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Environmental Impact and Remediation of Residual Lead and Arsenic Pesticides in Soil

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1. Introduction

Chemical control of insects is considered one of the most beneficial developments of civilization (Klassen & Schwartz, 1983). As long ago as 1000 B.C., sulfur compounds were used to control insects in Asia Minor (National Academy of Science, 1969). However, the extensive use of chemicals to control pests has developed only in the last 150 years. The first example of large-scale effective chemical control of an insect pest occurred in 1867, with the use of Paris green (copper acetoarsenate) to control Colorado potato beetle, *Leptinotarsa deecemlineata* (Say). Paris green was later used to control codling moth, *Laspeyresia pomonella* (Linnaeus), on fruit trees (Klassen & Schwartz, 1983). Due to its effectiveness in controlling gypsy moth, *Porthetria dispar* (Linnaeus), lead arsenate replaced Paris green in New England in 1892. Lead arsenate was later used to control codling moth in apple, plum, and peach orchards (Klassen and Schwartz, 1983; Peryea, 1998a).

This chapter will focus on the inorganic pesticide lead arsenate ($PbHAsO_4$) and its effects on the environment. Both lead (Pb) and arsenic (As) have been used to produce a large number of chemical and manufactured products. Some of these products have been used in agriculture as defoliants, insecticides, and fungicides to control pests in apple, plum, and peach orchards, turf, vegetable crops, and on cattle. From the late 1800s to about 1947, lead arsenate was the most commonly used insecticide for control of codling moth in deciduous tree fruit orchards in countries throughout the world, including the USA, Australia, Canada, New Zealand, England, and France, because of its low cost, high efficiency, and low phytotoxicity (Focus, 2006; Peryea and Kammereck, 1997 and Shepard, 1951). The wide use of lead arsenate significantly increased its annual production during the early 1900s. Worldwide, lead arsenate production increased from 2,268 metric tons in 1908 to more than 41,000 metric tons in 1944. Even though the total amount of lead arsenate used on orchards is not known, this pesticide was applied frequently and at high application rates. Annual application rates as high as 215 kg Pb ha^{-1} and 80 kg As ha^{-1} were recommended for apple orchards (Peryea and Creger, 1994**).** Such high application rates helped minimize the development of resistant insects, a problem that farmers were facing with other insecticides. Moreover, the fact that lead arsenate has multiple sites of action made it unlikely that insect resistance could be achieved with single mutations (Georghiou, 1983). Lead arsenate was used as an insecticide until the introduction of the organochlorine dichlorodiphenyltrichloroethane (DDT) in the 1940s (Peryea 1998a; Wolz et al., 2003). However, lead arsenate continued to be used in some locations into the 1970s and was not officially banned until 1988 (Focus, 2006).

2. Environmental effects of lead arsenate pesticides

2.1 Occurrence of lead arsenate in the environment

In the early 1900s, fear and concern arose about the potential for retention of excessive pesticide residues on fruits and vegetables treated with lead arsenate. This concern became a reality in 1919, when western pears were condemned in Boston because of excessive arsenic residues (Klassen & Schwartz, 1983). Arsenate residue was also observed in fruits grown on lead arsenate contaminated soils in Canada. Arsenic concentrations in fruit juice and juice concentrate were higher when prepared from skin and cores. Arsenic concentrations in fruit and fruit products were influenced by the size of fruits at spraying and by spraying frequency (Bishop & Chisholn, 1966).

As a result of repeated lead arsenate application, lead and arsenic concentrations increased significantly in orchard soils. In one orchard soil studied, lead concentration ranged from 500 to 1500 mg kg^{-1} and arsenic concentration ranged from 200 to 500 mg kg^{-1}, whereas the concentrations found in uncontaminated soil normally range from 2 to 300 mg kg^{-1} for lead and 0.1 to 20 mg kg^{-1} for arsenic (Alloway, 1995). In an apple orchard with 70 years of lead arsenate use, Frank et al. (1976) reported lead concentrations in the range of 6.4 to 774 mg kg^{-1} and arsenic concentrations from 7.4 to 121 mg kg^{-1}. The extent of contamination is considerable in former fruit growing areas. It has been estimated that approximately five percent of the soils in New Jersey are affected with lead arsenate, for example, while about 188,000 acres in Washington State and 50,000 acres in Wisconsin are contaminated (Focus, 2006).

