

ANALYTICAL REVIEW OF PESTICIDE FORMULATION TRENDS AND APPLICATION: THE EFFECTS ON THE TARGET ORGANISMS AND ENVIRONMENT

***¹Eze S.C., ²Mba C.L. and ³Ezeaku P.I.**

¹Department of Crop Science, Faculty of Agriculture, University of Nigeria, Nsukka

²Department of Geography, Faculty of the Social Sciences, University of Nigeria, Nsukka

³Department of Soil Science, Faculty of Agriculture, University of Nigeria, Nsukka

E-mails: simon.eze@unn.edu.ng (**Corresponding Author*), ²chinedu.mba@unn.edu.ng

³peter.ezeaku@unn.edu.ng

Abstract: Pest control is a major problem militating against food security in Africa, especially Nigeria. The development of various pesticides used in combating agricultural pests resulted in pesticide residues on crops and environment especially in developing countries due to higher pest pressure and subsequent overuse of pesticides. This paper therefore, examined the agricultural pesticide development trends, application methods, and the impact on the target pests, food and environments. Synthetic pesticides have characteristic rapid action that lures farmers into its application in agriculture. Synthetic pesticides, though effective have numerous negative environmental impacts such as pest resurgence following resistance to continuous application in addition to air, food and water pollution. Bio-pesticides, unlike the synthetics usually have slow speed actions and long lasting effects on the target with little or no mammalian toxicity, ecologically friendly, and no harmful residue on the environment. Most recently was the advent of nanotechnology which gave birth to Nanopesticides. Nanoparticles hold great potentials in various contents including agricultural pest control. They have no toxic chemicals and no adverse effects on food. There is need for public awareness of these rapidly growing technologies in order to guide the public on the choice of agricultural pesticides and their impacts on environment

Keywords: Bio-pesticide, Synthetic pesticide, Agricultural pests, Nanoparticles.

INTRODUCTION

A pesticide may be described as any physical, chemical or biological agent that will kill undesirable plant or animal pest (Ecobichon, 1996, FAO, 2002). In general, a pesticide is a chemical or biological agent (such as a virus, bacterium, antimicrobial, or disinfectant) that deters, incapacitates, kills, or otherwise discourages pests from attacking crops, animals or crop and animal products that constitute food (Gilden et al, 2010). Some pesticide products are available for domestic use, while a large number are available for commercial and restricted uses. Pesticides are used extensively in agriculture to protect commodities from damages caused by insects, weeds and other pests. The forms and application method vary

*Received Jan 11, 2016 * Published Feb 2, 2016 * www.ijset.net*

with the site, duration, target crop or animal and type of pesticide. Some are applied directly on the target, in the soil, in the air while others are released as fumigants. However, people who are concerned about the environment question the safety of pesticides in relation to food, water quality, farm workers and non-target beneficial organisms given that their use in the production and storage of crops is profitable (Kuniuki, 2002). But the truth is that with the current agricultural methods and technologies, it is not possible to provide the quantities of food currently needed for the number of people living in the earth. Pesticides allow us to increase our harvests and feed more people on the earth. The Council on Scientific Affairs (1997) classified pesticides into two broad types based on their origin: Synthetic pesticides and Biopesticides. Most recently was the advent of nanotechnology which gave birth to Nanopesticides.

Nanotechnology tries to manipulate matter on the scale of atoms and molecules, and the term is generally used when referring to materials with sizes ranging from 0.1 to 100 nm (Bowman and Hodge, 2007). Materials with a particle size less than 100 nm in at least one dimension are generally classified as nanomaterials. The development of nanotechnology in conjunction with biotechnology has significantly expanded the application domain of nanomaterials in various fields. Conventional pesticides have been reported to have potential health hazards and threat to food security globally (Koirala *et al.*, 2009). Some pests are difficult to control with available technologies and large differences exist in the efficacy of pest control. In Northwest Europe, during 2001-2003, efficacy was as high as 71%, in South Asia 42%, in West Africa 43% and in East Africa 32% (Oerke 2006). Pesticide residues are also a more frequent issue in developing countries due to higher pest pressure and subsequent overuse of pesticides, often of doubtful quality. Again, pests appear to be economically more important than disease in relation to food security and safety because some pests are disease vectors while others create entrance for pathogens. The Food and Agriculture Organization (FAO 2008) reported that climate change is likely to increase pest pressure and the incidence of mycotoxins. This paper therefore examines the benefits and problems associated with pesticide developments and application on food and environment.

