Pesticides: Classification, Detection, and Degradation



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Introduction

Human population has always followed a geometrical progression, whereas food production shows an arithmetic progression. The huge pressure of providing food at low costs has forced farmers to use pesticides. According to the Federal Insecticide, Fungicide and Rodenticide Act, a pesticide is defined as any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any insects, rodents, nematodes, fungi, weeds, or any other form of life declared to be pests; it is any substance or mixture of substances intended for use as a plant regulator, defoliant, or desiccant (Benson 1969; What are Pesticides/Definition/Types/Uses and Effects 2016). According to the Food and Agriculture Organization, a pesticide is any substance or mixture of substances intended for preventing, destroying, or controlling any pest, including vectors of human or animal disease, or unwanted species of plants or animals causing harm during or otherwise interfering with the production, processing, and storage or marketing of food agriculture commodities, wood or wood products, or animal feed stuffs, or which may be administered to animals to control insects arachnids or other pests in or on their bodies (Zacharia and Tano 2011). These chemicals may be growth regulators, defoliants, desiccants, fruitthinning agents, or agents for preventing the premature fall of fruits that are applied in the field or on food during storage and transport. The evolution of pesticide use is represented in Fig. 1.

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First generation pesticides (Highly toxic compounds) eg: calcium arsenate, HCN, lead arsenate, Bordeaux mixture etc.

Second generation pesticides (synthetic organic compounds eg: DDT)

Third generation pesticides coupled with green revolution

Fig. 1 Schematic representation of the evolution of pesticides (Zacharia and Tano 2011; Compelling Evidence of Human Health Effects of Pesticides n.d.)

The green revolution brought an excessive use of pesticides to enhance productivity and reduce crop loss (Singh 2000; Conway and Barbier 2013). The widespread use of pesticides, environmental persistence, and potential hazards to wildlife initiated research on the impact of pesticides on the ecosystem (Conway and Barbier 2013). Thereby, studies revealed that the entire population is exposed to a mixture of pesticides through food, water, and air. The effect of pesticides on different classes of people is summarized in Table 1.

Pesticide formulations usually contain active and inert ingredients. The active component kills the pest, whereas the role of inert components is to improve the efficiency of the active ingredient. These inert ingredients are not tested thoroughly and are seldom disclosed on the product labels, with most of them being toxic when inhaled or absorbed by the skin. The health effects of different classes of pesticides can be categorized as shown in Table 2.

Pesticide available in the market can be classified as shown in Table 3.

Figure 2 shows the cycle of pesticide exposure and represents the course of a pesticide's journey after application on farmland.

In most cases, the degradation products of pesticides are far more toxic than the original pesticides; for example, photodieldrin is several times toxic than dieldrin. The degradation of common pesticides was investigated in detail by Benson et al., who confirmed that the degradation products of most pesticides are far more toxic than the parent pesticides. Photodegradation and other modes of degradation for common pesticides are shown in Fig. 3.

Eugina et al. investigated the amount of heavy metals in pesticides, fertilizers, and soil. Soil samples from rice farming areas in Albufera Natural Park were selected for the study (Gimeno-García et al. 1996). Significant amounts of heavy metals are found in pesticides due to insufficient purification for reducing the cost of production. Fertilizers such as superphosphate contain high concentrations of Cd, Co, and Zn, whereas CuSO₄ and FeSO₄ showed a high content of Pb and Ni. Similarly, pesticides showed the presence of high concentrations of Cd, Fe, Mn, Zn, and Ni.

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Infants and exposure in womb	Pregnant women	Adults and farmers
Premature birth, low birth weight, cancer, brain tumors,	Pregnancy complications, miscarriage; children with	Memory loss, loss of coordination, reduced speed of
neuroblastoma, leukemia, underdeveloped brain, paralysis,	birth defects, oral clefts, neural tube defects, heart	response to stimuli, reduced visual ability, asthma,
birth defects, developmental disabilities, fetal death	defects, limb defects, and leukemia	allergies, cancer, hormone disruption, paralysis, stroke,
		etc.