Lead and arsenic concentrations in orchards soils vary depending on the type of orchard (peach, plum, or apple), soil type, organic matter content, rate and frequency of pesticide application, and management practices after old trees are removed. Lower soil lead and arsenic concentrations were observed in peach orchards and vineyards than in apple orchards, due to the infrequency and lower rate of lead arsenate application in the former (Frank et al., 1976)**.** When replanting orchards, some farmers, after removing the old trees, shift the rows when replanting new trees in order to protect them from lead and arsenic toxicity. Under this management practice, there is little disturbance of the surface, and lead and arsenic concentrations will be much higher in the surface soil compared to their levels under management practices in which fields are plowed after removal of old trees and then planted with agronomic crops such as corn, wheat, and soybean for two or three years before being replanted with new trees. Lead and arsenic concentrations in the surface soil under this management will be lower due to the mixing of the surface and subsurface soil. This practice will increase lead and arsenic in subsurface soils, which, in turn, will increase the potential for vertical movement of lead and arsenic to ground water, especially if these soils are sandy.

Because lead and arsenic generally do not dissolve, biodegrade, or decay, are not rapidly absorbed by plants, and do not readily move through the soil profile, they remain in the soil long after their use (Wu et al., 2010). When lead arsenate reaches the soil, it undergoes hydrolysis, separating into lead and arsenic, which are bound to soil particles and organic matter and become immobilized. Lead is only slightly soluble and therefore accumulates in the surface soil (0-15 cm depth). Arsenic is slightly more soluble and will move through the soil profile (Focus, 2006). Arsenic mobility is enhanced by addition of phosphorus (Peryea & Kammereck, 1997). Arsenic is more mobile compared to lead regardless of the soil type and texture (Eflving et al., 1994). When lead is applied to soil, it will react with sulfate,

phosphate, and carbonate to formed complexes such as lead sulfate ($PbSO_4$), lead carbonate (Pb_3 $(OH)_2$ CO_3), and chloropyromorphite ($Pb_5(PO_4)_3Cl$). These compounds vary in their solubility in the soil. Lead is also adsorbed directly to clay minerals and indirectly by forming complexes with organic matter (such as humic and fulvic acids) that is adsorbed onto soil solids (Harrison & Laxen 1984). In some cases, lead has accumulated in orchard soils in amounts equal to the application rate. In a survey of soils from 31 apple orchards, soil lead concentration averaged 821 mg kg^{-1}, almost equal to the 817 mg kg^{-1} applied, while mean soil arsenic concentration was 188 mg kg^{-1}, considerably lower than the 245 mg kg^{-1} that was applied (Frank et al., 1976).

2.2 Lead and arsenic toxicity

Neurological impairment in children and hypertension in adults are the main health problems associated with chronic high lead levels in the blood. Lead toxicity in humans also affects red blood cells and their stem cells, the kidney, heme biosynthesis, vitamin D metabolism, and the neurobehavioral development of newborns, infants, and children (Carrington & Bolger 1992; Dudka & Miller 1999; Needlemann et al., 1990; Wolz et al., 2003). It has been suggested that blood Pb levels should be no higher than 6 µg dl^{-1} in children to avoid neurological symptoms and no higher than 25 µg dl^{-1} in adults to prevent hypertensive symptoms. Blood Pb levels above 10 µg dl^{-1} could result in spontaneous abortion and potential damage to the fetus in women who are pregnant. Dietary exposure that results in these blood levels of concern was estimated to be 60 µg Pb per day for children age 6 and younger, 150 µg Pb per day for children 7 years and older, 250 µg Pb per day for pregnant mothers and 750 µg Pb per day for adults (Carrington & Bolger, 1992).

In humans, circulatory disorders, skin cancer, and internal cancer are the main hazards related to arsenic exposure (Chaney & Ryan 1994; Dudka & Miller, 1999). Although arsenic is readily absorbed by humans, 40 to 70 percent of As intake is absorbed, metabolized, and excreted within 48 hours. The minimal risk level (MRL) for chronic oral ingestion of arsenic has been estimated to be 0.3 µg arsenic kg^{-1} day^{-1} (ATSDR, 1998; Wolz et al., 2003). Arsenate (V) and arsenite (III) are the dominant inorganic species of arsenic in soils (Chaturvedi, 2006). Arsenate is the predominant species in aerobic soils and arsenite is dominant under anaerobic conditions (Chaturvedi, 2006; Smith, 1998). Inorganic arsenic is very toxic to plants because phosphate and arsenate are analogs and are therefore absorbed by the same transport system (Meharg, et al., 1994; Meharg, 1992). When arsenic is absorbed into the plant it interferes with plant metabolic processes, uncouples phosphorylation, and inhibits phosphate uptake, resulting in purpling of lower leaves, symptoms that are similar to those of phosphorus deficiency (Cox & Kovar, 2001; Gang et al., 2006).