1 Definitions

1.1 Synthetic pesticide

The British broadcasting corporations English Dictionary defines synthetic as products made from chemicals or artificial substances rather than from natural ones.

Synthetic pesticides are therefore, substances of chemical or artificial origin which are valued for their pesticidal, medicinal or therapeutic properties (Copper and Dobson, 2007).

1.2 Biopesticides

Biopesticides are defined as pesticides derived from such natural materials as animals plants, bacteria and certain minerals e.g. canola oil and baking soda (EPA, 2007). It includes whole fresh plants to purely isolate bioactive phytochemicals or their formulations which are effective against pest and pathogens (Prakash and Rao, 1996).

1.3 Nanopesticides

Huang *et al.* (2007) defined nanobiotechnology as a multidisciplinary integration of biotechnology, nanotechnology, chemical processing, material science and system engineering into biochips, molecular motors, nanocrystals and nanobiomaterials. Nanopesticides or nano plant protection products represent an emerging technological development that, in relation to pesticide use, could offer a range of benefits including increased efficacy, durability, and a reduction in the amounts of active ingredients that need to be used (Nair, et al, 2010).

2.0 Pesticide development trends

The concept of pesticide is not new. The first known pesticide was elemental sulphur dusting used in ancient summer about 4,500 years ago in ancient Mesopotamia (EPA, 2007). By the 15th century, Chinese people were using arsenic, mercury and lead to control and kill garden pests. Graeme (2005) reported that 1940's and 1950's are considered to have been the start of the pesticide era. Daly *et al.* (1998) said that from 1940's, scientists began to produce large amounts of synthetic pesticides and their use became widespread.

Biopesticides on the other hand, had been used by many people a very long time ago. Plant extracts were likely the earliest agricultural biopesticides as history records that nicotine was used to control plum beetles as early as 17th century (University of Arkansas, Ohio State University). The 19th century saw the introduction of two more natural pesticides (biopesticide) pyrethrum which is derived from chrysanthemums and rotenone which is derived from the roots of tropical vegetables (Miller, 2002). Experiments involving biological controls for insect pests in agriculture dates back as far as 1835, when Agostine Bassi demonstrated that white muscadine fungus (*Beauveria bassiana*) could be used to treat an infectious disease in silkworm (University of Arkansas, Ohio State University). As the costs of over-using synthetic chemicals became apparent, there was resurgence in academic and industrial research related to biopesticide development and with rapid expansion of organic

agriculture (Frost and Sullivan, 2009). According to the researchers, the development and adoption of biopesticides had increased especially since the mid 1990's.

2.1 Pesticide classification/application

Pesticides are classified according to their functions: insecticides control insects, rodenticides control rodents, herbicides control weeds and fungicides control fungi and so on. They have enabled farmers to produce some crops profitably in otherwise unsuitable locations, extend growing seasons, maintain product quality and extend shelf life (Copper and Dobson, 2007). Pesticide application refers to the practical way in which pesticides are delivered to their biological targets. Bateman (2003) reported that public concern about the use of pesticides has highlighted the need to make this process as efficient as possible in order to minimize their release into the environment and human exposure (including operators, bystanders and consumers of produce).

