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Analytical Methods for Performing Pesticide Degradation Studies in Environmental Samples

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1. Introduction

Pesticides are groups of artificially synthesized substances, toxic and non-biodegradable in the environment, that persist after application and are subject to some chemical processes of degradation, hydrolysis, oxidation, and photolysis by the ecosystem (Ormad et al., 1997; Ariaz-Estevéz et al., 2008). According to Law 7802 of 11 July 1989, pesticides and similar substances are defined as those products and agents of physical, chemical or biological processes intended for use in the production, storage and processing of agricultural products, in pastures, in the protection of native or implanted forests and other ecosystems, and also in urban, aqueous and industrial environments, whose purpose is to change the composition of the flora or fauna, to preserve them from the harmful action of living organisms considered to be harmful (Mahalashmi et al., 2007). This group of substances can be classified according to the purpose for which they are intended, the mode or period of action, or the chemical function such as: insecticide (insects), fungicide (fungi), rodenticide (rodents), molluscicide (snails), defoliant (leaf harvesting), dissecting (foliage). They are extensively used as insecticides, herbicides and nematocides, and they are included in the classes of organochlorides, organophosphates, and pyrethroids. More than 500 different formulations of pesticides have been used in the environment, largely in agricultural activities, for many decades. Pesticides are widely studied as environmental contaminants because of their extensive use in the control of pests affecting agricultural crops, homes, and gardens. Because of their chemical characteristics, they represent a type of pollutant that shows variable persistence and biochemical and photochemical degradation (Bandala et al., 2007).

Some studies show that, less than 1% of the total quantity of pesticides used in agriculture reaches its target. The remainder contaminates soil and other environmental compartments, air, and surface and groundwater. The fact that they are not biodegradable, together with their continued use, makes them a significant problem and a critical issue, with potentially damaging and unforeseen consequences for the future (Kapustka et al., 1996; Bandala et al., 2002; Acero et al., 2008; Veiga et al., 2006). In 1995, US \$1.6 million in actual pesticides were sold in Brazil. That amount increased to \$2.5 million in 2007 (Andreu & Picó, 2004). The use of pesticides in the world has increased five fold in the last 30 years (Nawab et al., 2003).

According to the World Health Organization (WHO), approximately three million people are intoxicated each year as a result of the use of pesticides. In addition to the toxicity to humans, the presence of these products in the environment poses a risk to water quality and the ecosystem (Veiga et al., 2006). When applied to the soil, they can reach other levels as a result of mobility, sorption, volatilization, erosion, and leaching, thereby contaminating various environments (Andreu & Picó, 2004; Nawab et al., 2003), as is shown in Fig. (1).

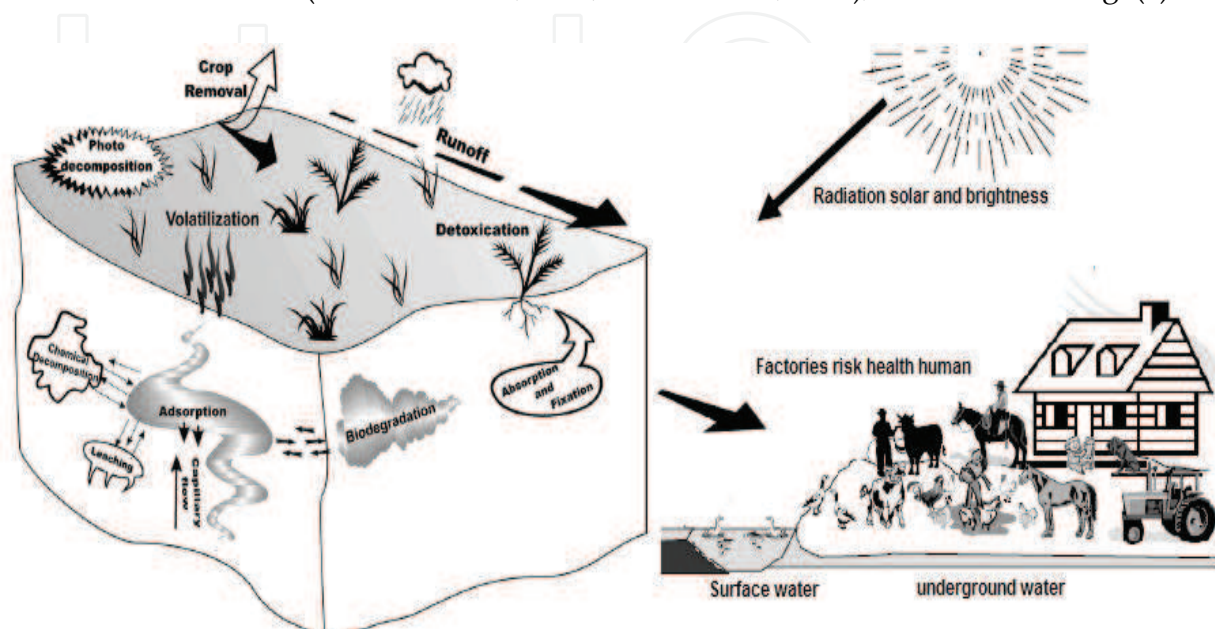


Fig. 1. Pesticide contaminants in the environment (Strandberg et al., 1998; Bavcon et al., 2002, adapted)

Other important aspects to be considered are the products of pesticide transformation (TP). There is great interest in studies on the formation of pesticide sub-products in the environment, since they can present a greater risk to the ecosystem than the original pesticides (Nawab et al., 2003; Sinclair & Boxall, 2003; Pozo et al., 2001; Sabik et al., 2000). On the other hand, some pesticide TP may present lower toxicity than the original substances from which they are formed (Borga et al., 1998). Thus, the results of pesticide use have not been completely elucidated because most studies are focused principally on the primary residues and not on their transformation products (Strandberg et al., 1998).

Some pesticides are considered to be persistent organic pollutants (POP) in the environment (Bavcon et al., 2002). These POP possess long half-lives and can accumulate in the environment and in organisms, being transferred throughout the food chain until they reach human beings (Kodaka et al., 2003). On the other hand, many pesticides can be degraded. The degradation processes generate a large number of sub-products in low concentrations that are considered to be beneficial for the systems for treatment and disinfection of crops, soils and groundwater, but hinder chemical analysis. Even in low concentrations, these residues can be prejudicial to human health and the environment because of the accumulative effect (Kapustka et al., 1996; Bandala et al., 2002). Pesticides are degradable by microbiological or chemical processes. Chemical degradation occurs by photolysis, oxidation and reduction reactions (Sassman et al., 2004), while biological degradation occurs through the action of environmental microorganisms (Nawab et al., 2003; Sassman et al., 2004; Ghardiri & Rose, 2001). The microorganisms are usually distributed in the first few

centimeters of the earth's surface, where the largest quantity of the organic compounds that serve as food, including the pesticides, exist (Navarro et al., 2004; Li et al., 2002; Monkiedje et al., 2003).

