Once applied, pesticides, depending on their physical properties (solubility, volatility, mobility, etc.), can be dragged into bodies of water, as suggested by Lara (1972), when he stated that rain is the main vehicle for transporting contaminants dispersed in the atmosphere, leading to the contamination of streams, rivers and even seas. Another interesting mechanism is the process of soil wear (leaching), which is associated with the process of contamination of groundwater (EDWARDS, 1973).

Once the water is contaminated with pesticides, Machado Neto (1991) considers that all the elements present in the ecosystem (biotic and abiotic) will also be. Based on this relationship, Luna (2004) correlated the contamination of pesticides in bodies of water with their effects on the populations present, in terms of measurable criteria, based on the number of dead organisms, percentage of cuttlefish eggs, changes in size and weight, percentage of enzyme inhibition, tumor incidence, among others.

An example of this was presented by Elfvendahl (apud CARVALHO, 2011), who studied the water and sediment of the Alto Ribeira Tourist Park (PETAR), located in the Ribeira Valley in São Paulo, and detected the presence of 20 different pesticides, 7 of which are extremely toxic to fish and species in marine environments.

Canuto et al. (2011), in a recent study, investigated the contamination of surface and groundwater by residues of atrazine, cyromazine and methyl parathion, applied to vegetable crops developed in Serra da Ibiapaba, municipality of Tianguá – Ceará (CE). By comparison between models, atrazine and cyromazine showed high potential for surface water contamination and high leaching potential for groundwater. Methyl parathion showed a medium potential for contamination of surface water and non-leachable to groundwater. The results showed the need for constant monitoring of the levels of these pesticide residues.

Andrade et al. (2011) evaluated the levels of pesticides used in the region of the Alto Paranaíba Directed Settlement Program (PADAP), in an area of 60,000 ha of intensive cultivation system in the Cerrado of Minas Gerais. The authors considered the relationship between environmental classification and the risk of groundwater contamination as a function of the active ingredients found. It was observed that about 70% of the pesticides used in this region were among the classes of highly dangerous and very dangerous products to the environment. Of the 45 active ingredients evaluated, approximately 38% showed potential for contamination to groundwater.

Lima et al. (2011) conducted a study in the Cumaru creek watershed, municipality of Igarapé-Açu (PA) with the purpose of evaluating the potential for groundwater contamination by pesticides. The sorption experiments carried out by the authors showed the low sorption of the pesticide dimethoate in the sediment of the unsaturated zone, mainly due to its mobility and low retention, indicating the high potential for groundwater contamination by this compound.

Silva et al. (2011), in turn, investigated the presence of pesticides in rice-growing areas in Rio Grande do Sul (RS) and Santa Catarina (SC). The current system of irrigated rice production in these regions requires a wide use of pesticides. The authors showed that in most samples, Fipronil was present followed by imazetapir, clomazone, imazapic and quinclorac. 27% of the groundwater samples analysed by the authors showed Fipronil levels above the potability limit proposed by the European Community.

Pesticide contamination can also interfere with the water supply system. In this sense, Brito et al. (2011) prospected on this subject in the Sergipe River basin. 30% of the water supply of the city of Aracaju - Sergipe (SE) comes from the Poxim River, whose recharge areas, previously occupied by native vegetation, have intense agricultural activity, mainly through the cultivation of sugarcane. In this study, the presence of Diuron was observed in the Poxim-Mirim River (upper part of the subbasin, where agricultural activities take place) and in the Poxim River (in the lower part of the sub-basin, where water is collected for public supply), at levels that can compromise water quality, especially in the rainy season, possibly caused by surface runoff from contaminated soil.

3.2.3 Soil contamination

Soil is the first destination of pesticides in the environment. The capacity of this compartment to retain these compounds allows us to infer about the tendency of the pesticide to contaminate surface or underground water bodies. This pesticide retention capacity in the soil depends on some characteristics of the soil itself combined with the physical and chemical properties of the pesticide.

In terms of soil, the first characteristic refers to hydraulic conductivity, which can simply be understood as the ability of the soil to drain any surface water towards groundwater. This characteristic defines the time of permanence of the pesticide in the soil, since it results in the greater or lesser speed of water flow in the soil, which in turn leads to the pesticides eventually dissolved in it.

According to Barbalho (2010), one aspect considered in the evaluation of the potential for contamination of underground aquifers by pesticides is the percentage of soil slope. Such information, associated with the potential for hydraulic conductivity, allows estimating the tendency of the pesticide, dissolved in water, to be transported along the soil, and consequently to diffuse in underground water bodies.



3.2.3.1 Soil and its characteristics

Soil is one of the main natural resources of fundamental importance for the development and diffusion of most plants. Of varied composition and dependent on the type of soil, from the physicochemical point of view, it has a mineral and organic composition, as well as water and air (BRADY, 1989; KOUSTAS; FISHER, 1998; LUCHINI, 1995).

Organic matter, called humus, originates from decomposing animal and plant remains, which is associated with living organisms such as: bacteria, insects, fungi, plant roots, among others. Humus is more present on the soil surface, constituting a colloidal system (ANDREA, 2000).

With regard to mineral matter, it can be inferred that the soil is constituted, even if variably, by fragments of rocks and primary minerals from the mother rock and secondary minerals, which are derived from the modification of the primaries, being mainly composed of clay, iron and aluminum oxides and hydroxides, and in some cases, calcium and magnesium carbonates, as well as other varieties (KOUSTAS; FISCHER, 1998).

The greater variety of conditions to which the soil is subjected, such as climatic conditions, slope of the terrain, organisms in the soil and the type of parent rock, will result in the different types of soil known (Table 2) (BRADY, 1989; ARMAS, 2005; ANDREA, 2000).

