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## Use of Botanical Pesticides in Modern Plant Protection

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### 1. Introduction

The European Union has made very clear political decisions to increase environmental awareness. A Thematic Strategy on the Sustainable Use of Pesticides was launched by the Commission of the European Communities in 2006. It was decided to minimize the hazards and risks to health and the environment caused by the use of plant protection products. In 2009, the European Parliament accepted a new framework directive on the sustainable use of pesticides. Directive 2009/128/EC fosters the development of plant protection and integrated pest management (IPM) in the EU. The directive states that “*when pesticides are used, appropriate risk management measures should be established and low-risk pesticides as well as biological control measures should be considered in the first place*”. Biological control comprises various technologies of which one option is the use of botanical products. Many kinds of plant species and technologies have been used in the production of botanical pesticides. Some but not many of the plant-based pesticides have already become established plant protection products (Isman 2006).

There are many methods to extract essential oils and liquids from plant material, the most popular being steam distillation. Other methods are expression, enfleurage, maceration, solvent extraction and pyrolysis. Pyrolysis has been thoroughly described by Tiilikkala et al. (2010), proving that slow pyrolysis has been known for thousands of years. It has been used in the production of charcoal (biochar), tar, pitch and wood vinegar. The liquids which are most useful as biocides and pesticides are tar and wood vinegar. Tar has mainly been used as a wood preservative. The production and use of wood vinegar has increased rapidly in Asian countries, including Japan, China, India and Thailand. As a result of active development numerous botanical pesticides have been put on the market during the last 10 years (Tiilikkala et al. 2010). Simultaneously, pyrolysis has also become a frequently used technology in waste treatment which may lead to a rapid increase in the production of liquids based on the use of organic matter.

The raw materials used for the production of botanicals will differ in different parts of the world because of divergent natural resources. In Finland we have a huge reserve of wood

material and thus it was decided at MTT Agrifood Research Finland to search for modern pesticides from birch. The defence mechanisms of birch (*Betula* sp.) and the chemical compounds involved have been well studied (Novriyanti et al. 2010). The defence mechanisms are activated when a plant is under stress. Pests (including mammals) and plant diseases often attack birches and disturb their normal growth. Strong defence mechanisms are needed to survive the attack by herbivores and birches react to these in various ways. Plant defence can be divided into constitutive defences and induced defences. The defence methods used by birches within these categories are chemical, physical and phenological, depending on the plant organ. All these methods are found in leaves, but in the bark and woody parts the main defence mode is chemical. Different models, such as the optimal defence, carbon-nutrient balance, growth rate and growth differentiation hypothesis have been developed to explain variations in plant defence against herbivores. However, in birch the defence mechanisms are very complex and variations may depend on the type of stress or consumer and the genetical regulation (Novriyanti et al. 2010).

Pyrolysis was the “leading technology” three hundred years ago in Finland when the country’s “bioeconomy” was based on pine tar trade in Europe. Consequently, pyrolysis was a self-evident technology for extracting plant-based pesticides from wood. However, much of our experience of the use of pyrolysis liquids as pesticides can be applied in the commercialization of all kinds of botanical pesticides. The route to bring an effective botanical to the market from the stage of an innovation is not predicated on the extraction technology but on many other factors of the commercialization procedure. REGULATION (EC) No 1107/2009 (EU commission 2009) is the most important guideline for SMEs planning registration of biological plant protection products in Europe.

The aim of this article is to demonstrate the potential of slow pyrolysis liquids as pesticides and give examples of the use and role of botanical pesticides in modern IPM programmes. The information requirements and the bottlenecks in the commercialization of botanicals are discussed.

## **2. Efficacy of pyrolysis liquids as plant protection products**

### **2.1 Usability of pyrolysis liquids as repellents and insecticides**

Efficacy studies on birch tar oil (tar and wood vinegar) have been in focus for several years at MTT and at the University of Helsinki. After screening possible organisms suitable for further investigation by treating pests, diseases and weeds with two birch tar oils either alone, as a mixture or together with Vaseline®, the most promising target organisms were found. It was proved that birch tar oil, when painted on fences and pots, most efficiently prevented the molluscs *Arianta arbustorum* and *Arion lusitanicus* (Lindqvist et al. 2010) from crossing the barriers to reach the food behind the fence or in the pots. In addition, repeated treatments with birch tar oil in combination with short intervals or mixed with Vaseline were needed to achieve a long-term effect against slugs and snails (Figures 1 and 2).