The extensive presence of pesticides in the water and soil has stimulated interest in finding solutions for the treatment and/or removal of residues from the environment. Many techniques, such as adsorption, filters, biological treatment, and degradation by advanced oxidative processes (AOP) that utilize TiO_2/UV as a catalyst, photo-Fenton reagents (FR) (Legrini et al., 1993), and ozonation processes with O_3 , O_3/UV , and $\text{O}_3/\text{H}_2\text{O}_2$ (Masten & Davies, 1994), are presently being studied for removal of pesticides.

Several analytical methods have been developed for the identification and quantification of pesticide residues and their by-products. Among the most widely used techniques are gas chromatography (GC) and liquid chromatography (LC), both in combination with mass spectrometer (MS) detector (Arnold et al., 1995). In conventional GC-MS methods for the determination of pesticides in environmental waters, solid phase extraction (SPE) and liquid-liquid extraction (LLE) are used for sample preparation. However, these methods require large volumes of organic solvents (Louter et al., 1996; Hyotylainen et al., 1998; Jongenotter et al., 1998). Therefore, several other extraction methods have been proposed, among them the technique of solid phase microextraction (SPME) (Louch et al., 1992; Zhang et al., 1994; Doong & Liao, 2001), which will be emphasized in this chapter. This review describes the current studies on degradation of pesticides and the aspects involved in the analysis of pesticides and their sub-products, sample preparation, methods of determination, and analytical techniques.

2. Environmental risk and the use of pesticides

Environmental pollution by pesticides depends on several variables, including the type and quantity of the products employed. The factors that influence the transport of these compounds to surface waters are their physical-chemical and biological properties and their capacity for degradation. These factors include solubility, vapor pressure, the partition coefficient of organic carbon with water (K_{oc}), and the octanol-water partition coefficient (K_{ow}). Compounds with a high solubility and low adsorption have resulted in major contamination of surface and groundwater. In addition, the pH and soil temperature, climatic conditions, landscape characteristics, including topography and drainage, and appropriate practices, also influence the pesticide content of water. Pesticides with a high solubility in water can easily contaminate surface and ground water. The increase of organic matter in the soil increases the capacity for adsorption of pesticides by reducing leaching. For example, cationic pesticides are strongly adsorbed by electrostatic interactions with negative charges in the soil surface. The weak bases with pK_a values close to the soil pH are strongly adsorbed. The acid pesticides are ionized, forming negative charges, and are not adsorbed by minerals in the soil because the negative charges cause repulsion in the interactions with soil organic matter (Jinno et al., 1996; Guo et al., 2000).

The process of pesticide degradation plays an important role in the removal of their residues from the aquatic environment to mitigate the problem of pollution. This process is governed by biotic and abiotic factors (including enzymatic catalysis by microorganisms) that can cause very complex reactions involving a variety of interactions of pesticides with microorganisms that are soil constituents. The adsorption also plays a key role in the dynamics of transmission, persistence, transformation, and bioaccumulation of pesticides

(Jonge et al., 1996; Gao et al., 1998). It depends on the characteristics of these compounds and the organic matter in the soil (Spark & Swift, 2002; Coquet, 2003; Ahmad et al., 2006). The pesticides that bind covalently to humic soil matter have functions similar to the components of humus, and the processes of interaction with organic matter are generally governed by oxidative reactions. Microorganisms have always been reported as mediators in both the interaction of pesticides with the soil and their degradation (Gevao & Semple, 2000; Dubus et al., 2001). The adsorption of weakly acid organic pesticides in the soil depends on the composition of the soil and its pH (Clause & Fabricius, 2002; Boivin et al., 2004; Wauchope et al., 2002), and may sometimes favor the leaching by surface and groundwater.

Some studies have shown major interactions between the adsorption and degradation of pesticides (Guo et al., 2000; Gevao et al. 2000), since the chemical adsorption reduces the access of microorganisms, thereby limiting the degradation and transport of these compounds (Selim et al., 1999; Koskinen et al., 2001; Moyer et al., 1972). In studies assessing the rates of microbial degradation of these substances, the authors concluded that, under certain conditions of temperature and pH, the pesticides may deteriorate even before being adsorbed by the soil (Park et al., 2003; Bolan et al., 1996; Dyson et al., 2002; Elliot et al., 2000; Roulier & Jarvis, 2003). In a study that involved the evaluation of the degradation of 2,4-D in ten types of natural soils, a high degree of adsorption was observed to be associated with high microbial activity (Bolan et al., 1996). The penetration of pesticides into the soil and groundwater can be realized by galleries and by infiltration (Worrall et al., 2007). Infiltration is more common and represents a potent source of environmental pollution of groundwater. Some of the properties that favor the environmental contamination by adapted pesticides are presented in Table 1 (Strandberg et al., 1998).

Parameter	Value
Water solubility	> 30mg/L
K _{oc} [*]	< 5, usually < 1
K _{ow} [*]	< 300
Speciation	Negatively, fully or partially charged at ambient pH
Hydrolysis half-life	> 25 weeks
Photolysis half-life	> 1 week
Field dissipation half-life	> 3 weeks

*K_{oc}= organic carbon content/ water partition coefficient

*K_{ow}= octanol-water partition coefficient

Table 1. Pesticide Properties Indicating their High Potential for Groundwater Contamination.

3. Degradation process

The degradation processes described in the literature demonstrate a great efficiency in the decontamination of systems contaminated by pesticides. Several factors influence the rate of degradation, such as the chemical structure of the pollutants, pH, iron concentration, hydrogen peroxide and the organic load. Because of the great potential of contamination by

pesticide residues and the variation in the time necessary for natural degradation, it is necessary to discover those processes that accelerate the decontamination of the affected environment. Thus, several degradation processes such as photocatalytic degradation, advanced oxidative processes, phytoremediation, bioremediation, ozonation and photo-Fenton reactions have been proposed. All these systems are considered to be efficient for pesticide degradation.