2.3 Risk assessment of lead arsenate exposure
2.3.1 Introduction

It has been reported that the health risk of living on old orchard land contaminated with lead arsenate is very low (Focus, 2006). Nevertheless, there is concern that when such contaminated land is converted to other uses such as vegetable crop production and residential development, (homes, schools, child care facilities, and parks) lead and arsenic will enter the food chain. It has been estimated that that over 6 million acres of farm land have been converted to non-agricultural uses (Focus, 2006). Because excess consumption of non-essential metals such as lead and arsenic can result in neurological, bone, and

cardiovascular diseases, impaired renal function, and various cancers even at low levels (Calderon, 2000; Jarup, 2002; Khan et al., 2003, Miller et al., 2004; Watt et al., 2000), there is a need for the development of risk assessment of these soils. The development of any risk assessment for these soils must consider both toxicity and exposure (Carrington & Bolger 1992; Pocock et al., 1984). Presently, each state has its own guidelines on the utilization of lead and arsenic contaminated orchard soils. However, with the increasing conversion of old orchard land to residential development or to other agricultural uses, a national effort is needed to prevent excessive human exposure to lead and arsenic.

2.3.2 Pathways of lead and arsenic uptake

Lead and arsenic can enter the human or animal body through direct or indirect pathways. A direct pathway is the unintentional consumption of lead and arsenic via the drinking of contaminated water or the inhalation and/or ingestion of contaminated soil and dust. An indirect exposure pathway is consumption of plants that have taken up Pb and/or As from the soil. The direct ingestion of lead and arsenic contaminated soils, especially by children, is considered the most important exposure route of arsenic and lead to the human body (Dudka & Miller. 1999). The segment of our population most vulnerable to lead poisoning is children below the age of 5 years, due to their unintentional ingestion of contaminated soil through hand to mouth activity or by breathing house dust brought inside the house on shoes (Chaney & Ryan. 1994). A recent risk analysis which is considered conservative stated that a soil arsenic concentration of 40 mg kg^{-1} and a soil lead concentration of 300 mg kg^{-1} do not result in excessive intake of arsenic and lead by humans as evaluated by the direct ingestion exposure mode (Dudka & Miller. 1999; US Environmental Protection Agency [USEPA], 1993).

2.3.3 Plant uptake of lead and arsenic

Even though plants do not readily take up lead and arsenic in large quantities, research has shown that some crops will remove lead and arsenic from lead arsenate contaminated soils. Plant lead concentration increased in some crops grown on lead arsenate contaminated soils, exceeding the 2.0 mg kg^{-1} Canadian residue tolerance level (Chisholm, 1972). Miller et al, (2004) observed that arsenic concentrations in agricultural produce grown on lead and arsenic contaminated soils near a Columbia mining area were below existing Canadian guidelines for arsenic content in commercially sold vegetables, but that lead levels in carrots, lettuce, and beetroots from some locations exceeded the recommended guideline of 2.0 mg kg^{-1} Pb. They concluded that the greatest risk was from consumption of contaminated soil particles adhering to vegetables, and that this risk can be reduced by washing and peeling vegetable crops before eating them. Carrot lead and arsenic concentrations increased when grown on lead arsenate contaminated soils (Zandstra & Dekryger, 2007).

In a growth chamber study, Codling et al. (2011, in press) measured lead and arsenic uptake by carrots grown on five orchard soils with history of lead arsenate use, with total soil arsenic and lead ranging from 93 to 291 and 350 to 961 mg kg^{-1}, respectively. Arsenic concentration in peeled carrots ranged from 0.38 to 1.64 mg kg^{-1} dry weight compared to 0.05 mg kg^{-1} in the control. Lead concentration in peeled carrot ranged from 2.67 to 7.32 mg kg^{-1}, compared to 0.19 mg kg^{-1} in the control. Lead concentration was higher in peeled roots compared to the peel and shoot, while arsenic concentration was higher in the shoot and peel than in peeled roots. This study demonstrated that carrots will accumulate lead in

edible tissue. Lead in food is less well absorbed by humans than lead in water, and further studies are needed to determine what fraction of lead and arsenic in such carrots are bioavailable to humans.