 Table 1
 Effects of pesticides on different classes of people (What are Pesticides|Definition|Types|

 Uses and Effects 2016)
 1

 Table 2
 Different categories of pesticides and their effects on humans

Organochlorine (Longnecker et al. 1997; Alavanja et al. 2004; Schade and Heinzow 1998)	Organophosphates and carbamates (Alavanja et al. 2004; Eskenazi et al. 1999; Senanayake and Karalliedde 1987; Karalliedde et al. 2000; Wesseling et al. 2002; Karami-Mohajeri and Abdollahi 2011)	Pyrethroids (Vijverberg and vanden Bercken 1990; Saillenfait et al. 2015; Shafer et al. 2005; Bradberry et al. 2012)	Herbicides (Bertazzi et al. 2001; Sterling and Arundel 1986; Kligerman et al. 2000; Wolfe et al. 1990)
Loss of sensation, hypersensitivity to light and sound, dizziness, tremors, nausea, vomiting, nervousness, neurological diseases, decrease in sperm count and mobility	Increased salivation, perspiration, narrowing of pupils, nausea, diarrhea, decreased blood pressure, muscle weakness and fatigue, paralysis Human toxicity caused a decline in their use and spurred search for new alternatives	Hyperexcitation, aggressiveness, lack of coordination, whole body tremors, skin allergies, cancers, reproductive or developmental effects, endocrine system effects	Birth defects, cancers, liver disease and other related illnesses; also affect wildlife and aquatic organisms; contaminate surface water and ground water

Detection of Pesticides

Chromatographic Techniques

Pesticide detection usually involves the steps shown in Fig. 4 (Omeroglu et al. 2012).

The major drawbacks of the chromatographic technique include the following (Wan and Wong 1996):

- 1. Large amounts of organic solvents are required.
- 2. Special purification techniques are required for these solvents, making them very costly.
- 3. The recovery of solvents along with their disposal are difficult.
- 4. The solvents are hazardous to the environment.

Common pesticides	Comments
1. Organochlorine pesticides (OCPs)	Introduced in 1950s and banned due to extreme toxicity. They are stable, thereby persistent in environment. OCP contaminants can be found in soil, river sediments, and costal marine sediments
	For example, CCl4, DDT, DDE, heptachlor, β-HCH, dieldrin
2. Organophosphate pesticides (OPPs)	Generalized during the Second World War, toxi to non-target species also
R P O (or S) R ₁	For example, acephate, parathion, malathion, phosmet
	Most of them are banned in the United States of America
3. Carbamates	Neurotoxin and acetylcholinesterase inhibitors, adverse effect on human development
	For example, aldicarb, carbaryl, methiocarb, pirimicarb, maneb
4. Pyrethroids	Interfere with cell signaling, adverse effect on male reproductive health suspected endochrine disrupters
H ₃ C H ₃ C H ₃ C H ₃ C COOF	For example, cyhalothrin, cypermethrin, deltamethrin
5. Neonicotinoids	Neuroactive insecticide with a structure similar to nicotine. It was first introduced in 1985. They are more toxic to insects than mammals. They have suspected toxicity to bees
	For example, clothianidin, imidacloprid, thiamethoxam
6. Chloroacetamides	Suspected to cause developmental abnormalities, reproductive toxicity, teratogenecity.
CINH2	For example, alachlor, metolachlor
7. Glyphosate	Usually and aqueous mixture of isopropylamine salt of glyphosate, a surfactant, antifoaming and coloring agents, biocides, and inorganic ions
	Glyphosate is an example of a compound where toxicity is due to the "inert" ingredient

Table 3 Different classes of pesticides available in the market along with their general structure

To reduce the impact of these effects, several strategies have been reported. Bushway et al. reported the use of miniaturization of scale, where a small portion of the extract is cleaned for analysis (Bushway et al. 1995). This reduces the solvent consumption and decreases the analysis time. Simplification of the analysis procedure is another accepted methodology, which can broadly be divided into two methods:

- 1. The thorough removal of analyte from the sample matrix, followed by washing the remainder with large amounts of solvent. They are then combined.
- 2. The sample is extracted only once. Small amounts of this extract are then used for subsequent clean-up as required.