The repellence of birch tar oil was also seen in a choice bioassay experiment with egg laying psyllids (*Trioza apicalis*) but did not affect flies (*Delia floralis*) (Tiilikkala & Segerstedt 2009). In a laboratory experiment in Greece, aphids (*Myzus persicae*) on eggplants were effectively killed (95 %) when sprayed once with birch tar oil (1% v/v aq solution) (Figure 3). However, the application seemed to be phytotoxic.

The repellence was observed in mammals as well. Field voles (*Microtus agrestis*) housed in a terrarium, avoided treated apple branches (Figures 4 and 5) if untreated branches or other food was available (Tiilikkala & Segerstedt 2009). Similarly, voles in the apple orchard injured birch tar oil-treated apple stems only when untreated trees were not available or when the vole population density was peaking. Orihashi et al. (2001) reported similar results in evaluating the deterrent effect of rosin and three wood tars on gray sided voles (*Clethrionomys rufocanus bedfordiae*) – high population density seemed to correlate with slight effect of rosin. Moreover, they proved that all tars were effective in repelling voles, but wood vinegar without tar did not inhibit voles from barking the tree material tested.



Fig. 1. Pots moved out from an experimental field where a high number of slugs (*Arion lusitanicus*) attacked the pots every night. Chinese cabbage was eaten by the slugs within one week when grown in pots without the birch tar oil treatment.





Fig. 2. Pots painted with a repellent made of birch tar oil (mixture of tar and wood vinegar). No slugs or snails were found from the pots and the test plants were untouched at the end of the experiment.

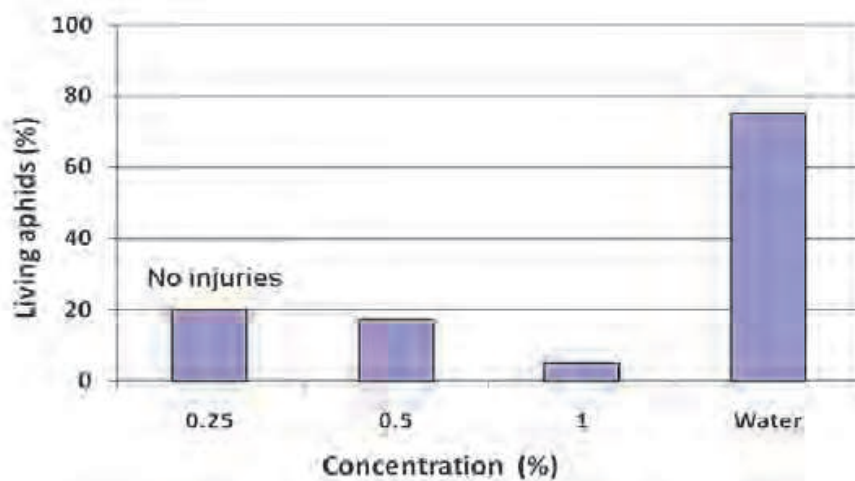


Fig. 3. Number of aphids on eggplant four days after spraying with birch tar oil. Three different concentrations were used: 1%, 0.5% and 0.25%. The last bar on the right refers to a birch tar oil free control.



Fig. 4. Branches of an apple tree were cut and treated with birch tar oil. Field voles did not touch the branches if untreated branches were available.



Fig. 5. Untreated branches of an apple tree were totally eaten within one day by field voles in a test terrarium.





Fig. 6. Moose repellents must be covered with a material to prevent the impact of rainwater. If not covered, wood vinegar will leach to the soil within a few days.

It has been observed that excessive moisture or rainwater will easily dilute active components of pyrolysis liquids (Figure 6). Efficacy tests may not show any impact if the repellents have not been protected against rainwater (Härkönen & Heikkilä 2009). Further evaluation of fractions made from wood tar revealed that all fractions contained repelling components (Orihashi et al. 2001). Beyond these results a literature review on the efficacy of wood vinegar used as a pesticide indicated that only a limited number of scientific publications are available (Tiilikkala et al. 2010). In spite of this wood vinegar has been widely used as a pesticide based on old traditions and knowledge of users and local producers.