Microorganisms are considered to be the principal agents for the degradation of pesticides in bioremediation processes. Considering that the earth is the home for an uncountable number of microorganism species, the pesticides applied to these soils probably suffer an accelerated degradation by these organisms. Bhalero et al (Wyss et al., 2006), were able to remove the pesticide endosulfan from the environment. They isolated 16 microorganismos from the soil for this purpose. *Aspergillus* of the funghii kingdom totally removed endosulfan after incubating the mushroom for 12 days with the pesticide. The levels evaluated were between 35.0 and 350.0 mg.L⁻¹. The results demonstrated that *Aspergillus* is a potent and easily acquired bioremediating agent that could be used to remove other pollutants from water and even soils.

Wyss et al., 2006, isolated and characterized the bacterium *Pseudomonas sp* for the hydrolysis of atrazine. This microorganism used atrazine as a nitrogen, citrate and carbon source, and for the production of electron donor molecules under aerobic conditions. The degradation of approximately 100.0 mg.L⁻¹ of atrazine occurred. The *Pseudomonas sp* was first cultivated in flasks under aerobic conditions previous to the experiments. The authors observed that concentrations of atrazine above 100.0 mg.L⁻¹ were toxic to *Pseudomonas sp*. Giacomazzi & Cochet, 2004, studied the transformation of the herbicide diuron in water by microorganisms present in the soil. The reaction was catalyzed by OH⁻ and H⁺ with organic and inorganic matter from soil dissolved in the aqueous phase. The proposed system presented good results for the chemical degradation of diuron. The authors suggest that microorganisms could be used to promote the biological treatment of polluted sewage water.

Phytoremediation is a degradation process that uses plants to degrade or assimilate contaminants through natural processes. The success of this process is largely the result of the photosynthetic activity and growth rate of plants. Olette et al., 2008, investigated the potential of the phytoremediation process to remove pesticides in water bodies. The ability of three aquatic plants - *Lemnos minor*, *Elodea canadensis* and *Cabomba aquatico* to degrade pesticides by exposing the plants to five concentrations varying from 0 to 1.0 mg.L⁻¹. *L. minor* was observed to be the most efficient for the capture of pesticides, followed by *E. canadensis* and finally *C. aquatico*. The percentage removal of pesticides ranged from 2.5% to 50% during four days of incubation and reached 100% after seven days of incubation.

In another study, Bouldin et al., 2006, investigated the removal of atrazine and lambda-cyhalothrin from water and sediment by hydroponic plants. They used *Juncus effusus* and *Luwigia peploides*. In this study, 98% degradation in just 48 hours of exposure of the pesticide to plants was observed. The results obtained by Bouldin and Olleta demonstrate the potential of efficient phytoremediation processes for removal of pesticide residues from the environment. Xia & Xiangjuan, 2006, investigated the disappearance of the persistent pesticide ethion from water by the process of phytoremediation. They used the plant *Eichlornia crassips*, which was able to degrade 98% of the ethion. The authors concluded that this plant could be used as an efficient, economical, and ecological alternative to hasten the removal and degradation of ethion in groundwater, industrial waste and other systems,

together with other types of pesticides. Amaya-Chavez et al., 2006, studied the efficiency of removal of methyl parathion from water and sediments by the plant *Typhya latifolia*. This plant was able to reduce the content of pesticides in the concentration range of 0 to 200.0 mg.L⁻¹, reaching 100% degradation during 10 days of exposure. Thus, *Typhya latifolia* may be a good candidate for phytoremediation of systems contaminated with methyl parathion.

Photocatalytic oxidation is a very advanced process used to remove and degrade pesticide residues from various environments such as soil, water and food. In recent years, several studies and reviews on advanced oxidative processes (AOP) (Wu et al., 2007; Lasa et al., 2005; Carp et al., 2004), which use UV light. Titanium dioxide is used extensively in most of these studies. It is one of the most extensively used processes among those mentioned because it is a readily available reagent, chemically robust and durable (Legrini et al., 1993; Kabra et al., 2004; Leyva et al., 1998; Oh et al., 2004; Moctezuma et al., Chen & Ray, 1998; Canle-Lopez et al., 2005). Moctezuma et al., 2007, studied the photocatalytic degradation of methyl parathion pesticides, using TiO₂ in aqueous suspension. The final products were phosphoric acid and CO₂. Furthermore, Mahalakshmi et al., 2007 demonstrated that the combination of TiO₂ and ZnO₂ was very effective in the photocatalytic mineralization reactions of carbofuran in water samples under solar radiation. They also assessed the total quantity of organic carbon (TOC) to confirm the extent and effectiveness of the mineralization process used in this study. Four intermediate products of the carbofuran pesticide were formed after only six hours of reaction. Various pathways for degradation of this compound were proposed.

Shemer & Linden, 2006, studied the degradation and the degradation products of diazinon using photocatalyzed reactions with the application of UV light and UV/H₂O₂ catalyst. The addition of H₂O₂ was very effective in this process, increasing the rate of removal of diazinon from aqueous samples. Upon photolysis, the hydrogen peroxide leads to the formation of strongly oxidant species such as the hydroxyl radical, which accelerates the degradation process. Chiron et al., 2000, used AOP to remove diazinon from aquatic environments. Similar to other studies, the hydrogen peroxide was very effective and efficient in reducing the burden of diazinon in the environment.

Chiron et al., 1997, studied the degradation of endosulfan in water samples using photocatalyzed reactions with (FeCl₃/H₂O₂) and (TiO₂/H₂O₂). The degradation was studied with a concentration of 35.0 g.L⁻¹, and the results showed that both catalysts were effective for the removal of pesticides and can be applied to other situations and environmental compartments. Arbeli & Fuentes, 2007, investigated the process of complete mineralization in the accelerated degradation of methyl parathion, parathion, diazinon and cypermethrin pesticides using ozonation reactions. The complete mineralization was assessed by intermediate products and the formation of CO₂. Ozonation has become a safe and promising process for the removal of pesticides from water samples, plant surfaces, and domestic waste.

3.1 Kinetic study of degradation

The time necessary for degradation of pesticides is important to assess whether pollutants are persistent in the environment. The disappearance of these compounds is related to several factors such as pH, temperature, light, oxygen, and quantity of organic matter, which alter the kinetics of degradation. The kinetic studies to assess degradation of organic pollutants can be performed and assessed by the rate of mineralization (Dyson et al., 2002). The rate of mineralization is determined by monitoring of inorganic compounds such as CO₂, Cl⁻, SO₄²⁻, NO₃⁻ and PO₄³⁻. The most common method of analysis to assess

mineralization is the determination of total organic carbon (TOC). It is a rapid measurement of high reliability and sensitivity to the level of $\mu\text{g.L}^{-1}$.