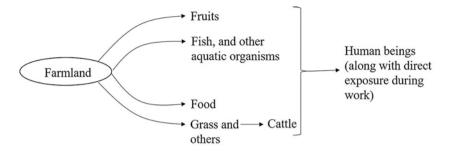


Fig. 2 Cycle of pesticide transfer after application (Alternative and Biological Pest Controls/Commons Abundance Network n.d.)

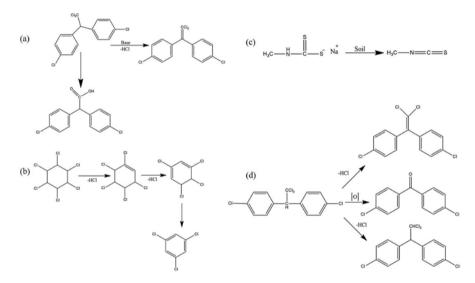


Fig. 3 Different modes of degradation and the products formed for different pesticides: (a) 1,1'-(2,2,2-trichloroethane-1,1-diyl)bis(4-chlorobenzene) (DDT), (b) benzene hexachloride (BHC), (c) methyl isocyanate, (d) p,p'-dichlorodiphenyldichloroethene (P, P'-DDE)

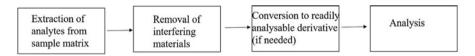


Fig. 4 Different steps involved in the chromatographic detection of pesticides

Liao et al. (1991) and Miyahara et al. (1994) reported the direct analysis of samples (where a clean-up step is omitted); however, this is not recommended due to the possibility of negative effects from complex matrices. Kadenczki et al. reported a multi-residue method in which extraction and column clean-up occurred in a single step (Kadenczki et al. 1992). In the early 1990s, researchers developed new extraction techniques, such as solid-phase extraction (which is mainly used for the trace enrichment of water samples before testing). Belardi and Pawliszyn

developed a solid-phase microextraction technique in which sorbent-coated silica fibers are used for the extraction of analytes from aqueous and gaseous samples and then used for analysis (Application of chemically modified fused silica fibers in the extraction of organics from water matrix samples and their rapid transfer to capillary columns n.d.). Later, a solid-phase microextraction (SPE) method was used for the detection of phenols and metal ions in water samples (Rosenfeld 1999; Huang et al. 1997). The major drawback of the SPE technique is the fact that the sorbents can be used only once and are quite expensive (Barker 2007). Matrix solid-phase extraction is a new member of the family of SPE family; it is commonly performed in supercritical fluid extraction (SFE) and pressurized liquid extraction (PLE) to retain water/unwanted matrix compounds (Barker 2007; Oniszczuk et al. 2013).

Supercritical Fluid Extraction

Carbon dioxide (CO_2) is safe, unreactive, readily available, relatively inexpensive, and has low critical pressure and temperature; thus, it is the most commonly used solvent in SFE (McHugh and Krukonis 2013). Important advantages of SFE include the following (McHugh and Krukonis 2013):

- 1. SFE is a viable approach for the extraction of individual and multiple pesticides from food, soil, and plants.
- 2. It reduces operation costs, time, labor, space, glassware, and laboratory space, among others.
- 3. Fatty foods require clean-up after SFE, whereas non-fatty foods do not require any clean-up.
- 4. SFE results in minimal pesticide loss.
- 5. Water and salts can have strong effects in the SFE process.
- 6. Satisfactory extraction efficiency can be achieved for pesticides with low polarity; for pesticides with high polarity, modifier addition is necessary. Kane et al. (1993) discussed in detail the relationship between the structure of an analyte and the mode of extraction.

Pressurized Liquid Extraction

PLE was introduced as a competitor for SFE by Dionex scientists (Hawthorne et al. 2000; Carabias-Martínez et al. 2005; Mustafa and Turner 2011). Figure 5 shows a schematic representation of the instrumentation of PLE.