 Table 2

 Soil types and their characteristics

TYPES OF SOIL	FEATURES
Sandy texture soil	It has a sand content > 70%. It has good aeration and little humidity (it does not retain water), leading plants and microorganisms to live more difficult in this type of soil. It also has clay and other compounds in smaller quantities. Its permeability is due to the larger grains of sand, which because they have more space between them, facilitate the passage of water, making it difficult to retain it.
Clay texture soil	It's not as sandy. It is less permeable, which provides slower passage and easier storage of more water than sandy soil. Some Brazilian soils, even though they have a lot of clay, have great permeability due to the high amount of aluminum oxides (gibbsite) and iron oxides (goethite and hematite), which form small grains, giving them a character similar to sandy.
Medium-textured soils	Medium in texture, they have a certain balance between sand, silt and clay contents. They usually have good drainage, good water retention capacity and average erodibility index. Therefore, they do not require special care, adapting to all irrigation methods.



Silty textured soils	They have a large amount of silt, and are usually very erodible. Silt does not aggregate like clay and at the same time its particles are very small and light;
Humiferous soils	They have a higher amount of humus compared to other types of soils. It is a generally fertile soil. They have about 10% of humus in relation to the total of solid particles. The presence of humus contributes to its ability to retain water and mineral salts, increasing its porosity and aeration. The grains are of varied and diversified sizes and the passage of water occurs according to the type of grain.
Calcareous soil	The amount of limestone in this type of soil is greater than in the others. From this type of soil, a white or yellowish powder is removed, which can be used to fertilize soils intended for agriculture and livestock. This soil also provides the raw material for the manufacture of lime and cement

Source: Musumeci (1992); Camargo et al. (1986).

3.2.4 Properties of pesticides

Soil contamination by pesticides is conditioned by the physical and chemical properties of these compounds, which can be measured in terms of volatility, adsorption, leaching, microbial metabolism and its persistence in the soil, the drainage potential of the soil, in addition to its physicochemical properties.

The tendency of pesticides to stick to the soil can provide information about the leaching potential of these compounds, that is, the greater tendency to be transported to other environments.

One way to quantify the tendency of the pesticide to associate with sediment or soil is given by the Organic Carbon Partition Coefficient (Koc), also known as the soil/water partition coefficient or adsorption coefficient. The Koc value indicates the potential mobility of the pesticide in the soil (EMBRAPA, 2006). Pesticides with Koc< 50 mL/g are considered to have high mobility, while values between 150-500mL/g are moderately mobile and, above 2,000mL/g, have low mobility in the soil (MILHOME, 2009).

Another factor that is influenced by soil characteristics is the degradation of the active ingredient and the extent of biodegradation, since the latter only occurs if it is bioavailable. Thus, the half-life in the soil (T50) is a quantity that can vary according to environmental parameters (GOSS, 1992). The half-life (T50) of the pesticide in the soil is very important in the evaluation of the contamination potential, since a high value of this parameter will result in a long period of its permanence in the soil and a low one will allow a faster dissipation (MILHOME, 2009).

The solubility of the pesticide in water is another parameter considered in studies evaluating the potential for soil contamination by these compounds. It can be understood as the measure of how readily a substance will dissolve in water, and is expressed in mg/L. The more soluble it is in water, the greater the ability of pesticides



to diffuse into water bodies. This aspect associated with soils with high drainage constitutes a danger to be considered in terms of contamination.

Domingues (2010) used the parameter of pesticide solubility to predict contamination. For the author, a solubility > 3 mg/L indicates the possibility of the pesticide contaminating the water table.

3.2.4.1 Assessment of the risk of contamination of surface and groundwater by pesticides

There are several ways to analyze the trend of environmental contamination by pesticides. Many require detailed information, such as that obtained by simulations of the dynamics of pesticides in the vertical profile of soils. Another way to analyze contamination trends is through some characteristics of these compounds. This includes analyses of trends in groundwater contamination, obtained by the screening criteria of the Environmental Protection Agency (EPA) (COHEN et al., 1995 apud MILHONE, 2009) and by the GUS Groundwater Ubiquity Score index (GUSTAFSON, 1989 apud EMBRAPA, 2006).

The method proposed by Gustafson (1989) to estimate the degree of leaching of a pesticide in the soil combines parameters such as half-life and the partition coefficient of pesticides in the soil. The result is expressed through a mathematical relationship (Eq. 1), called the Groudwater Ubiquity Score (GUS) model or index, in which it points to the time/speed with which the substance reaches the groundwater (Table 3).

 Table 3

 GUS Evaluation Criteria

Criterion	GUS
Does not leach	< 1.8
Transition Track	1.8 < GUS < 2.8
Probable leaching	> 2.8

Source: Gustafson (1989).

The GUS index can be obtained from equation 1.

$$GUS = log(DT50solo)x(4 - logKoc)$$
 (1)

To conclude, it should be understood that there are several categories of pollutants or contaminants, which when associated with the characteristics of the soils, may or may not be transported. Not settling in the soil, they can propagate in several directions, reaching the water table and the food chain. Remaining in the soil, they will



be part of the food chain via absorption by crops. Information on the properties of pesticides, such as adsorption, half-life in soil and water; and water solubility are necessary for this analysis.

Analyses of surface water contamination trends can also be predicted by the characteristics of the active ingredients, using the criteria proposed by GOSS (1992). The method combines the parameters water solubility (S), partition coefficient (Koc) and soil half-life (T50) (Table 4).

 Table 4

 Criteria and baseline parameters of the GOSS method for surface waters

Sediment-associated transport potential						
	DT50solo(d)	KOC (mL.g-1)	S(mg. L-1)			
High potential	≥ 40 ≥ 40	≥ 1000 ≥ 500	- ≤ 0,5			
Low potential	< 1 ≤2 ≤4 ≤ 40 ≤ 40	- ≤ 500 ≤ 900 ≤ 500 ≤ 900	- - ≥ 0,5 ≥ 0,5 ≥2			
Transp	oort potential dissolved	l in water				
	DT50solo(d) KOC (mL.g-1) S(mg. L-1					
High potential	> 35 < 35	< 100,000 ≤ 700	≥1 ≥ 10 and ≤ 100			
Low potential	- ≤1 < 35	≥ 100.000 ≥ 1000	- - < 0.5			

T50: half-life; KOC: coefficient of adsorption to organic matter; S: solubility in water.