## 2.2 Weed control with pyrolysis liquids

In a weed control experiment Tiilikkala & Segerstedt (2009) showed that birch tar oil could control broad-leaved weeds such as *Chenopodium album* and *Stellaria media*. Preliminary field experiments already showed the potential of wood vinegar as a herbicide (Figure 7). In weed control acetic acid is probably the most important component (Tiilikkala unpublished data). Experimental work with the pyrolysis liquids has shown clearly that the efficacy of botanicals depends very much on the application technology. Sprayers developed for use with synthetic chemicals are not well suited for the application of wood vinegar. It is obvious that the development of plant-based pesticides should be linked to the development of novel application technologies. With suitable application technology wood vinegar can be used for control of broad-leaved weeds including invasive alien species such as *Heracleum sp.* (Figure 8).





Fig. 7. One spray with wood vinegar controlled weeds in a carrot plot effectively (left). On the right, dense weed vegetation completely smothered the carrots.



Fig. 8. Birch tar oil proved to be an effective herbicide for control of giant hogweed (*Heracleum* sp). The oil was poured inside the gut vessel of the weed which did not recover after the treatment.



### 2.3 Use of pyrolysis liquids as a fungicide

Preliminary results of a laboratory experiment indicated that birch tar oil (10 and 30 % v/v aq solution) inhibited growth of wood rotting fungi (*Cylindrobasidium evolvens*, *Libertella* sp. *Stereum hirsutum* and *Chondrostereum*) on Petri dishes (Tiilikkala & Segerstedt, 2009). The same effect was seen on the cut surfaces of birch branches treated with birch tar oil (Figure 9). In laboratory conditions, volatile components of birch tar oil effectively inhibited growth of potato late blight (*Phytophthora infestans*) fungi (Figure 10). A similar control effect was difficult to achieve outdoors when the same product was sprayed with conventional equipment (Tiilikkala & Segerstedt 2009).

Many control technologies have been developed to inhibit fungi that cause discolouration on timber. It has been shown (Velmurugan et al. 2009) that wood vinegar made from bamboo and broad-leaved trees is effective against sapstaining fungi. The results revealed that compounds of Chikusaku-eki and Mokusaku-eki markedly inhibit fungal growth and the product possesses both antifungal and antioxidant properties as well as potential for use as a natural preservative in woodworking industries. The antifungal efficiency of wood vinegars was reported to be strongly dependent on their phenolic compound content (Baimark et al. 2009).



Fig. 9. One cut surface of a birch log (left) was dipped in birch tar oil and photographed after storage for one year outdoors. Many kinds of wood rotting fungi were growing on the untreated cut surface (right) but not on the treated surface.



Fig. 10. Untreated potato leaves covered with potato late blight mycelium (left) and leaves sprayed with birch tar oil before inoculation with the fungi.

### 3. Toxicology of birch tar oil

Hagner et al. (2010a) reported that the risk to the soil environment caused by birch tar oil (concentration 500–1360 L/ha) is insignificant and short-term compared to many synthetic plant protection products. A proper dose of the pyrolysis liquid when sprayed on the soil surface activated soil organisms shortly after the application (Figure 11). The authors concluded that pyrolysis liquids could be listed as “Minimal Risk Pesticides” like many essential oils in the USA.