There is a possibility that lead arsenate contaminated lands may be used for rice production. A greenhouse study was conducted to determine arsenic uptake by rice from two lead arsenate contaminated soils under flooded conditions (Codling, 2009). Flooding reduced grain yield and increased grain arsenic concentration in both soils. Lead concentration in the grain decreased with flooding for one of the soils but increased for the other. Lead and arsenic concentrations observed in the rice grain would not be expected to become a human health risk. However, the bioavailabilities of lead and arsenic in this rice grain need to be determined. Arsenic and lead concentrations in the straw and husk were much higher than in the grain. Straw from rice grown on these soils under flooded conditions could indirectly become a human health risk because rice straw is used for livestock feed and bedding.

2.3.4 Animal uptake of lead and arsenic

Herbivores and their predators that live in old orchards with history of lead arsenate use are at risk of lead and arsenic contamination (Elfving et al., 1978). Earthworms, for example, have been shown to concentrate lead from these soils (Ash & Lee, 1980; Morgan & Morgan, 1999. Worm eating birds will accumulate lead from consuming these worms. Animals such as meadow voles have been shown to accumulate high levels of lead and arsenic in their liver, kidney, and bones compared to control animals (Haschck, 1979). Predators of these animals such as owls, hawks, and foxes potentially will accumulate lead and arsenic in their tissue. Animals grazing on these contaminated soils unintentionally consume large amounts of soil containing lead and arsenic (McGrath et al., 1982). Even though there is no evidence of human lead and arsenic toxicity from eating animal tissue that was grazed on lead arsenate contaminated soil, there is a potential for lead and arsenic entering the human food chain via this route.

3. Remediation of lead arsenate contaminated soil

3.1 Introduction

Several remediation methods have been proposed and used for remediating lead arsenate contaminated soils, including removal and replacement of surface soil, chemical treatment *in situ*, establishment of a grass cover to prevent erosion and direct contact with humans, and phytoremediation (Peryea 1998b; Codling & Ritchie 2005). Physical removal of contaminated soil by excavation is acceptable and has been used. The cost of excavation, however, is quite expensive, with cost ranging from US$ 25,000 to US$ 1 million per acre, depending on the depth of soil removed, availability of a disposal site, and cost and availability of replacement uncontaminated soil (Peryea 1998a). This method would not be applicable for the large areas that are contaminated with lead arsenate. Remediation by dilution, such as by mixing contaminated surface soil with uncontaminated subsurface soil, may not be acceptable because arsenic in the subsoil may leach to the ground water.

3.2 In situ remediation of lead and arsenic

In situ inactivation methods reduce the hazards associated with contaminated soils through the use of chemicals that change the ionic and/or molecular species of metals to stabilize the

metal chemically and physically in place (Berti & Cunningham, 1997; Brown et al., 2004). This method has been used effectively to sequester either lead or arsenic in soils contaminated from metal smelters, leaded gasoline, lead paint, lead batteries, cattle dips, and arsenic treated lumber. Remediation of lead arsenate contaminated soils, however, is more challenging because of (1) the vast amount of lead arsenate contaminated soil throughout the world (Peryea & Kammereck 1997), and (2) some of the common *in situ* remediation methods that have been proven effective for the remediation of lead contaminated soils result in the release of arsenic from lead arsenate contaminated soil, thereby creating a new environmental problem (Codling, 2007; Peryea 1991b). Phosphate, for example, has been shown to be very effective in sequestering lead in contaminated soils (Chaney & Ryan 1994; Ruby et al., 1994), but this remediation method is not suited for lead arsenate contaminated soil; because arsenate and phosphate exhibit similar physicochemical behavior in soil and compete directly for sorption sites on soil particles, the use of phosphate on a lead arsenate contaminated soil will promote arsenic release from the soil into the soil solution phase, threatening the ground water (Dupanport & Peryea 1991b; Eflving et al., 1994**;** Peryea & Kammereck 1997; Peryea, 1991). Increasing the number of adsorption sites via the addition of high oxide minerals such as iron and manganese might allow for the resorption of arsenate after its release caused by phosphate competition during lead sequestration.