Several authors have dedicated themselves to the study of the degradation kinetics to evaluate the persistence of the pesticides in the environment. Penuela & Barcelo, 1998, described the use of TOC to monitor the products of catalytic degradation of triazophos with TiO_2 catalyst. The results showed that the triazophos absorbs light in the presence of TiO_2 and is degraded in 4.5 hours. The rate of carbon dioxide formation is an indication of the disappearance of the pesticide. Prevot & Pramauro, 1999, also observed the complete disappearance of 2,3,6-trichlorobenzoic acid after 60 minutes of irradiation in the presence of TiO_2 . The degradation of this substance increased considerably at $\text{pH} = 3$, while the rates were lower at other pH values. Blanco et al., 1996, studied the degradation kinetics of pesticides in water samples by ultraviolet light. They observed that the degradation became effective after irradiation for a period longer than five hours. In another study, Konstantinou et al., 2001, investigated the photochemical degradation of herbicides (atrazine, prometryn and propazine) in different types of natural waters (river, sea and lake) and soils. The monitoring showed that the compounds exhibited degradation kinetics with very different periods of irradiation, being greater than 10 hours for the three types of matrices. Hermam et al., 1999, investigated the degradation kinetics of methyl pirimiphos in water with different photocatalytic irradiation times. The results showed that over 98% of the pesticide disappeared after 10 minutes of irradiation with 1.5×10^{17} photons per second. Complete (100%) degradation of the pesticide occurred upon irradiation with 1.4×10^{16} photons per second over a longer period (30 minutes). Shankar et al., 2004, studied the influence of pH on the degradation kinetics of pesticides in aqueous solutions. The results indicated that the degradation was rapid in solutions at pH between 2 and 7, reaching 100% degradation. At pH's above 7, the degradation rates were below 60%. A similar study was conducted by Kuo, 2002, who investigated the kinetics of degradation of the carbofuran pesticide between pH 4 and 7, using TiO_2 as the catalyst. The results showed that the degradation was slow at pH's above 7. Uygun, 1997, studied the rate of degradation of pesticides in stored carrots. The studies were performed under sunlight and ultraviolet light of 280-300 nm. The degradation of pesticides occurred after 3 to 5 hours of solar irradiation, while the degradation by UV radiation required 10 hours. Rafqah et al., 2005, investigated the rate of degradation of sulfuron methyl by a photocatalytic process in the presence of two different titanium dioxides, Degussa P_{25} and Millennium PC_{500} . The times necessary for the disappearance of the pesticide in the presence of Degussa P_{25} and Millennium PC_{500} were 20 and 80 minutes, respectively, the efficiency of TiO_2 (P_{25}) being the greater. Wang & Lemley, 2001, studied the rate of degradation of the pesticide 2,4-D in natural waters by treatment with Fenton, combined with the photocatalytic degradation of pesticides with TiO_2 . Rapid degradation by the Fenton reaction occurred in the presence of hydrogen peroxide; otherwise, the process was very slow.

4. Environmental analysis of the pesticides and the sub-products

The intensive use of pesticides and the consequent contamination of surface water, soil, flora, fauna and groundwater by their residues, including the products and degradation sub-products, require the use of reliable, sensitive methods for the analysis of contamination by these pesticides. Several analytical methods were developed for identification and quantification of pesticides and their degradation products in the environment. Among the main analytical techniques used are high performance liquid chromatography (HPLC) and gas chromatography (GC), since they possess the selectivity, sensitivity and high capacity

necessary for identification and quantification of pesticides and their degradation by-products (Sabik et al., 2000; Wang & Lemley, 2005; Gennaro et al., 2001; Sasano et al., 2000; Pereira et al., 1990; Faria et al., 2007; Sandra et al., 1995; Carreteur et al., 1996).

4.1 Sample preparation

The methods for extraction of pesticides and clean-up of environmental samples are extremely important for their quantitative determination in the matrices of interest. The extraction techniques used to concentrate the analytes include liquid-liquid extraction (LLE), solid phase extraction (SPE) and solid phase microextraction (SPME). The SPME technique is promising and has the advantage of not using a solvent for extraction.

The LLE extraction is based on the partition of the sample between two immiscible phases (organic and aqueous) and was used in the analysis of pesticides in water and food samples. It was used for many years as an official technique of the U.S. Environmental Protection Agency (U.S. EPA) (Watts et al., 1989). It is a classical technique based on repeated extraction of 1.0 or 0.5 L of sample with organic solvents using a separatory funnel. Its main advantage is the ability to extract a wide range of compounds with a wide range of polarities.

Solid phase extraction (SPE) is a technique commonly used as a method for pretreatment of samples in trace analysis of micro-contaminants in aqueous samples. It was introduced in mid 1970 (Pichon, 1998), and it was marketed in 1978 as an alternative to LLE. The analytes contained in an aqueous matrix are extracted together with the interfering compounds after passage through a sorbent cartridge. A selective organic solvent is commonly used to extract the analytes of interest. The selection of the SPE method depends on the physico-chemical properties of the pesticides and their concentrations, so as to process the ideal volume of solvent (Thurman et al., 1990). Sasan et al., 2000, determined the pesticides and herbicides in aqueous samples using SPE. The efficiency of the extraction method for the identification of 30 compounds was demonstrated. Using the same extraction method, Carreteur et al., 1996, analyzed pesticides in samples of sea water using SPE. The technique was very efficient for the extraction of analytes at ng.L^{-1} concentrations, allowing rapid preparation of the sample at the local of collection with good performance. Other studies have focused on the triazines and their degradation products extracted by this technique (Pichon et al., 1994; Dugay et al., 1998). Penuela et al., 1996, performed the analysis of endosulfan in water samples using SPE with C18 cartridges, which permitted the study of its isomers at low concentrations. In another study, Penuela et al., 1998, used SPE to monitor the kinetics of degradation of Alachlor in water. The method was efficient for the extraction of pesticides, including for various degradation products. The pre-concentration with SPE in studies of photodegradation is a good technology, making it possible to measure the organic pollutants and identify the degradation products in low concentrations. Faria et al., 2007, proposed a new method for extraction of pesticides. To do so, they associated the SPE with a polymer supported on silica. The new system presented a high potential for extraction at gL^{-1} concentrations. However, alternative methods reduce or eliminate the use of solvents in the preparation of samples for chromatographic analysis (Chiron et al., 2000), this being one of the limitations of this technique compared to more traditional methods.