Source: Milhome et al. (2009)

It is noteworthy that the evaluation of contaminant transport by the GOSS criterion presupposes two diffusion mechanisms: 1) via sediment, i.e., the movement of contaminants in the soil is associated with the amount of soil grains that have been leached by runoff water; 2) solubilized in water, that is, compounds that have high values of solubility in water.

Table 5 lists the factors that interfere with soil contamination by pesticides.



Table 5Properties of pesticides in the soil and physical constants that quantify them

PROPERTIES	FEATURES	CONSTANTTHAT QUANTIFIES PROPERTY
Volatility	The volatility of pesticides in the soil is very variable, as is their tendency to lose to the atmosphere. In some cases, the pesticide is selected for its very high vapor pressure that allows it to penetrate the pores of the soil, to reach the organisms.	Henry's law constant (KH) and vapor pressure (PV) are parameters related to the volatility of the compound. The first indicates the distribution of the species between the liquid phase and the gaseous phase, depending on the temperature. The second defines the equilibrium concentration rate between water and air.
Adsorption	The tendency to be adsorbed by soils is largely determined by the characteristics of the pesticide itself as well as that of the soil that is added. The presence of certain functional groups with -OH, -NHR, -CONH2, -COOR and -NR, in the molecular structure of the chemicals, stimulates adsorption.	Parameters such as soil organic matter adsorption coefficient (Koc) and half-life (T50) are rarely mentioned in the literature because they are dependent on environmental factors, such as soil type, climate, among others. The Koc value indicates the potential for pesticide mobility in the soil. Koc< 50 (high mobility pesticides); 150 <koc<500 (barceló;="" (low="" (moderately="" 1997).<="" 2,000="" above="" and="" ground)="" hennion,="" mobile)="" mobility="" on="" th="" the=""></koc<500>
Leaching	The tendency of pesticides to leaching into the soil is directly related to their adsorption potential. The movement of water may favor leaching, which is carried out more quickly in sandy soil with a reduced amount of clay and organic matter;	The result expressed through a mathematical relationship called the GUS model (Groudwater Ubiquity Score) in which it points to the time/speed with which the substance reaches groundwater: GUS < 1.8 (Does not leaching); 1.8 < GUS < 2.8 (Transition Range); GUS > 2.8 (probable leaching).
Microbial metabolism	The biochemical degradation exerted by organisms is perhaps the single most important method of removing pesticides from the soil, since the presence of certain polarized groups in the molecules of pesticides provides points of attack to the organism, such as -OH, -NHR, -CONH2, -COOR and -NR;	
Persistence in soils	The persistence of pesticides in soils is the sum of all reactions, movements and degradations that influence them, in general organochlorines are the ones with the longest persistence time compared to other organosynthetic pesticides.	Half-life in soil (T50) reveals the stability of the compound under certain conditions.
Water solubility	High solubility in water indicates tendency of the compost to be removed from the soil. Therefore, compounds that have high solubility values are more likely to be carried by rain or irrigation water and reach water bodies.	It is understood as the measure of how readily the substance will dissolve in water and is expressed (mg/L). It is the maximum amount of pesticide that will be dissolved in 1L of water. Domingues (2010) used the following standard as an evaluative parameter for contamination prediction: when >3mg. L-1 there is a possibility of contaminating the water table.

Source: Andréa (2000); Bollag (1990), Musumeci (1992) and Roberts (1998).



Milhome et al. (2009) evaluated GUS indices for some pesticides in the Baixo Jaguaribe region, being considered to have high potential for contamination for groundwater, atrazine, imidacloprid, metolachloror, nicosulfuram, thiamethoxan, azoxystrobin, 2,4 D, methamidophos, propiconazole and triazophos. In the same work, he evaluated the risk of contamination of surface waters through the GOSS method, with the compounds chlorpyrifos, difenoconazole, paraquat and propiconazole, considered to have high contaminating potential, and can be transported dissolved in water or associated with sediment. Cypermethrin, endosulfan and esfenvarelato also presented a high risk of surface water contamination by sediment-associated transport and the pesticides atrazine, azoxystrobin, fenitrothion, imidacloprid, lambdacyhalothrin, metolachlor, methyl parathion, thiamethoxan and triazophos, by transport dissolved in water. The work demonstrated that the identification of the contaminating potential of pesticides applied in the Baixo Jaguaribe region through the use of the models, served as a subsidy to the environmental agencies during the execution of water resources monitoring programs, which can later be associated with data on water quality in the region.

Another study conducted by Ferracini et al. (2001) analyzed the potential for contamination of groundwater and surface waters of the Lower São Francisco River by pesticides applied to mango and grape crops, using criteria from the Environmental Protection Agency, the GUS index and criteria proposed by GOSS. All the criteria used took into account the properties of the products applied, not requiring high costs or much time for gathering information and evaluating the potential for contamination. The results obtained reinforce the importance of providing information on the physicochemical properties of pesticides, especially the adsorption coefficient, whose value allows the prediction of the mobility of the compost in the soil. This factor, integrated with the knowledge of the degradation time of the product up to half of its initial concentration (half-life) in the soil, provides information about its influence on the potential for water contamination. The results of this work provide knowledge of pesticides with the greatest potential for contamination of water resources, which should be prioritized in environmental monitoring "in loco".