Another *in situ* method that has been considered for the remediation of lead arsenate contaminated soils is biomethylation, in which the soil is flooded after application of a carbon source such as apple pomace. Under the high carbon and flooded condition, biomethylation of arsenic will occur (Peryea, 1991b). However, the quantity of lead arsenate contaminated land and the topography of these sites would make biomethylation difficult and expensive (Focus, 2006).

3.2.1 Long term study of *in situ* remediation of lead arsenate contaminated soil

Codling (2007) determined the effect of amendment with calcium carbonate, iron, and phosphate on water-extractable lead and arsenic in two orchard soils with history of lead arsenate use. A soil from Maryland (Thurmont sandy loam) had total lead and arsenic concentrations of 677 and 133 mg kg^{-1}, respectively, and a soil from Washington State (Burch) had total lead and arsenic concentrations of 482 and 93 mg kg^{-1}, respectively. Calcium carbonate, iron oxide, and phosphorus (as potassium phosphate) were mixed with these soils as individual treatments and as combinations. Soils and amendments were mixed and allowed to incubate for 60 weeks. Each treatment was sampled at 2, 4, 6, 8, 10, 16, and 60 weeks for water-extractable lead and arsenic. Iron oxide treatment without calcium carbonate did not change water-extractable arsenic concentration for both soils, compared to the control. The phosphate and iron+phosphate treatments increased water-extractable arsenic compared to the control (Figure 1, only Thurmont data shown). In these treatments, water-extractable arsenic concentrations were higher than the recommended drinking water limit of 10 μg L^{-1}. Application of phosphorus and iron plus phosphorus increased water-extractable lead concentration for both soils with and without calcium carbonate, compared to the control and the iron alone treatment (Figure 2, only Thurmont data with calcium carbonate shown). The higher water-extractable lead concentrations observed with the iron plus phosphorus treatment suggests that iron reacted with phosphorus making it less available for lead precipitation. Because of these observed increases in water-extractable lead and arsenic caused by application of iron and phosphorus to lead arsenate

contaminated soils, this *in situ* remediation method should not be use without further studies to determine the appropriate ratio of iron to phosphorus needed to sequester lead and arsenic in these soils.

3.3 Phytoremediation of lead arsenate contaminated soil

Using plants to remove toxic metals from soils, a process known as phytoremediation, is an inexpensive alternative to conventional methods (Lim et al 2004). In order for a plant to be considered a hyperaccumulator, it must accumulate at least 1000 mg kg^{-1} of the metal in the above ground tissue. Chaney et al. (1994) demonstrated that *Alyssum murale* Waldst. & Kit. will accumulate nickel from high nickel serpentine soil. Francesconi et al. (2002) and Ma et al. (2001) demonstrated that Chinese brake fern (*Pteris vittata* L) and silver fern *Pityrogramma calomelanos* (L) can hyperaccumulate arsenic. Some researchers do not believe phytoremediation of lead arsenate contaminated soil holds much promise because it is slow, potentially taking decades or longer to effectively remove the contaminant. While other researchers believe that phytoremediation is a cost effective, non-intrusive technology that needs improvement (Alkorta, et al., 2004). Alkorta, et al. (2004) stated that improvement of the capacity of plants to tolerate and accumulate metals by genetic engineering should open up new possibility for phytoremediation. They also suggested that a better understanding of metal uptake and translocation mechanisms and the external effects of phytoremediation should also increase its application. Research is ongoing to identify plants that could potentially be used as accumulators of lead and/or arsenic on lead arsenate contaminated soils. In a greenhouse study, Codling & Ritchie (2005) tested Eastern gamagrass [*Tipsacum dactyloides* (L.)] for lead and/or arsenic accumulation from two lead arsenate contaminated orchard soils. This species was chosen because the plant has an extensive root system and is used to reduce soil erosion on disturbed soils. Eastern gamagrass did not remove substantial amount of arsenic from these soils, making this species a poor candidate for phytoremediation of lead arsenate contaminated soils.
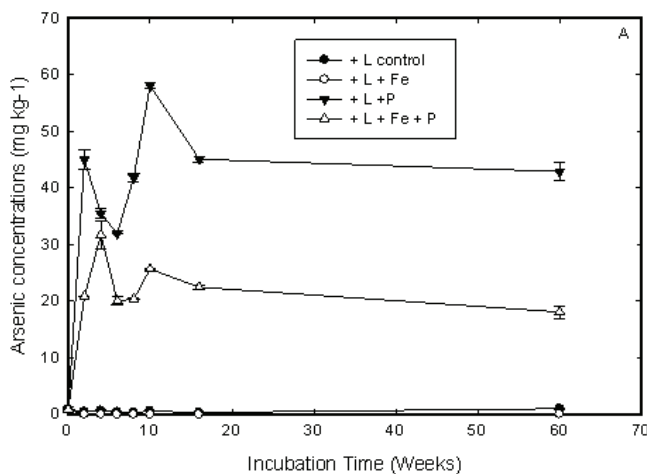