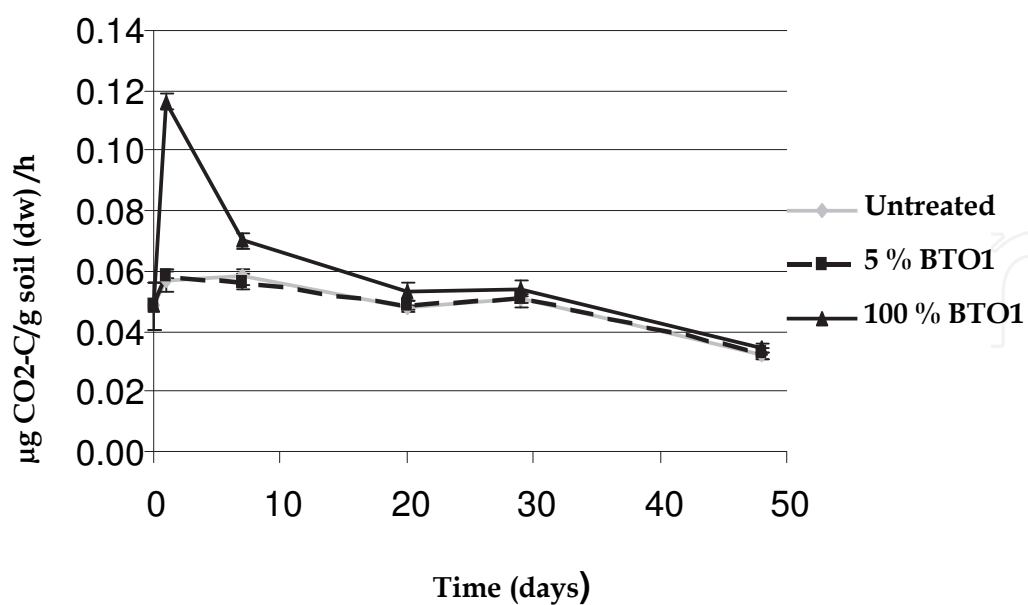


Fig. 11. Impact of a birch tar oil treatment (BTO1) on the activity of soil microbes (mean values + S.D., n=5). Time is given in days from the start of the pot experiment. The bioactivity of soil microbes is presented as CO<sub>2</sub> emission.

In their toxicity tests with a wide spectrum of aquatic organisms Hagner et al. (2010b) reported that these biota are invariably sensitive to birch oil distillates. However, the authors suggested that birch tar oil does not pose a severe hazard to aquatic biota (Figure 12).

Due to variations in manufacturing techniques, pyrolysis liquids differ in chemical composition and, consequently, the toxicological studies are divergent (Schmid et al. 1996). Very little is known about the toxicity of birch tar and wood vinegar, although the liquids have been used for hundreds of years in East European countries like Russia (Nozdrin et al. 2004). The lack of knowledge about the toxicology of pyrolysis liquids has been noted in many publications (Orihashi et al. 2001).

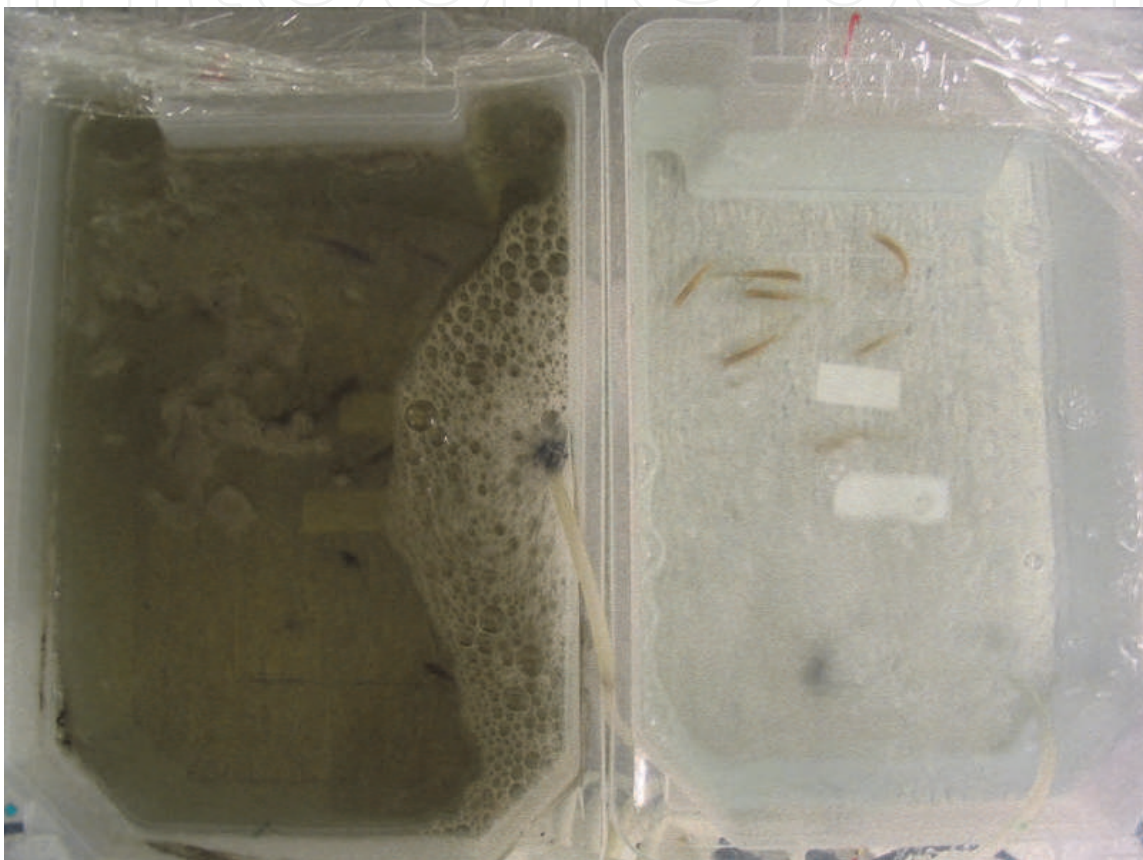


Fig. 12. Test fish swimming in a box treated with birch tar oil (left) and in a control box without birch tar oil (right). No negative impact was recorded on fish although the fish were hardly visible because of the birch tar oil treatment.