PLE is very similar to Soxhlet extraction and has been described as a "green" technology for the extraction of nutraceuticals from food and herbal plants (Hawthorne et al. 2000; Mustafa and Turner 2011). Suchen et al. compared the

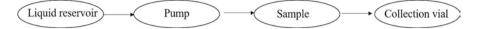


Fig. 5 Schematic representation of the instrumentation of PLE (Hawthorne et al. 2000)

efficiency of PLE with Soxhlet extraction; the authors concluded that PLE showed better efficiency than Soxhlet extraction for indicator polychlorinated biphenyls, some organochlorine pesticides, more volatile hexachlorobenzenes, as well as semi-volatile compounds. However, the major limitation of PLE is the high cost of the instrument (Suchan et al. 2004).

Gel Permeation Chromatography

Gel permeation chromatography (GPC), also known as size exclusion chromatography, involves the separation of molecules on the basis of their size (López-Mesas et al. 2000). GPC is commonly used for the determination of molecular weight.

Analysis of Pesticides

Durand et al. (1989) discussed the accuracy of various analytical techniques, such as gas chromatography (GC), mass spectroscopy (MS), GC-MS, and liquid chromatography (LC)-MS, for chlorotriazines and organophosphorus pesticides. It was concluded that GC methods offer better detection of 1–2.5 orders of magnitude, whereas an LC-LC-diode array (DA) is more easily applicable for soil samples (Durand et al. 1989). Balinova and Balinov (1991) reported the use of GC coupled with an electron capture detector for the analysis, detection, and estimation of nine soil applied herbicides with different chemical structures (Balinova and Balinov 1991). A specially packed column was used for the study; Fig. 6 shows the recovery of herbicides using various extraction solvents (Balinova and Balinov 1991).

A specially packed column was prepared by combining 3% OV-225 and 5% SE-52 in a ratio of 1:4:0.9, coupled with consecutive filling; it was reported to be simple, reliable, rapid, and effective for the detection of pesticides, with OV 225 at the side of injector and SE-52 at the side of the detector. Raju and Gupta (1991) first reported the use of spectroscopic methods for the determination of endosulfan in soil and water (Raju and Gupta 1991). Sulfer dioxide (SO₂) from endosulfan was liberated using p-toluene sulfonic acid, which was then absorbed in malonyldihy-drazide followed by estimation using p-aminoazobenzene and formaldehyde in HCl medium. This method provided 98–99% recovery from soil samples and approximately 99% recovery from water samples, which was reported to be superior to other methods for recovery (Raju and Gupta 1991). Figure 7 shows the ultraviolet-visible (UV-vis) spectra of endosulfan (Raju and Gupta 1991).

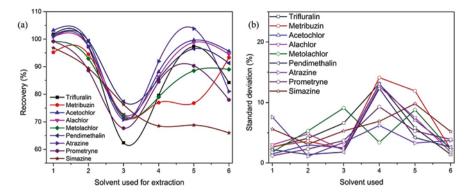
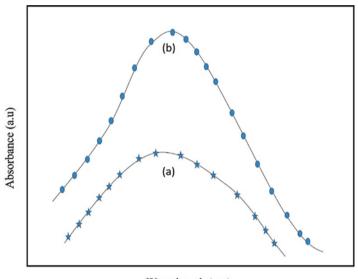


Fig. 6 (a) Recovery of various herbicides using various solvents: (1) acetone, (2) acetonitrile, (3) methanol, (4) acetone-water, (5) acetonitrile-water (9:1), (6) hexane-water (9:1) and (b) the corresponding standard deviations (Balinova and Balinov 1991)



Wave length (nm)

Fig. 7 Ultraviolet-visible spectra of the dye: (a) the blank reagent and (b) amount of endosulfan (Raju and Gupta 1991)

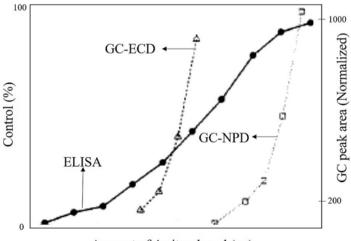
de Bertrand et al. (1991) reported the use of liquid chromatographic diode array determination (LC-DAD) for the estimation of carbamate pesticides in soil. LC-DAD provides a way to improve selectivity, with detection limits of approximately 25 ng/g corresponding to an absolute injected amount of 5 ng; it was reported to be effective for the detection of different carbamate pesticides at low levels of 0.1–1 μ g·g⁻¹ (de Bertrand et al. 1991). The significance of this work is evident by the fact that carbamates are unstable compounds, thermolabile, and quickly decomposed by alkali, which make their analysis extremely complicated.