Sabik et al., 2000, used SPE and SPME to analyze triazines in water samples. They discussed the advantage of SPME over SPE, since it dispenses the use of solvent. However, a large number of pesticides, including triazines and their degradation products, are easily determined and monitored efficiently at trace concentrations (ng.L^{-1}) in water samples with SPE.

Chiron et al., 2000, highlighted SPME, a widely used extraction method, because it does not require the use of solvents and is simple, fast and efficient. Jinno et al., 1996, analyzed residues of some pesticides in plant samples using SPME with a PDMS fiber. The results showed that it is a technique capable of extracting traces of pesticides from aqueous solutions and from the surface of plants under domestic conditions. Sabik et al., 2000, measured pesticides in surface water and groundwater using SPME as the extraction method; Polydimethylsiloxane/Divinylbenzene (PDMS/DVB), Carbowax/Divinylbenzene (CW/DVB) and Polyacrylate (PA) fibers were tested. The CW-DVB fiber in saline solutions was more efficient for atrazine and its degradation products and was suitable for extraction of more polar compounds.

There exists a discussion about the difficulty of quantitative analysis using SPME, conversely, the studies shown below presented good results for quantitative determinations using SPME. Miege & Dugay, 1998, analyzed pesticides in aqueous samples using SPME. The most adequate fiber was PDMS (100 μm), which was able to extract organochlorine pesticides of low solubility and some organophosphates. The PA fiber was shown to be ideal for the extraction of pesticides containing nitrogen and phosphorus. The data indicated that the measurable limits were from 5.0 to 100.0 ng.L^{-1} . Navalon et al., 2002, developed a method for determination of the herbicide oxidiazon in water, soil, wine and human urine samples, using the Headspace and PDMS fiber. The best responses were obtained by extraction for 25 minutes at a temperature of 100 °C.

Carvalho et al., 2008, determined organochlorine pesticides in sediments and studied their strong interaction with organic matter using SPME in headspace mode (HS-SPME) with a PDMS fiber. The method presented detection limits of 0.005 to 0.11 ng.g^{-1} of sediment and a good linearity in the 6.0- to 1000.0- ng.g^{-1} range. Xiang et al., 2008, investigated SPME using a new polythiophene (PTH) fiber to determine organochlorine pesticides in water. The results proved the ability of the new fiber to extract these compounds from aqueous samples. The detection limit was 0.5 to 10.0 ng.L^{-1} , and the calibration curve was linear in the appropriate range, 10.0 to 100.0 ng.L^{-1} ($R^2 > 0.982$). The method had the advantage that the fiber is robust, with durability greater than that of the PDMS fiber used by Carvalho et al, 2008.

Gupta et al., 2008, proposed an improved SPME method using a Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS) fiber with a PTFE tube for the analysis of organophosphate pesticides. The proposed combination presented good linearity in the range from 0.03 to 150.0 $\mu\text{g.L}^{-1}$, with 78% recovery and detection limits between 6.1 to 21.8 ng.L^{-1} . The method is efficient, but requires a longer time to process the samples than the conventional SPME method. Seeking innovation, Djozan & Ebrahimi, 2008, covered the fiber with methacrylic acid and ethylene glycol by means of copolymerization for the analysis of atrazine and triazines in water by SPME. The new fiber was highly efficient, even for the analysis of rice and garlic. Similarly, Zeng et al., 2008, used ceramic material and carbon of high thermal stability as a support for SPME fibers for the analysis of organophosphorus pesticides in water samples. The method presented an LOD of 5.2 to 34.6 ng.L^{-1} and a good linearity between 0.05 to 200.0 ng.mL^{-1} .

Silva & Cardeal, 1999, developed a method for the determination of organophosphorus pesticides in water samples using SPME. A good linearity of the method was obtained in the 0.20 to 20.0 ng.L^{-1} range, with correlation coefficients above 0.999. The accuracy of the method was 5.7 to 10.2% for all the pesticides evaluated, resulting in lower limits of detection, from 0.008 to 0.020 ng.L^{-1} . Capobianco & Cardeal, 2005, proposed a method for the analysis of organophosphorus pesticides (co-ral, DDVP, Di-syston, phorate, phosdrin and

malathion) in freshwater fish, water and food samples by applying the SPME technique. The correlation coefficients for the curve obtained were between 0.997 and 0.999, with a relative standard deviation of 4.40 to 15.13%. The detection limits ranged from 0.05 $\mu\text{g.L}^{-1}$ to 8.37 $\mu\text{g.L}^{-1}$, and the measurable limits were 0.09 $\mu\text{g.L}^{-1}$ to 8.70 $\mu\text{g.L}^{-1}$.

Among the techniques mentioned, SPME extraction preserves all the advantages of SPE, such as simplicity, low cost, and easy automation, and eliminates the disadvantages such as clogging of the cartridge and use of solvents. All the studies for the analysis of pesticides by SPME furnished good results. This fact indicates that this approach is recommended for the analysis of trace organic compounds in environmental samples. Other studies (Fernandez-Alvarez, 2008), have proposed changes in methods and alternatives for the analysis of other undesirable compounds in ecosystems.

Basher et al., 2007, compared the efficiency of extraction of organophosphorus pesticides from groundwater by SPME and by liquid-phase microextraction (LPME). The SPME method was more effective at higher concentrations (LOD between 3.1-120.5 ng.L^{-1}), while the LPME method was more effective at low concentrations (LOD between 0.3-11.4 ng.L^{-1}). Lambropoulou & Albanis, 2005, successfully developed a LPME method to determine traces of some insecticides (dichlorvos, mevinphos, ethoprophos, carbofuran, chlorpyrifos methyl, phenthoate, methidathion and carbofenothion) in water samples. Their method exhibited good linearity. The detection limits were in the 0.001 to 0.072- $\mu\text{g.L}^{-1}$ range with relative recoveries from 80 to 104%. In another work, also using LPME, Xiong & Hun, 2008, analyzed organosulfur pesticides (malathion, chlorpyrifos, buprofezin, triazophos, carbofuran and pyridaben) in environmental samples of water. The method presented good linearity (0.80 to 850 $\mu\text{g.L}^{-1}$) and a correlation coefficient of 0.9901 to 0.9988, with limits of detection of 0.21 to 3.05 $\mu\text{g.L}^{-1}$. Thus, LPME is a promising technique for environmental analysis at trace levels.

4.2 Analytical techniques

The analytical techniques for the determination of the pesticides in environmental samples request appropriate sensibility and precision. Gas chromatography coupled to mass spectrometry is among the most frequently used tools. This analytical tool has promoted the quantification of pesticides and their sub-products in the ppt level.