#### 4. Chemical composition of pyrolysis liquids

The characterization of fast pyrolysis liquids has been continued for a long time. The products contain many organic components and the composition is very complicated. According to literature, the main organic components of liquids from fast pyrolysis are methanol and acetic acid (Tiilikkala et al. 2010). Other components are acetone, methyl acetone, acetaldehyde, allyl alcohol, furan and furfural, as well as formic, propionic and butyric acids. The settled tars can be fractionated into light and heavy oil fractions. The former consists of aldehydes, ketones, acids and esters. Various phenols, including a high proportion of cresols and pitch, are present in the heavy oil fraction.



The chemical composition, physical properties and fuel oil quality of fast pyrolysis liquids has been extensively developed and described by Oasmaa & Meier (2005). Similar information on slow pyrolysis products is needed. The production of a standard wood vinegar from divergent plant material is a challenging task for the SMEs which produce biochar, charcoal and wood vinegar. Practical quality criteria for pyrolysis products are needed and technology for quality assurance should be developed (Tiilikkala et al. 2010). The variability of botanical products is a well known phenomenon and carefully considered e.g. in the production of botanical medicine (Shane-McWhorter 2001).

## 5. Registration of biological plant protection products

Isman (2006) wrote that pyrethrum has been approved as a pesticide worldwide, but the commercialization of other botanical insecticides is variable. The use and marketing of wood vinegar has grown rapidly in many Asian countries but not in Europe (Tiilikkala et al. 2010). Isman (2006) listed several barriers to commercialization of botanical insecticides and, respectively, Tiilikkala et al. (2006) discussed the regulatory problems of pyrolysis liquids in Europe. Regulatory barriers to all biological control agents were dealt in the report of the REBECA Project (Ehlers 2006). The authors of the REBECA report concluded that SMEs applying for registration of new botanicals should be financially supported by specific programmes and should be given detailed guidance by the regulatory authority. The REBECA group suggested that funding could come from various sources, such as rural development agencies, IPM and organic action plans, promotion of SMEs or taxes on pesticides. A follow-up of the commercialization of wood vinegar in Finland has proved that innovative SMEs rarely have sufficient resources to obtain e.g. the toxicological data which is required for the registration of all kinds of pesticides.

## 6. Conclusion

In the future the use of pesticides will be tightly regulated because of well-documented environmental risks in the use of synthetic chemicals (Ongley 1996). This may lead to a growing demand for biological plant protection agents including use of botanicals. Based on hard data and scientific publications it seems evident that plant extracts are biodegradable and thus will not cause similar environmental risks as many of the widely used synthetic chemicals. The option of replacing fossil oil-based chemicals with plant extracts fits well with food and agriculture policies directed to the future (Lee & Neves 2009). Sustainable food security cannot rely on the use of fossil oil as has been the case for a long time in the highly developed countries. Local resources must be utilized in agriculture and thus also recentralized production of biopesticides should become a common practise. In fact, this is already the case in many parts of the world where farmers have never had money to buy synthetic chemicals. The development of organic farming as predicted by FAO (2009) may boost the use of botanical pesticides and biological pest control globally.

Various extraction technologies will be used for production of plant-based liquids. Many kinds of raw material can be used as the source of the bioactive molecules. Slow pyrolysis is a powerful technology, because different types of materials can be processed. The price of the by-products, such as tar and wood vinegar, will be reasonably low which will make it possible for all farmers to use pyrolysis liquids as pesticides. In the future, production of biochar or agrichar will increase the volume of pyrolysis liquids substantially if claims

(Verheijen et al. 2009) concerning the positive impacts of biochar in agriculture can be proved. One of the main challenges will be the production of liquids with standard quality. This problem applies to all extraction methods and producers who are using plants or waste as raw material for the production of green chemicals.