An advantage of using LC coupled with a UV-vis variable detector is to enhance the selectivity by working at different wavelengths. The use of LC-DAD is simple, less time consuming, and allows simultaneous determination of 1-naphthol (de Bertrand et al. 1991).

Durand et al. (1991) reported the use of thermospray LC-MS for the determination of pesticides (Durand et al. 1991). The effect of four different mobile-phase compositions with reversed-phase methanol-water (50:50) + 0.05 M ammonium nitrate, methanol-water (50:50) + 0.05 M ammonium formate, acetonitrile-water (50:50) + 0.05 M ammonium formate were compared for the determination of carbamate and chlorotriazine pesticides (Durand et al. 1991). The results showed 3–3.5 orders of improvement in PI mode for carbamates, with the exception of pirimicarb, carbaryl, and α -naphthol (Durand et al. 1991).

Taylor (1991) developed a method using GC and LC for the general pesticide screening of soil samples from mixer/loader sites (Taylor 1991). Samples were extracted in methanol-acetone mixture, concentrated, and then analyzed using capillary GC with flame ionization detection and an LC-diode array (Taylor 1991).

Organophosphate derivatives of O-nitrophenol have been used quite extensively as herbicides, insecticides, and fungicides (Taylor 1991). Wong et al. used enzymelinked immunosorbent assay (ELISA) and GC for the detection of organophosphate pesticides (Wong et al. 1991). ELISA is less time consuming, low cost, and has the advantage of running the analysis without an extensive sample work-up (Wong et al. 1991). Figure 8 shows a comparison of the results obtained for ELISA, GC-electron capture detector, and GC-nitrogen phosphorus detector (Wong et al. 1991). Based on this study, it was concluded that GC and ELISA showed good agreement; furthermore, ELISA can be effectively used to detect 4-nitrophenol and parathion in the same sample.



Amount of 4-nitrophenol (pg)

Fig. 8 Comparison of the efficiency of ELISA against GC-electron capture detector and GC-nitrogen phosphorus detector for the detection of 4-nitrophenol (Wong et al. 1991)

Later, King and Nam (1996) coupled ELISA with SFE for the detection of pesticides (King and Nam 1996). Kizza and Yaw reported the use of multidimensional column with ultraviolet detection for the determination of nitrate, nitrite, and organic pesticides in soil solution (Nkedi-Kizza and Owusu-Yaw 1992). A convective-dispersive transport model with a sorption term was used to model the transport of NO₃⁻, NO₂⁻, and Baygon through the column (Nkedi-Kizza and Owusu-Yaw 1992).

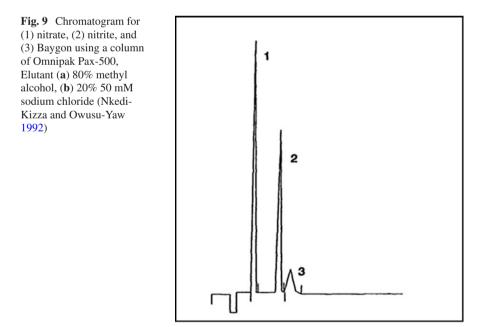
$$\frac{R\delta C}{\delta p} = \frac{1}{P} \frac{\delta^2 C}{\delta X^2} - \frac{\delta C}{\delta X} \tag{1}$$

Where

And
$$P = \frac{vL}{D}$$
 $X = \frac{x}{L}$.