Rosa et al. (2006) evaluated the leaching potentials of some agrochemicals towards groundwater in the Alto Vale do Itajaí region and concluded that:



- in the Alto Vale do Itajaí region, about 39 active ingredients of herbicides, 33 of insecticides and 32 of fungicides are used in the crops of corn, onions, tobacco, rice, beans and pasture. In onion crops, about 50 active ingredients of agrochemicals are used;
- the GUS index showed results in the classification of the leaching potential towards groundwater of the active ingredients;
- about 43% of the herbicides are classified as having leachate potential (GUS ≥ 2.8) and about 37% have zero potential (GUS ≤ 1.8). A smaller percentage of active ingredients of insecticides and fungicides are classified as having leaching potential by the GUS index. There are 14.29% of insecticides and 11.43% of fungicides with leaching potential.

3.2.5 The Diffusion of Pesticides

Pesticides are directly propagated in the environment through the various processes of mobility of their molecules in the environment, as well as the various processes that contribute to their degradation in the environment (Table 6).

Table 6Dynamics/fate of pesticides in the environment

Process	Consequence	Factors		
Transfer (process that relocates the molecule without changing its structure)				
Physical drift	Movement by the action of the wind	Wind speed, droplet size		
Volatilization	Evaporation loss of soil, plant or aquatic ecosystem	Steam pressure, wind speed, temperature		
Adsorption	Removal by interaction with plants, soil and sediment	Mineral content and organic matter, type of mineral, moisture		
Absorption	Root absorption or animal ingestion	Cell membrane transport, contact time, susceptibility		
Process	Consequence	Factors		
Transfer (process that	relocates the molecule without	changing its structure)		
Leaching	Lateral and vertical translocation through the ground	Water content, macropores, soil texture, mineral content and organic matter content		
Erosion	Movement by the action of water or wind	Rainfall, wind speed, particle size of mineral and organic matter with adsorbed molecules		
Degradation	(process that alters the chemic	al structure)		
Photochemistry	Breakdown of the molecule due to absorption of sunlight	Chemical structure, intensity and duration of sunlight, exposure		



Microbial	Microbial degradation	Environmental factors (pH, humidity, temperature), nutrient conditions, organic matter content
Chemistry	Alteration by chemical processes such as hydrolysis and oxy-reduction reactions	High or low pH and environmental factors
Metabolism	Chemical transformation after absorption by plants and animals	Ability to be absorbed, metabolized, and interact with organisms

Source: Pierzynski; Sims; Vance (1994 apud RIBAS, 2009).

Regarding the leaching potential of pesticides, Andrade et al. (2011) estimated values for herbicides used in intensive agriculture areas in the Alto Paranaíba region (MG). The active ingredients with the greatest leaching potential and that should be considered in later stages of environmental risk assessment were taken as a basis, mainly due to mobility, in the following order: imazetapir>fomesafem>metribuzim>nicosulsulmon>atrazine>ametrine>chlorimuron-ethyl >bentazone, with estimates of leaching losses in the first 80 cm of soil of 38.7; 26,5; 1,86; 1,02; 0,797; 0,535; 0.056 and 0.035%, respectively.

In this work, special attention was given to the herbicides imazetapir and fomesafem, as their physicochemical characteristics are highly favorable to leaching under the conditions studied by the authors. The herbicides diuron, linurom, alachlor, trifluralin, fluazifop-p-butyl, paraquat, glyphosate, lactofem and oxyfluorfem showed very low mobility, showing no risk of contamination for the groundwater of the region studied.

Scorza Júnior et al. (2012) determined the sorption and degradation of the insecticide thiamethoxam in two agricultural soils in Mato Grosso do Sul (typical Dystrophic Red Latosol with a very clayey texture and a typical Dystrophic Red Latosol with medium texture in Mato Grosso do Sul), at two depths (0-30 and 50-70 cm), evaluating its leaching and dissipation in the field. The results obtained showed, in both soils and depths, the low affinity of Thiamethoxam for the solid phase of the soils. The degradation of this insecticide also proved to be quite slow, in both soils and depths, with half-life values between 96 and 618 days. In the field, a rapid dissipation of thiamethoxam was observed soon after application. The leaching of thiamethoxam was restricted to 50 cm depth to both soils, indicating low potential for contamination for groundwater.

Another way of assessing the toxicity of pesticides in soils was conducted by



Botelho et al. (2011). In this work, it was investigated whether the type of soil influenced the toxicity of the insecticides aldicarb and fipronil, the herbicides diuron and clomazone+ametrine and the ripeners ethyl-trinexapac and sulfotenturon-methyl, used cultivation of sugarcane, in the fungi Metarhiziumanisopliaee Beauveriabassiana. These were inoculated in clayey and sandy soil, before and after the addition of the products. Aldicarb reduced the population of these fungi in both soil types, with less toxic effect on clay soil, while fipronil had little effect on the survival of B. bassiana in both soil types. Diuron showed less toxic effect for B. bassiana, and, conversely, greater toxic effect for *M. anisopliaenosoil sandy. Clomazone+ametrine*, ethyl-trinexapac and sulfometuron-methyl reduced the survival of fungi in both soil types, with less toxic effect on clay soil. The authors concluded that the pesticides studied and used in sugarcane cultivation were toxic to *M. anisopliaee B. bassiana*, both in clayey and sandy soils. The effect was smaller in the clayey soil and greater when the addition of pesticides to the soil occurred just before or after the inoculation of the fungi.

Marion et al. (2012) evaluated the soil toxicity condition in different vegetable crops in the municipality of Santa Cruz do Sul, comparing the conventional system with the ecological-based system, through ecotoxicological tests using Eiseniafetide (Annelideo) as a test organism. Soils of conventional and ecological properties were sampled, in areas suspected of contamination, at a depth of 0 to 10 cm. The organism was exposed to the samples to determine its mortality after 7 and 14 days. Samples collected from the ecological properties showed no toxicity. However, of the samples collected from conventional farms, two showed toxicity, with 100% and 20% mortality, respectively. In the first collection, mortality was probably caused by the synergy of pesticides used in the lettuce crop, especially Mancozeb, metalaxyl-M, Iprodione and deltamethrin. In the second collection, mortality occurred, which was attributed to the use of abamectin, emphasizing that, as well as the mortality of organisms, the surviving individuals had low mobility and morphological alterations. The results showed that the use of pesticides in conventional quantities causes soil contamination, reducing its environmental quality. The absence of mortality of organisms in samples of ecological properties revealed that this system does not cause toxicity to the test organisms, being recommended as environmentally correct for this agricultural activity



3.2.5.1 The diffusion in humans and the toxicity of pesticides

In the words of Carvalho and Pivoto (2011), the contamination of pesticides in humans is the result of the diffusion of these substances on three fronts: environmental, occupational and food.