Gennaro et al., 2001, investigated the process of degradation of the pesticide carbofuran using photocatalyzed reactions. The progress of the degradation of the pesticide was monitored using the techniques of HPLC and GC, both being coupled to mass spectrometer (MS) detectors. The intermediate products from carbofuran could only be identified by the GC/MS method because it presented greater selectivity, specificity, and capacity for identification.

Sasano et al., 2000, proposed the analysis of pesticides in water samples using the GC/MS technique. The authors used an automated system that consisted of pneumatic valves that introduced the sample directly into the sample injector chamber, with rapid evaporation of the solvent. They determined 29 pesticides and herbicides. The system achieved a recovery of over 75% and a relative standard deviation ($n = 6$) of 10%. Sabik et al., 2000, described the determination of herbicides of triazines group and their degradation products in water samples using the GC/MS, HPLC-UV and HPLC/MS techniques. The technique was relevant because it became possible to propose reaction pathways for the degradation of atrazine.

Nélieu et al., 2000, analyzed the atrazine degradation products by LC and HPLC using UV and MS detectors. The results indicated that mass spectrometry is a more efficient detector. Some

of the degradation products were not identified by HPLC/MS or HPLC/MS/MS. Sandra et al., 1995, investigated the degradation of the organophosphate methyl pirimiphos in water by artificial light. The analysis of the intermediate degradation products was achieved by GC/MS, HPLC-UV, HPLC/MS analysis and total organic carbon (TOC) techniques. The best results were obtained by GC/MS, and it was possible to identify all the degradation products of methyl pirimiphos. The formation of inorganic ions was verified through TOC. Prevot et al., 1999 and Ravelo-Perez et al., 2008, investigated the photocatalytic degradation of acid solutions of 2,3,6-trichlorobenzoic acid (2,3,6-TBA) in the presence of TiO_2 . Several aromatic intermediates were detected by GC/MS with HS-SPME extraction. These intermediates have indicated the occurrence of hydroxylation, dechlorination, decarboxylation and oxidation-reduction reactions. Pereira et al., 1990, identified a number of pesticides including atrazine, alachlor, and metoxichlor and their degradation products in surface water using gas chromatography and mass spectrometry with an ion trap analyzer. The method resulted in the determination of approximately 1.0 ng.L^{-1} , with detection limits of up to 60.0 pg.L^{-1} .

Faria et al., 2007, proposed a method of analysis for six pesticides (imazethapyr, imazaquin, metsulfuron-methyl, bentazone, chlorimuron-ethyl and tebuconazole), by GC and HPLC with mass spectrometer detectors. The method involved the immobilization of the pesticides on a silica support immersed in water. The proposed system presented a good potential for extraction and concentration of pesticides in aqueous samples. It had the advantage of being a low-cost extraction method.

Faria et al., 2007 and Sandra et al., 1995, developed a GC/MS method for the analysis of two metabolites of the herbicide chlorotriazine and 11 pesticides in water samples. The recovery index for all the analytes studied was 105-116% for concentrations in the range of $0.5 - 1.0 \text{ ng.mL}^{-1}$, with detection limits of 0.05 ng.mL^{-1} .

In another study, Charreter et al., 1996, determined pesticides in water samples using sequential GC/MS with Ion trap analyzers, in electron impact (EI) and chemical ionization (CI) modes. In this study, the detection limits for both types of ionization were 0.2 to 5.0 ng.L^{-1} . The selectivity increased significantly with the use of EI-MS/MS, compared to CI. Steen et al., 1997, analyzed triazines using the working conditions of Charreter. Magnuson et al., 2000, also determined the degradation products of triazines by GC/MS, but noted a problem of coelution of the two main products, deethylatrazine (DEA) and deisopropylatrazine (DIA). The strategy to avoid coelution was to combine the products with two different compounds, octadecyl and ammelide, so as to increase the polarity of the molecule.

Uygun, 1997, investigated the degradation of chlorvenvifós by GC/MS, HPLC/UV and gel permeation chromatography (GPC) techniques. The main degradation product in all the samples was trichloroacetophenone, and the GC/MS technique was the only one able to identify this compound. The results also indicated that the degradation of chlorvenvifós is significantly lower at temperatures below 5°C .

Penuela & Barcelo, 1998, studied the degradation of endosulfan in water samples using the GC/MS and GC/ECD techniques. The endosulfan sulfate was determined in only a few samples because the proposed method indicated that the degree of recovery was low (70-86%) and the limit of detection was high ($0.5-540.0 \text{ ng.L}^{-1}$) for the levels under study.

Penuela & Barcelo, 1996, studied the degradation of Alachlor in water samples by GC/ECD and GC/MS. Three products were identified (2-hydroxy-2,6'-diethyl-N-methylacetanilide, 8-ethyl-1-methoxymethyl-4-methyl-2-oxo-1,2,3,4-tetraquionoline and hydroxyalachlor). The pesticide was highly stable when exposed to irradiation by natural light during a period of

20 h. However, in the presence of 15.0 mg.L^{-1} of FeCl_3 catalyst, the method became very effective for the destruction of Alachlor.

Bandala et al., 2007, studied the degradation of aldrin, and its products were analyzed by GC/MS. Three degradation products were identified: dieldrin, chlordane and 12-hydroxydieldrin. In the presence of H_2O_2 , 93% degradation of aldrin was achieved.

A review of methods for the determination of pesticides and their degradation products in environmental samples using different types of detectors was performed. The methods most used in the analysis were GC with an electron capture detector (ECD), nitrogen and phosphorus detector (NPD) or mass spectrometer (MS) detector and the technique of liquid chromatography with UV and MS detectors. The best detector among the studies discussed was the mass spectrometer. A summary of some studies described in the literature regarding the pesticides examined, types of samples and techniques used are presented in Table 2.

Kouloumbos et al., 2003, investigated the products of photocatalytic degradation of diazinon in aqueous suspensions using GC/MS/MS and HPLC/MS/MS. The photocatalytic degradation of diazinon catalysed by titanium dioxide was observed to proceed essentially through a hydroxylation mechanism. The results show that the combination of GC/MS/MS with EI, positive and negative ion CI, and LC/MS/MS with electrospray ionization represent a powerful analytical approach for the confirmation of the structure of photocatalytic intermediates.

Kowal et al., 2009, developed an ultraperformant liquid chromatography-tandem spectrometry (UPLC/MS) method for the analysis of metabolites of the pesticide N,N-dimethylsulfamide (DMS) in aqueous matrices. More than 600 samples of drinking water, surface water, and groundwater have been examined successfully using this method. The method furnished a relative standard deviation of 15% ($n=10$) and a limit of detection of 10.0 ng.L^{-1} .