The efficacy of wood tar as a biocide has been known for thousands of years, but evidence to prove all the claims about the efficacy of wood vinegar as a plant protection product needs to be verified. However, it is obvious that pyrolysis liquids can be used as raw material for making repellents, insecticides, molluscicides, herbicides and fungicides. In most of the products the efficacy is based on a mixture of many components. This is one of the main difficulties in the registration of botanicals as pesticides. The registration procedure has been developed for registration of one single active (synthetic) ingredient but not for mixtures of green chemicals. In practice, the efficacy of botanicals depends very much on the formulation of the product and on the application technology. Water can wash wood vinegar from plants and repellents, which means that rain or soil moisture can eliminate the efficacy of the vinegar in a short time. Standard efficacy studies must be adjusted to the functions of botanicals. Very often more frequent use of botanicals is needed compared to use of synthetic chemicals and the push and pull theory must be known e.g. in control of insects and other mobile pests. Formulation of slow-release products will increase the efficacy of botanicals such as wood vinegar (Lindqvist et al. 2010).

Pyrolysis liquids have been used for thousands of years without any records of the risks on the environment. However, this kind of historical information is not usable in the registration process of pesticides. Official data proving environmental impacts must be obtained for every product from laboratories which have an official quality system. Scientific evidence has proved that birch tar oil is an environmentally friendly product (Hagner et al. 2010a, 2010b). Similarly, it has been shown that essential oils do not pose any threat to the environment (Misra & Pavlostathis 1997). However, it is still uncertain if scientific publications are valid documents in the registration process for biological plant protection products.

Biodegradability of botanicals may be an important factor which will increase demand for plant-based products. On the other hand, we have found that the rapid biodegradability of botanicals may hinder the registration process. It is very difficult to obtain data indicating the spread of botanicals in water, because all measurable components break down in soil within a few days. There is no single active ingredient or decomposition product which could be used as an indicator of the leaching risk. No data - no progress in registration.

Risks to human health are a very important factor which must be analysed and documented before the registration of all kinds of pesticides. Many of the tar and wood vinegar products have been used as skin ointments and thus spread intentionally on the skin of patients. However, this kind of historical knowledge does not alleviate the need to obtain scientifically sound data proving the low risks of every single botanical pesticide on human health. It is generally well known that plant-based components may cause e.g. allergic reactions in sensitive people. Botanicals consist of hundreds of components as a mixture and the impacts of the mixtures must be studied in depth.

Commercialization of synthetic chemicals is very expensive because of the need for hundreds of documents which are required for the registration process of an active ingredient and a plant protection product. Only economically strong companies have been able to fulfil the demands for information. The SMEs which produce botanical pesticides do

not have the resources to cover all the costs of registration. Public funding is needed from many sources as was suggested in the reports of the REBECA Project (Ehlers 2006).

Botanicals may have an important role as pesticides in the modern world. However, it will take a long time before the potential of new innovations can be realized. The whole agribusiness is tightly committed to the use of fossil oil-based agrochemicals and the structure of the business must be radically changed before full-scale commercialization of botanicals is possible. While waiting for the business to change, much research work needs to be done to justify the claims of the already known and used plant-based products. Studies on ecotoxicology and toxicology need a lot of time and funding. Simultaneously the application technology used for spraying synthetic chemicals needs to be rebuilt so that modern technologies will adapt to the needs of the modern plant protection products – botanicals.

## 7. Acknowledgment

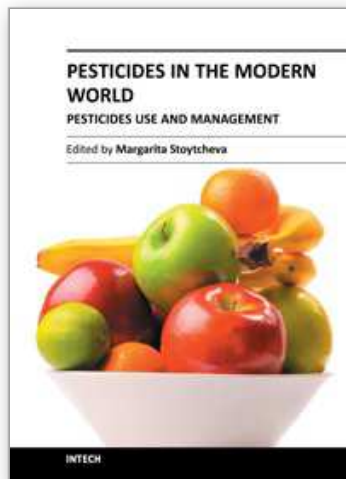
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## **Pesticides in the Modern World - Pesticides Use and Management**

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This book brings together issues on pesticides and biopesticides use with the related subjects of pesticides management and sustainable development. It contains 24 chapters organized in three sections. The first book section supplies an overview on the current use of pesticides, on the regulatory status, on the levels of contamination, on the pesticides management options, and on some techniques of pesticides application, reporting data collected from all over the world. Second section is devoted to the advances in the evolving field of biopesticides, providing actual information on the regulation of the plant protection products from natural origin in the European Union. It reports data associated with the application of neem pesticides, wood pyrolysis liquids and bacillus-based products. The third book section covers various aspects of pesticides management practices in concert with pesticides degradation and contaminated sites remediation technologies, supporting the environmental sustainability.

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