According to Ribas (2009), the effects on health can be of two types: **1**) Acute, or those that result from exposure to concentrations of one or more toxic agents. They are capable of causing apparent effective damage in a 24-hour period; **2**) Chronic, or those that result from continued exposure to relatively low doses of one or more products.

Table 7 presents a summary of the main acute and chronic effects caused by exposure to the main pesticides available according to the pest they control and the chemical group to which they belong.

 Table 6

 Effects of exposure to pesticides

Classification	Chemical group	Acute intoxication	Chronic poisoning
	Organophosphates and carbamates	-Weakness - Abdominal cramps -Vomiting - Muscle spasms -Seizures	Delayed neurotoxic effects Chromosomal alterations Contact dermatitis
INSECTICIDES	Organochlorines	-Nausea -Vomiting - Involuntary muscle contractions	Liver damageCardiac arrhythmiasKidney injuriesPeripheral neuropathies
	Synthetic Pyrethoids	Irritations of the conjunctivaeSneezingExcitementSeizures	-Allergies - Bronchial asthma - Irritations on the mucous membranes -Hypersensitivity
	Dithiocarbamates	-Dizziness -Vomiting - Muscle tremors - Headache	Respiratory allergiesDermatitisParkinson's diseaseCancers
FUNGICIDES	Phenthalamides		- Teratogenesis
	Dinitrophenols and pentachlorophenol	- Difficulty breathing -Hyperthermia -Seizures	- Cancers (PCP formation of dioxins) - Chloroacnes
HERBICIDES	Phenoxyacetics	- Loss of appetite -Seasickness -Vomiting - Muscle fasciculation	Induction of liver enzyme productionCancersTeratogenesis
	Dipyrydils	-Nosebleed -Weakness -Fainting	- Liver damage - Contact dermatitis - Pulmonary fibrosis

Source: WHO (1990); OPS/WHO, (1996).



The toxicity of pesticides can be measured through physicochemical, toxicological and ecotoxicological studies. Based on these parameters, pesticides can be categorized in terms of environmental hazard into four categories, namely: products that are highly hazardous to the environment (Class I), products that are very dangerous to the environment (Class II), products that are dangerous to the environment (Class III) and products that are not very dangerous to the environment (Class IV). This classification consists of "in vitro" laboratory tests in which there is exposure of a population of animals, in which an attempt is made to establish a lethal dosage (LD) of the pesticide in 50% of the animals studied (WHO, 1990; OPS, 1997) (Table 8).

 Table 7

 Classification of pesticides according to effects on human health

Toxicological Class	Toxicity	DL50	Colored Stripe
I	Extremely toxic	≤ 5 mg/kg	Red
II	Highly toxic	between 5 and 50 mg/kg	Yellow
III	Moderately toxic	between 50 and 500 mg/kg	Blue
IV	Low toxic	between 500 and 5000 mg/kg	Green
-	Very little toxic	Above 5000 mg/kg	-

Source: WHO (1990); OPS/WHO (1996).

Some examples of pesticide toxicity, in terms of toxicological classes, can be shown in Table 9.

 Table 8

 Examples of pesticides categorized on the toxicity scale

Trade name	Chemical Group	Toxicological Class	Band Color	Purpose
AFALON®	Urea	III- Medium	BLUE	Herbicide
TOP® BRIDE	Strabillurins	III- Medium	BLUE	Fungicide
DITHANE®	Alquelenobis	III- Medium	BLUE	Fungicide/Acaricide
PYRAT®	Pyrazole	III- Medium	BLUE	Acaricide
THIOBEL®	Bis(thiocarbamate)	III- Medium	BLUE	Fungicide/Insecticide
VERTIMEC	Avermectins	III- Medium	BLUE	Acaricide/Insecticide
CIPERTRIN®	Pyrethroid	II- High	YELLOW	Insecticide
FOLIDOL®	Organophosphate	II- High	YELLOW	Insecticide
FOLISUPER®	Organophosphate	II- High	YELLOW	Insecticide/Acaricide



Pyrethroid	II- High	YELLOW	Insecticide	
Glyphosate	II- High	YELLOW	Herbicide	
Organophosphate	II- High	YELLOW	Insecticide	
Pyrethroid	II- High	YELLOW	Insecticide	
Organophosphate	II- High	YELLOW	Insecticide	
Chlorocyclodiene	II- High	YELLOW	Acaricide/Insecticide	
Ariloxifen-	I-Extreme	RED	Herbicide	
Oxypropionic Acid	I-EXITCINE	NED	i leibicide	
Aryloxyalkanoic			Herbicide	
acid +	I Extromo	RED		
iridinocarboxylic	I-EXIIEME			
acid				
	Glyphosate Organophosphate Pyrethroid Organophosphate Chlorocyclodiene Ariloxifen- Oxypropionic Acid Aryloxyalkanoic acid + iridinocarboxylic	Glyphosate II- High Organophosphate II- High Pyrethroid II- High Organophosphate II- High Chlorocyclodiene II- High Ariloxifen- Oxypropionic Acid Aryloxyalkanoic acid + iridinocarboxylic	Glyphosate II- High YELLOW Organophosphate II- High YELLOW Pyrethroid II- High YELLOW Organophosphate II- High YELLOW Chlorocyclodiene II- High YELLOW Ariloxifen- Oxypropionic Acid Aryloxyalkanoic acid + iridinocarboxylic II- Extreme RED	

Source: Gonçalves (2008).