Hernández et al., 2008, investigated the metabolites of pesticides in food and water by liquid chromatography with time-of-flight mass spectrometry (HPLC/TOFMS). This technique has been successfully applied in multi-residue target analysis and has allowed the safe identification of metabolites in samples, as well as their quantification.

In other study, Jeannot & Sauvard, 1999, determined pesticides in water samples using HPLC/MS/MS-APCI in positive mode. The method showed good linearity from 0.05 to 10.0 ng.L^{-1} , correlation coefficients from 0.9993 to 1.0 and detection limits from 0.02 to $0.1 \text{ } \mu\text{g.L}^{-1}$. The study furnished the identification and quantification of pesticides and their conversion products in drinking water.

Comprehensive two-dimensional gas chromatography (GCxGC) is a relatively new technique, developed in the nineties, and has great power of separation for complex samples, such as multi-residue analyses of pesticides. Banerjee et al., 2008, optimized a method for multi-residue analysis of pesticides in grapes using comprehensive GCxGC/TOFMS and GC/TOFMS. The method resolved the co-elution problems observed in full scan, one-dimensional analysis and promoted chromatographic separation of 51 pesticides within a 24-min run time with mass-spectrometric confirmation. The detection limits for GC/TOFMS were 2.0 to 19.0 ng.g^{-1} and detection limits for GCxGC/TOFMS were 0.2 to 3.0 ng.g^{-1} . Multiresidue analysis by GCxGC/TOFMS presented distinct advantages over the GC/TOFMS analysis. The technique shows promise and good separation of all co-eluted as well as closely eluted compounds with high sensitivity in the analysis of the pesticides studied.

Khummueng et al., 2006, determined residues of nine fungicides in vegetable samples using GCxGC/NPD. The concentrations ranged from 1.0 to 1000.0 $\mu\text{g.L}^{-1}$. Excellent linearity was observed for these standards in the range from 0.001 to 25.0 mg.L^{-1} . The limit of detection (LOD) and limit of quantification were less than 74 and 246 ng.L^{-1} . Degradation of one fungicide (ioprodine) was readily identified by the characteristic band in the 2D plot between the parent and the decomposition product. The study showed that GCxGC/NPD has a potential for the routine analysis of fungicides in food and vegetables samples, providing a low LOD and LOQ and a good repeatability and reproducibility of peak response. Dalluge et al., 2002, also determined 58 pesticides in food extracts using GCxGC/TOFMS. All the pesticides of interest could be identified using their full-scan mass spectra. This determination of pesticides in vegetable extracts serves as an example. It was demonstrated that GCxGC improves the separation dramatically and is very suitable for the analysis of complex food samples. The authors mention that the analytes of interest can be better separated from one another when using GCxGC, but, more importantly, they are also separated from matrix compounds, which tend to seriously interfere in the 1D-GC/MS procedure. Consequently, the quality of the TOF/MS mass spectra obtained by GCxGC is much better than those obtained with 1D-GC, as was illustrated in this study for serious pesticides. Zrostlíková et al., 2003, determined trace level residues of 20 pesticides in complex food matrices using GCxGC/TOFMS. The repeatability of retention time as R.S.D. ranged from 0.28 to 0.56% and 0.29 to 0.78% in the first and second dimensions, respectively. Good linearity ($R^2 = 0.9982\text{--}0.9996$) was achieved in the concentration range of 5-500 ng.mL^{-1} for standards in ethyl acetate. In this study and that of Dalluge, GCxGC/TOFMS was demonstrated to be a powerful tool for solving the problems with reliable confirmation of pesticide residues at the very low concentration levels required for the analysis of some types of samples such as baby food.

Gilbert-López et al., 2010, studied 105 pesticide residues in olive oil using fast liquid chromatography-electrospray time-of-flight mass spectrometry (LC/TOFMS) with two sample treatment methods: matrix solid-phase dispersion (MSPD) and liquid-liquid extraction. Data obtained shows that higher recoveries were obtained with LLE. The limits of detection obtained using both sample treatment methods were lower than 10 $\mu\text{g.kg}^{-1}$ for more than 85 analytes. The HPLC/MS technique provided good precision and accuracy without requiring expensive instrumentation for the sample treatment step, and it consumed relatively low amounts of solvent and generated little waste material.

Cus et al., 2010, identified the presence of 117 pesticide residues in vinification process of different grape varieties. Pesticides were determined by two different multi-residue methods. Seventy-one pesticides and dithiocarbamates were determined by GC/MS. Another 45 pesticides were determined by HPLC/MS/MS. The LOD was 0.01 mg.L^{-1} . Dithiocarbamates and some pesticides that are rapidly degraded, such as chlorothalonil, were not detected in this study. However, the study demonstrated the persistence of many pesticides during the vinification process. The range of concentrations of pesticides detected was 0.01-0.013 mg.L^{-1} .

Ayala et al., 2010, used high performance liquid chromatography with mass spectrometry (HPLC/ESI/MS) to study the degradation of bromoxynil and trifluralin through an ozonation process. This mass spectrometry method provides necessary information about the degradation products during the process that can lead to a proposal of a transformation route for the pesticides studied. In another study, Ayala et al., 2010, evaluated the degradation of bromoxynil and trifluralin in natural waters by photoradiation with a UV

Pesticides	Degradation products	Analytical Technique	Method Extraction	References
Aldrin	Dieldrin, chlordane and 1,2-hydroxy-dieldrin	GC/MS e GC/ECD	LLE	Ormad et al., 1997
Carbofuran	2,3-dichloro-2,2-dimethylbenzofuran-7-carbonato , carbofurafenol and benzofuran	HPLC,UV-vis and GC/MS	LLE	Mahalakshmi et al., 2007
36 kinds of different pesticides studied	Their respective degradation products	GC/ECD,GC/MS, GC/NPD, LC/MS and LC/UV	LSE/SPME	Bandala et al., 1998
Propan, terbutiron, propiclor, chlortoluron, thiran, ácido fenoxiacético, 2,4,5-triclorofenoxid o, uracil, 5 bromuracil and bromotimol	Propham, propachlor, 3-3(3-hydroxy-4-methylphenyl)-1,1-dimethylurea, chloro-4-methylphenyl, urea, 3-3chloro-4-methylphenylamine e chlortoluron	GC/MS	SPME	Veiga et al., 2006
Mechlorprop , dichlorprop, 2,4-D, 4-chloro-2-methylphenol, 2,4-dichlorophenol , bentazon, bromoxynil, yonyxil, dicamba dinoseb and DNOC	4-chloro-2-methyl phenol CMP) and 2,4-dichlorophenol, (DCP)	GC/MS	SPME	Ghadiri et al., 2001
29 kinds of pesticides and herbicides	-	GC/MS	SPE	Olette et al., 2008
Triazines	Chloromethoxy , methylthiotriazines, metribuzin, metamitron, triazinones and hexazinonetriazinone and hexazinone	GC/MS, LC/MS, GC/MS, LC-UV	SPME	Bouldin et al., 2006
Pirimifós metal	4-hydroxy derivative, phosphorothioic acid,	GC/MS, GC/MS-MS	LLE/SPME	Herrmann et al., 1999