 $R = 1 + \frac{\rho K_D}{\theta} \quad p = \left(\frac{vt}{L}\right)$

Here, *R* is the retardation factor, *C* is the solution concentration $(\text{mg}\cdot\text{L}^{-1})$, *p* is the pore volume, *P* is the Peclet number, *x* is the distance, *t* is the time in hours, *L* is the length of the column, *D* is the hydrodynamic dispersion coefficient $(\text{cm}^2\cdot\text{h}^{-1})$, ρ is the bulk density, K_D is the sorption coefficient $(\text{mL}\cdot\text{g}^{-1})$, and θ is the volumetric water content. Figure 9 shows the chromatogram for nitrate, nitrite, and Baygon (Nkedi-Kizza and Owusu-Yaw 1992). They concluded that the new high performance liquid chromatography (HPLC) analytical method is a versatile



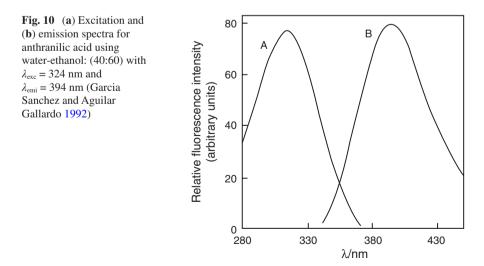
Retention time (min)

technique for the simultaneous determination of nitrate, nitrite, and pesticides with UV absorbance in the range of 210–254 nm and sample injection requirement of 20 μ L.

Garcia Sanchez and Aguilar Gallardo (1992) used hydrolysis-induced fluorescence spectrometry for determination of azinphos-methyl residue in soil (Garcia Sanchez and Aguilar Gallardo 1992). Figure 10 shows the excitation and emission spectra for anthranilic acid. The results obtained were reported to be better than that of HPLC (Garcia Sanchez and Aguilar Gallardo 1992).

Basta and Olness (1992) reported a method for the simultaneous resin extraction of alachlor, atrazine, and metribuzin in soil extracts. Pesticides were extracted using anion exchange, cation exchange, and non-polar resin followed by an analysis using dual-column chromatography (Basta and Olness 1992). Gael et al. investigated the determination of atrazine, simazine, cyanazine, deethylatrazine, and deisopropyl atrazine in soil samples (Durand et al. 1992). They compared the results for (1) GC-MS-MS (with collisionally activated dissociation and multi-reaction monitoring), (2) GC-LRMS (low-resolution mass spectroscopy) (with low resolving power of 1000) and (3) GC-HRMS (high-resolution mass spectroscopy). The authors concluded that GC-MS-MS with multi-reaction monitoring and GC-HRMS are useful techniques for the detection of chlorotriazines in soil, with GC-MS-MS having more selectivity than GC-HRMS (Durand et al. 1992). The major limitation is that the limit of detection of GC-MS-MS and GC-HRMS, which is approximately 1.5-2 orders of magnitude lower than that of a triple quadrupole or a single quadrupole GC-MS (Durand et al. 1992). GC and HPLC are time-consuming, expensive, and require specialized instrumentation.

The use of ELISA for the detection of pesticides was first reported in 1980 (Lawruk et al. 1993). The detection of pesticides using magnetic particle-based ELISA was reported by different groups; the use of this method for the detection of metolachlor was first introduced by Lawruk et al. (1993). This magnetic



particle-based system was reported to be rapid and sensitive. The authors also showed detection limits of parts per billion, thereby satisfying the sensitivity requirements for environmental monitoring. Later, Dequaire et al. reported the use of a disposable immunomagnetic electrochemical sensor with a magnetic particle-based solid phase and a Nafion-film-coated screen-printed electrode for the detection of pesticides (Dequaire et al. 1999). These devices were reported to be simple, cost-effective, and highly efficient (Dequaire et al. 1999).