In Brazil, between 2001 and 2007, there were 19,794 cases of acute pesticide poisoning distributed in the Brazilian regions as follows: Southeast (9,699 cases), South (3,559), Northeast (2,981), Midwest (2,439) and North, with 1,116 cases (GONÇALVES, 2008).

3.3 GEOGRAPHIC INFORMATION SYSTEMS (GIS/GIS)

Geoprocessing and geotechnologies can be understood as a group of technologies for collecting, processing, analyzing, and making available information with geographic reference. Generally speaking, they are made up of hardware, software, and peopleware, which together constitute powerful tools for decision-making. Among the geotechnologies, the following can be highlighted: Geographic Information Systems, digital cartography, remote sensing, global positioning system and topography (ROSA, 2005).

The name Geographic Information Systems (GIS) is widely used and in many cases is confused with geoprocessing. Geoprocessing is the most comprehensive concept and represents any type of processing of georeferenced data, while a GIS/GIS processes graphical and non-graphical (alphanumeric) data with an emphasis on spatial analysis and surface modeling (BURROUGH, 1987).

Rosa and Brito (1996) suggest a way of dividing the categories of geoprocessing techniques in terms of interpretations of spatial information:

 Techniques for collecting spatial information (cartography, remote sensing, GPS, topography, alphanumeric data collection);

- Spatial information storage techniques (databases object-oriented, relational, hierarchical, etc.);
- Techniques for treatment and analysis of spatial information (data modeling, geostatistics, logical arithmetic, topological functions, networks, etc.);
- Techniques for the integrated use of spatial information, such as GIS –
 Geographic Information Systems, LIS Land Information Systems, AM/FM –
 Automated Mapping/Facilities Management, CADD Computer Aided Drafting
 and Design.

GIS/GIS can be understood as a set of computational tools composed of equipment and programs that, through techniques, integrate data, people and institutions, in order to make it possible to collect, store, process, analyze and offer georeferenced information produced through available applications, which aim at greater ease, security and agility in human activities related to monitoring, planning and decision-making related to geographic space (ROSA, 2005).

Rosa (2005) draws attention to the confusion when referring to GIS/GIS, specifically, to software and not to technology. The difficulty of communication between professionals who use the same nomenclature to refer to different concepts is noticeable. Thus, for a more complete understanding, it is necessary to explain the main components of a GIS, The other elements to be defined are: *hardware*, data, users, and analysis methodologies (Table 10).



Table 9

GIS/GIS Components

COMPONENT	CHARACTERISTIC
Software	Formed by a set of programs (managed by a certain operating system), whose basic purpose is to collect, store, process and analyze geographic data, taking advantage of the increase in speed, ease of use and security in the handling of this information, pointing to a multi, intra and interdisciplinary perspective of its use.
Hardware	Set of equipment necessary for the <i>software</i> to perform the functions described. It is the physical component of the system involving the computer and its peripherals, or auxiliary equipment. Briefly, it includes the computer and peripherals, such as printer, <i>plotter</i> , scanner, tablet, storage drives (floppy disk drives, hard disk, CD-Rom, DVD, magnetic tapes, and ZIP <i>Drivers</i>). Communication between computers can also be mentioned, being carried out through a network environment.
Data	Raw material that feeds the system, allowing the generation of information, which is nothing more than the meaning attributed to the data by a given user. The power of information is undoubtedly indisputable. However, what has revolutionized the traditional processes of using information is the way it can be quickly processed and used for different purposes by the way it is presented, that is, georeferenced or mapped.
	The data used in a GIS can come from several sources, generically classified as primary (direct survey in the field or products obtained by remote sensors) and secondary (maps and statistics), which are derived from primary sources.
Users	People who have common goals form an organization or work group. GIS by itself does not guarantee the efficiency or effectiveness of its application. As in any organization, new tools only become effective when you can properly integrate them into the entire work process. For this, it is not enough just to invest, but to train personnel, users and managers to maximize the potential use of a new technology.
Methodologies or Analysis Techniques	They are directly linked to the knowledge and experience of the professional who, based on a defined objective, submits their data to a specific treatment in order to obtain the desired results. This aspect shows that the quality of the results of a GIS is not only linked to its sophistication and processing capacity. Much more than that, it is proportional to the user experience.

Source: Rosa (2005).

These components relate hierarchically in levels, being the level closest to the user, the human-machine interface is what determines how the system is operated and controlled. In the intermediate there are spatial data processing mechanisms (input, editing, analysis, visualization and output); and at the innermost level there is a geographic database management system that controls the storage and retrieval of spatial data (MORELLI, 2004).

GIS can be applied in several areas such as: regional and urban planning, spatial analysis, biology, planning of works (buildings), protection of the environment and nature, address management, statistics, land use, hydrology, climatology, meteorology, transportation, irrigation, mining, geology, medicine, forest and natural resource management, among others (MACHADO, 2002; IAP, 1994).

Montamoros (2005) demonstrated that the construction of a GIS/GIS helped the work of farmers in Ecuador in banana production. After understanding the slope of the soil, the absorption capacity of certain types of pesticides and their potential risk of leaching, it was possible to relate the parameters of contaminated areas in regions close to rivers.

Another example was demonstrated by Eklo (2009), in which he mapped potato farms in Norway, and through spatial analysis of the soil combining topography of the relief, soil type and presence of cracks on the surface, he built a GIS/GIS system, which revealed the potential risk of leaching and surface runoff of pesticides used in the region. The study collaborated in the change of agricultural practices.

Lee and colab. (2008), in a study carried out on agricultural farms in South Texas/USA after the construction of a GIS/GIS, it was possible to demonstrate that the intense use of some types of pesticides in irrigated regions would lead to a high potential for contamination of surface and groundwater, also alerting the danger to which the local population was subjected, since these waters were part of the supply system of the cities for human consumption.