Fig. 1. Water-extractable arsenic in limed iron- and phosphorus-amended lead arsenate contaminated Thurmont soil during incubation at 26 °C. Values are mean and standard deviation (n=3).
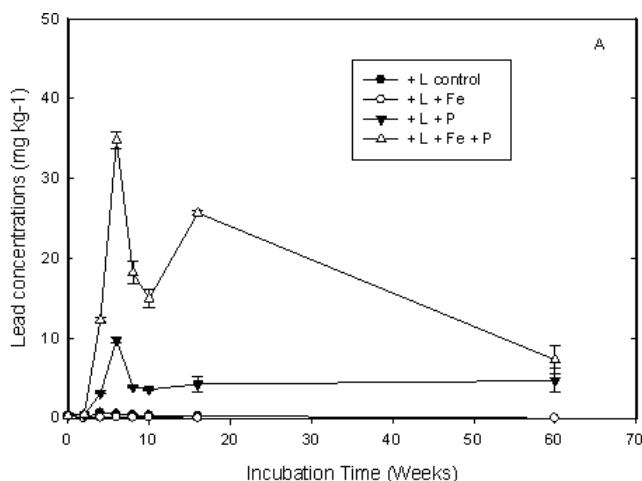
Fig. 2. Water-extractable lead in limed iron- and phosphorus-amended lead arsenate contaminated Thurmont soil during incubation at 26 °C. Values are mean and standard deviation (n=3).

4. Conclusions

The existence of large areas of lead arsenate contaminated orchard soils and their increasing conversion to vegetable crop production and to residential development has created a potential risk to public health. Young children are especially at risk because of their unintentional consumption of soil. Children exposed to lead may develop neurobehavioral impairment, while arsenic is a human carcinogen. Humans can also be exposed indirectly to lead and arsenic through the consumption of vegetable crops grown on contaminated soils, although the bioavailability of lead and arsenic in vegetable crops consumed by human and animals is not known. Because hundreds of thousands of acres have been contaminated with lead arsenate, removal of contaminated soil and replacement with clean surface soil is not economically feasible. Chemical *in situ* treatment with phosphorus, although effective in sequestering soil lead from other sources, has been shown to increase the leaching of arsenic to ground water in lead arsenate contaminated soils. Application of iron oxide has been shown to be effective in sequestering arsenic in lead arsenate contaminated orchard soils. Using plants to remove metals from contaminated soil (phytoremediation) is a method that is being considered for removing lead and arsenic from soils, but even if lead and arsenic accumulating plants are identified, this method may be too slow to be practical. Further research needs to be done on remediation of lead arsenate contaminated soils. Presently, each state has its own guidelines on the utilization of lead and arsenic contaminated orchard soils. However, with the increasing conversion of old orchard land to residential development or to other agricultural uses, a national effort is needed to prevent excessive human exposure to lead and arsenic.

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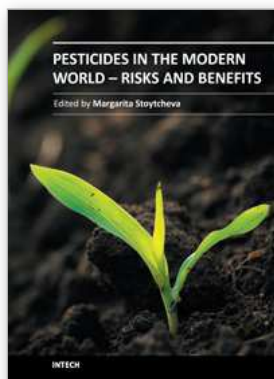
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Edited by Dr. Margarita Stoytcheva

This book is a compilation of 29 chapters focused on: pesticides and food production, environmental effects of pesticides, and pesticides mobility, transport and fate. The first book section addresses the benefits of the pest control for crop protection and food supply increasing, and the associated risks of food contamination. The second book section is dedicated to the effects of pesticides on the non-target organisms and the environment such as: effects involving pollinators, effects on nutrient cycling in ecosystems, effects on soil erosion, structure and fertility, effects on water quality, and pesticides resistance development. The third book section furnishes numerous data contributing to the better understanding of the pesticides mobility, transport and fate. The addressed in this book issues should attract the public concern to support rational decisions to pesticides use.

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