Rogers et al. introduced the use of a reusable fiber-optic enzyme biosensorbased technique for the detection of pesticides and insecticides (Rogers et al. 1991a, b, c). Kotoucek and Opraviliva reported the use of fast-scan differential pulse voltammetry for the detection of nitro-based pesticides using dropping mercury electrodes (Kotouček and Opravilová 1996). Vijay Kumar et al. reported the use of various spectroscopy techniques for the detection of organophosphate pesticides (Kumar et al. 2013), including the use of UV-visible spectroscopy, Fouriertransform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy, X-ray diffraction, and electrochemical methods for the detection of pesticides. This brought out the significance of other techniques for the detection of pesticides. Timperley et al. reported the use of UV-vis spectroscopy for the characterization of 18 different organophosphorous nerve agents and pesticides (Timperley et al. 2006). The significance of this work arises from the fact that organophosphorous pesticides and nerve agents usually do not show significant absorbance in the UV region and can be converted by suitable chemical modifications, as shown in Fig. 11 (Timperley et al. 2006).

Venugopal et al. reported the spectrophotometric detection of Malathion (Venugopal et al. 2012). Samples were prepared as discussed by Norris et al. (1954). The proposed method does not require any solvents and is simple, along with being less expensive (Venugopal et al. 2012). The nature of the interactions, degradation mechanisms, and pH dependency of reactions with atrazine (2-chloro-4-ethylamino-

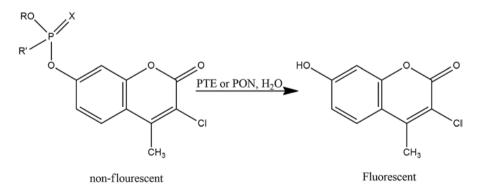


Fig. 11 Chemical modification of an oroganophosphorous pesticide, which is non-fluorescent to fluorescent compound (Timperley et al. 2006)

6-isopropylamino-8-triazine), which is one of the most commonly used herbicides with a half-life between 2 months and 5 years, were reported by Martin-Neto et al. (2001) and Sposito et al. (1996). Atrazine undergoes abiotic degradation with hydroxyatrazine (AT-OH), which is nonphytotoxic. Wang et al. reported the existence of weak hydrogen bonding interactions (proton transfer), and hydrophobic interactions between atrazine and humic compounds extracted from soil (Wang et al. 1990a, b). Later, Welhouse and Bleam reported that a lone pair of electrons on nitrogen is highly delocalized in the triazine ring, thereby existing in four different isomeric forms; it has a strong tendency to form complexes with amide or carboxylic acid groups (Welhouse and Bleam 1992). Gamle et al. and Wang et al. proposed that the surface Bronsted acidity of soil colloids catalyze the conversion of AT to AT-OH.

UV-vis spectroscopy studies by Martin-Neto et al. showed that the degradation/ conversion of atrazine is highly pH dependent (Wang et al. 1990a). When the pH of the solution is above 3.5, the peak at 223 nm (corresponding to AT) retained its shape, even after 4 days. On changing the pH to 2.3 or on increasing the acidity, the peak intensity of the AT band reduced by 25% and a new band corresponding to AT-OH started to appear. This was followed by an increase in the reaction rate as the pH was increased to 1.7. Martin-Neto et al. elucidated the application of FTIR spectroscopy for following the pH dependency and degradation rate of atrazine (Sposito et al. 1996; Martin-Neto et al. 2001). The results obtained using FTIR spectroscopy exactly matched the results obtained from UV-Vis spectroscopy, confirming the fact that spectroscopic techniques will open new areas for the detection and estimation of various pesticides.

Conclusion

The use of pesticides for enhancing food production resulted in extensive environmental pollution, coupled with a dramatic decrease in food production. Pesticides and their degradation products are extremely toxic—not only to human beings, but also to other living organisms. The photo degradation products of Aldrin are far more toxic than the parent compound; they are transferred through various natural resources, thereby contaminating the natural resources in the process. The major limitations of chromatographic techniques include the requirement for a large amount of solvent, long analysis time, need for expert technicians, and high costs for running the experiments. These limitations have resulted in the development of new techniques based on spectroscopy for the detection and estimation of pesticides. The major advantage of these techniques is that they induce less harm to the environment and other living beings.

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