Kamińska (2004), in a review article, corroborates the advantages of using GIS/GIS as an important tool for environmental monitoring, suggesting that its main advantages in pesticide research could be summarized as:

- Help create necessary data on the environment, vegetation cover, ways in which pesticides enter the biota (i.e. aquifer depth, soil texture and type, etc.);
- Allow recording changes in time with respect to spatial extent;
- Allow calculation of buffer zones and execution of spatial analysis, in order to define the exposure levels at desired points, lines, polygons (e.g., residence unit, water, stream, vegetable field);
- Facilitate the way to add new information to the databases (i.e. remote sensing information from different sources, transmitted by satellites and on-board platforms), and update current data.

4 MATERIAL AND METHODS

4.1 CHARACTERIZATION OF THE STUDY SITE

The municipality of Petrolina, 09°23'35"S and 40°30'27"W, is located in the Sertão do São Francisco, State of Pernambuco, bordering to the north by the municipality of Dormentes-PE, to the south by the State of Bahia, to the east by the



municipality of Lagoa Grande-PE, and to the west by the State of Bahia and the municipality of Afrânio-PE (Figure 6). At a distance of 722 km from the capital, Petrolina has an area of 4,756.8 km², and its main economic activity is agriculture, favored by the irrigated projects present in the region, with the cultivation of fruit trees for export, vegetables, corn and beans (SILVA, 2009).

CEARÁ PARAÍBA PIAUÍ RECIFE BAHIA PETROLINA LEGENDA ALAGOAS SEDE DO MUNICÍPIO LIMITE INTERMUNICIPAL CAPITAL DO ESTADO LIMITE INTERESTADUAL ESTADO DE PERNAMBUCO REGIÃO DE ESTUDO 0 20 40 120

Figure 6 Location of the municipality of Petrolina in the State of Pernambuco

Source: Author (2012).

According to Köeppen's classification, the climate of Petrolina is of the BSwh' type, which corresponds to a Semi-Arid Tropical region, with summer rains, from January to April. The average annual rainfall is 431.8 mm (CPRM, 2005).

The Municipality of Petrolina is located in the Sertão do São Francisco, State of Pernambuco, with an area of 4,756.8 km², and its main economic activity is agriculture, favored by the irrigated projects present in the region, with the cultivation of fruit trees for export, vegetables, corn and beans (SILVA, 2009).

The largest irrigated area in the Northeast is located in the São Francisco River basin, as it has the highest water availability in the Region. Despite the small percentage of irrigable area in the Northeast, irrigation is of great importance, as the hydrographic basins of the semi-arid region have a water deficit during almost the entire year. On the other hand, the semi-arid region has environmental conditions that represent comparative advantages for irrigated agriculture, which, if well exploited, can



be transformed into competitive advantages (EVANGELISTA, 1999).

According to the Brazilian Institute of Geography and Statistics (IBGE) (2012), through published data on municipal agricultural production (PAM), in 2010 the municipality of Petrolina recorded great diversity and quantity of agricultural production. It should be noted that in that year the following were produced: 1440 tons of tomatoes, 240 tons of corn, 480 tons of melon, 600 tons of watermelon, 5000 tons of cassava, 120 tons of castor beans, 270 tons of beans, 4000 tons of onions, 3600 tons of sugar cane, 1120 tons of sweet potatoes, 49 tons of rice, 141480 tons of grapes, 2380 tons of passion fruit, 160000 tons of mango, 2645 tons of papaya, 1190 tons of lemon, 71400 tons of guava, 13200 tons of coconut-of-the-bay and 49500 tons of banana. Such diversity suggests an intense use of pesticides, which allows us to infer the need for effective environmental monitoring associated with planned and rational agricultural practices.

The hydrographic basin, which has the largest irrigable area in the Northeast is the São Francisco basin, which is under the administration of the São Francisco Valley Development Company (CODEVASF), with a potential irrigable area in the public perimeters of 150.2 thousand ha. In this basin, the Middle São Francisco region stands out, with an irrigable area of 84.8 thousand ha (where the Jaíba Irrigation Project is located) and the sub-medium São Francisco region, with an irrigable area of 53.7 thousand ha, in which the Petrolina/Juazeiro irrigation pole is located (BANCO DO NORDESTE, 2012).

Also according to data from the Brazilian Geological Service (CPRM) (2005), the municipality of Petrolina is inserted in the domains of the São Francisco River Macro Basin, the Pontal River Basin and the Small Inland Rivers Basin Group. Its main tributaries are: the Jardim River and the streams: Baixa Salina, da Pedra Preta, Baixa do Procópio, Bom Jesus, Terra Nova, da Grota Grande, do Maçarico, Baixa do Coveiro, Baixa do Boi, Goela do Mocó, do Estandarte, da Porca, Baixa do Malaquias, Barreiro, Baixa do Morro Branco, Baixa das Panelinhas, Satisfied, do Caboclo, Barra da Cabeceira, do Dormente, São Bento, do Encantado, da Caieira, do Pontal, do Tanque Novo, do Tigre, Salina, Santa Fé, Sítio Novo, Baixa do Moronjongo, Baixa do Eugênio, Baixa do Gergelim, Baixa do Quarenta e Nove, do Barreiro, Baixa dos Velhos, Baixa da Vassoura, Baixa do Caldeirão, Baixa da Imburana Grande, do Corredor, Varginha, dos Cachorros, do Simão, Imburana, Cavalo Morto, Baraúna, Baixa do Santinho, Cruz, Baixa do Juá, Salina, Baixa do Serafim, Baixa do Socorro,

Baixa do Mulungu, Formosa, Areia, Viração, Espanto, Simão, Baixa da Marreca and Lagoa de Pedra.