	O.O.S-trimethyl ester			
Atrazine	Diethylatrazine and diisopropylatrazine	GC/MS/MS	SPME	Shankar et al., 2004
Pirimiphos-methyl	Phosphate, sulfate and nitrate anions	GC, HPLC, GC/MS, TOC and LC/MS	SPE	Kuo et al., 2002
2,3,6-Trichlorobenzoic	Dichlorobenzene isomers, 1,2,5-trichlorobenzene, 2,3,5-trichlorophenol, 2,3,6-trichlorophenol, 2,3,6-trichlorohydroquinone, 2,3,6-trichlorohydroquinone	GC/MS	LLE	Uygun, 1997
Chlorfenviphos	1-(2,4-dichlorophenyl)ethanol, 2,4-dichlorobenzoic acid and 2,2-dichloro-1-(2,4-dichlorophenyl)vinyl alcohol	GC/MS	LLE	Rafqah et al., 2005
Endosulfan	Endosulfan diol, endosulfan ether, endosulfan lactone, endosulfan hydroxyether and endosulfan dialdehyde	GC/MS	SPE	Wang & Lemley, 2001
Alachlor	2-hydroxy-2,6-diethyl-N-methylacetanilide, 8-ethyl-1-methoxymethyl-4-methyl-2-oxo-1,2,3,4-tetraquinoline and hydroxyalachlor	GC/MS	SPE	Gennaro et al., 2001
Parathion, atrazine and alachlor	Atrazine amide, deethylatrazine, simazine amide, deisopropylatrazine, hydroxyatrazine amide, chlorodiamino-s-triazine and deisopropylatrazine amide	GC/MS, LC/MS	LLE	Sabik et al., 2000
Triazines, phenoxyacids and organophosphorus compounds	Atrazine amide, deethylatrazine, deisopropylatrazine amide, deisopropylatrazine simazine amide, chlorodiamino-s-triazine, ammelie and hydroxyatrazine amide	GC/MS, LC/MS/MS	LSE/LLE	Picho et al., 1998

Diazinon	2-isopropil-6-metil-pirimidin-4-ol (IMP) and 2-isopropil-6-metilpirimidin-4-il fosfato (dizoxon)	UV-vis, GC/MS	LSE/SPME	Chiron et al., 1993
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Table 2. Studies of the Determination of Pesticides and their Degradation in Environmental Samples

lamp and with a combination of UV and hydrogen peroxide (H₂O₂). The concentration of these compounds was monitored by high performance liquid chromatography with a UV detector using the wavelengths of 237 and 220 nm to quantify trifluralina and bromoxynil, respectively. The study showed that the UV/H₂O₂ process enhanced the oxidation rate in comparison to direct photolysis.

Chung et al., 2010, validated a method of multi-residue analysis by liquid chromatography with a sequential mass spectrometer detector (HPLC/MS/MS). Ninety-eight pesticides, including organophosphorus and carbamates, were determined in various types of food, edible oil, meat, egg, cheese, chocolate, coffee, rice, tree nuts, citric fruits and vegetables. The method was suitable for the practical determination of multi-class pesticides in food. It presented good linearity in the range of 1 to 20 µg.L⁻¹. The coefficients of determination were greater than 0.995 for all the compounds studied. The limit of detection was of 2 µg.kg⁻¹, and the limit of quantification (LOQ) was 10 µg.kg⁻¹. The average recoveries, measured at 10 µg.kg⁻¹, were in the 70-120% range for all of the compounds tested.

5. Conclusion

Degradation methods have been extensively used and proposed as an alternative for the complete destruction of pesticide residues, or as a means of obtaining less harmful compounds in different environmental matrices and especially in water. The main methods proposed include photoirradiation, advanced oxidative processes (AOP), phytoremediation and bioremediation. AOP allied with irradiation was efficient in the elimination of harmful pesticide residues and has also been used to study the degradation products to determine the kinetics of formation and disappearance of more toxic products and to establish the routes of degradation and their relative importance.

Chromatographic techniques such as gas chromatography with mass spectrometer detector are proposed for the determination of pesticide residues and their degradation products because of the selectivity, sensitivity and relative speed of analysis. However, liquid chromatographic techniques with mass spectrometer detectors are more suitable for the analysis of more polar compounds because the samples are analyzed directly without the need for derivatization.

Commonly used extraction processes involving analytical methods such as LLE, SPE or SPME are associated with the chromatographic techniques. Considering the use of solvents and the formation of residues by LLE and SPE methods, methods using SPME are considered more advantageous. Moreover, several studies have shown that the SPME technique is selective, rapid and of low cost.

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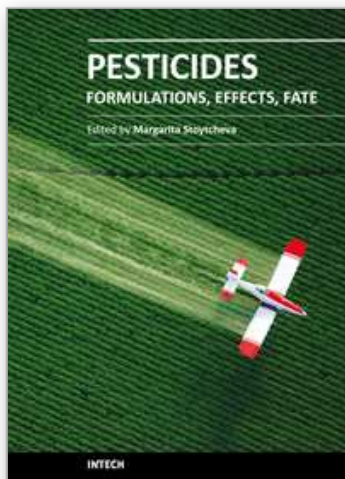
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This book provides an overview on a large variety of pesticide-related topics, organized in three sections. The first part is dedicated to the "safer" pesticides derived from natural materials, the design and the optimization of pesticides formulations, and the techniques for pesticides application. The second part is intended to demonstrate the agricultural products, environmental and biota pesticides contamination and the impacts of the pesticides presence on the ecosystems. The third part presents current investigations of the naturally occurring pesticides degradation phenomena, the environmental effects of the break down products, and different approaches to pesticides residues treatment. Written by leading experts in their respective areas, the book is highly recommended to the professionals, interested in pesticides issues.

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