The main collecting bodies, present in the municipality of Petrolina and, therefore, of accumulation are: the dams Baixa do Icó (1,300,000m3), Cacimba Velha (1,300,000m3), Cruz de Salina (4,021,375m3), Morros (1,860,000m3), Pau Ferro (2,068,937m3), Poço da Onça (1,200,000m3), Terra Nova (1,220,625m3), Vira Beiju (11,800,000m3), Barreira Alegria (2,880,000m3), Roça (741,700m3), Consolação, Comprida and Rajada (CPRM, 2005).

The lagoons present in Petrolina are: Marreca, Nova, Craíba, Junco, Areia, Pajeú, Capim, Tapera, Cabaças, Caldeirão, Espinho, Tabuleiro, Saco, Peixe, Cavalos, Veado, Boi, Curral Velho, Pau-Ferro, Muquém, Boa Vista, André, Arroz, Sovaco, Alagadiço, Redonda, da Formosa, Barro and Simão (CPRM, 2005).

All watercourses, except for the São Francisco River, have an intermittent flow regime and the drainage pattern is dendritic (CPRM, 2005).

The municipality of Petrolina is inserted in the geoenvironmental unit of the sertanejo depression, which represents the typical landscape of the semi-arid northeast, characterized by a very monotonous planation surface, predominantly smooth-undulating relief, cut by narrow valleys, with dissected slopes. Residual elevations, ridges and/or hillocks punctuate the horizon line. These isolated reliefs bear witness to the intense cycles of erosion that affected a large part of the northeastern hinterland (CPRM, 2005).

With respect to the soils of the region, in *the Long and Low Slopes* of the smooth undulating relief there are *Planosols*, poorly drained, medium natural fertility and salt problems; *Topos and High Slopes*, the non-Calcium Brunos *soils*, shallow and high natural fertility; *Tops and High Slopes* of the undulating relief occur the *Podzolic soils*, drained and medium natural fertility and the *Residual Elevations* with *the Litholic* soils, shallow, stony and medium natural fertility (CPRM, 2005).

The main pedological classes in the area are Latosols, Podzolic Soils (Ultisols, Alissolls, Luvisols and Plintosols), Vertisols, Cambisols, Quartzarentic Neosols (Quartz Sands). Among which, the soils Vertisols, Cambisols-Vertic, Shallow and Shallow Podzolics and Planosols stand out for their poor drainability (CPRM, 2005).

4.1.1 Study material

For this work, data were collected from the analysis of pesticide residues from



the main fruit matrices produced in Petrolina between the years 2009, 2010 and 2011, in a total of 107 samples, such as acerola, guava, mango, papaya and grape, analyzed by the Unit of Pesticides and Contaminants in Food and Alcoholic Products – LABTOX, located in Recife-PE, at the Pernambuco Institute of Technology. Labtox receives daily the most diverse fruit matrices produced by the Irrigated Fruit Growing Center of the São Francisco Valley for analysis of about 400 compounds (pesticides).

4.2 CONSTRUCTION OF INDICATORS FOR THE ANALYSIS OF ENVIRONMENTAL VULNERABILITY POTENTIALS

4.2.1 Hydraulic conductivity profiles of Petrolina soils

The hydraulic conductivity profiles of the soils in the region of Petrolina were estimated from the combination of some information about the different soil classes and their soil type/infiltration capacity relationship, based on the information Gomes (1996a, b) and Barbalho (2010) (Table s11, 12). Such behavior will reflect the greater or lesser tendency of contamination of the water table.

Table 10Estimated hydraulic conductivity of the main Brazilian agricultural soils, considering the classes of 1st, 2nd and 3rd categorical levels, as a function of texture, structure, aggregate stability and soil depth

Solo Class	Dominant Texture	Dominant Structure	Aggregate Stability	Depth	Hydraulic Conductivity
Red, Eutrophic, Dystroferic, Aluminoferric, Eutrophic and Dystrophic Latosols	Clay	Sub- angular blocks	Stable	Profound	Discharge
	Sandy Clay	Granular	Not very stable	Profound	Average
	Sandy	Granular	Not very stable	Profound	Average
Red-yellow, acriferous, crico. Dystroferic, Dystrophic and Eutrophic	Clay	Sub- angular blocks	Stable	Profound	Discharge
	Sandy Clay	Granular	Not very stable	Profound	Medium/High
	Sandy	Granular	Unstable	Profound	Discharge
Latos soils Yellow Acriferric, ' crico, Dystroferic, Dystrophic and Eutrophic	Clay	Sub- angular blocks	Stable	Profound	Average
	Sandy Clay	Sub- angular blocks	Stable	Profound	Average



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	Sandy	Sub- angular blocks	Stable	Profound	Average
Dystropic and Eutropheric Red Nitosols	Clay	Angular blocks	Stable	Relatively Shallow	Discharge
Eutrophic, Dystrophic and Eutrophic Red Ultisols	Clay	Sub- angular blocks	Stable	Shallow	Average
	Sandy Clay	Sub- angular blocks	Stable	Shallow	Average
Red-yellow Ultisols Eutrophic, Dystrophic, Aluminum	Clay	Sub- angular blocks	Stable	Shallow	Average
	Sandy-clay	Sub- angular blocks	Stable	Shallow	Medium/Low
Dystrophic and Eutrophic Yellow Ultisols	Clay	Sub- angular blocks	Stable	Shallow	Medium/Low
	Sandy-clay	Sub- angular blocks	Stable	Shallow	Average

Source: Gomes et al. (1996a, b).

Table 11Hydraulic conductivity profiles of soils

Hydraulic Conductivity Profiles	Classes		
(Order of Magnitude in m/s)	or Soil Associations		
Very High - > 1O-3	Quartzarenic Neosols		
High - 10-3 to 10-5	Latosols		
Average – 10-6	Ultisols, Nitosols		
Low 10.7 to 10.9	Cambisols, Plintosols, Litholic		
Low – 10-7 to 10-8	Neosols, and Gleisols.		

Source: Barbalho (2010).

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