Nevertheless, these chemicals pose some risks if used improperly or used too frequently. Schillhorn (1999) in his review of agricultural pest managements noted that in Asia, pesticides are often sold through unlicensed dealers and shopkeepers. Some of these dealers may be familiar with agro-chemicals, but in many rural shops one may find pesticides sold next to food products such as milk or bread. Although the availability of pesticides in rural areas is important, the benefit of such availability has to be weighed against consumer safety, proper storage, and the need to educate farmers about proper use. He also stated that recent development of pesticide resistance in China and India is to a large extent the result of uncontrolled marketing to poorly informed farmers. However, there is insufficient data, to really assess the risk, especially of newer products. For example, it has been claimed that in certain parts of India, the daily food borne intake of pesticide residues is approximately 0.51 mg (Alam 1994). This is well above accepted levels, but the impact on public health and reproduction has not yet been fully investigated.

2.2 Biopesticide (plant extract)

Over the past 10 years, the rapid development of new techniques, such as molecular biology, genetic engineering, protein engineering and others are all gradually improving the biopesticides production (Gao, 2006). However, the field had developed excellent application prospects with extensive social and economical benefits. The superior characteristics of biopesticides attracted more attention than ever before and made them a hot spot of research in biotechnology institutions and companies. The research and application of biopesticides had been well developed and gradually replaced the highly toxic conventional synthetic

pesticides in the market. In recent years, production of conventional pesticides declined by 2% per year (Cheng *et al.* 2010), while biopesticides' output increased at the annual rate of 20%. In China, the research and application of biopesticides began in early 1950s. In 2005, the total demand for all kinds of biopesticides in China reached 145,000 tons, while the total sales were valued at about 0.8 to 1 billion yuan (Zhu, 2009). Zhu (2009) predicted that biopesticides could replace more than 20% of conventional chemical pesticides in the next 10 years. However, there were more than 30 research institutions and 200 biopesticide enterprises (about 2000 conventional pesticide manufacturing enterprises) in China, with annual production of approximately 100,000 tons (Cheng *et al.* 2010).

2.3 Nanopesticide

Nanomaterials of inorganic and organic origin are used for nanoparticles (NPs) synthesis by a variety of physical and chemical methods (Sasson *et al.*, 2007). According to the researchers, synthesis of NPs involve size reduction by top-down methods such as milling, high pressure homogenization and sonication while bottom-up processes involve reactive precipitation and solvent displacement (Attama, 2015). Among inorganic materials, metal oxide NPs such as, TiO₂, ZnO, AgO and MgO and others are of particular interest as they are physically and optically stable with tunable optical properties (Makhluf *et al.* 2005). It has been reported that Photocatalytic (TiO₂, ZnO) and microbiocidal (AgO and MgO) NPs are employed for pesticide degradation, detection and control food spoilage respectively (Baruah and Dutta, 2009). Chitin and Chitosan are naturally-occurring products with interesting antimicrobial and eliciting properties and their derivatives have been getting more attention in recent years. These products can be used in a number of ways to reduce disease levels and prevent the development and spread of pathogen, thus preserving yield and quality crop products (Badawy *et al.* 2005).

3.0 Pesticide application

According to United States Environment Protection Agency (E.P.A, 2008) the hundreds of application methods available can be categorized into three major groups such as sub-surface, surface and aerial applications.

3.1 Sub-surface application methods:

This method involves injecting the pesticide into the ground to control subterranean insects and other sub-surface methods such as incorporating the pesticide into the soil (Weselak et al, 2007). One example of this method is seed treatment. In this method pesticides are applied to the seeds prior to planting in the form of a seed treatment or coating to protect it against soil

borne risks to the plants. Additionally these coatings can provide supplemental chemicals and nutrients designed to encourage growth. Nwachukwu and Umechuruba (2001) reported that plant extracts have played significant role in the inhibition of seed borne pathogens such as *Fusarium oxysporium* and improvements of seed quality and emergence of plant seeds.

3.2 Surface application:

This method involves applying pesticides, repellants, and disinfectants directly to the surface. An example is application of pesticides to flour boards, leaf surface etc (Bateman, 2003).

3.3 Aerial application:

This is application of pesticides via aircrafts, back pack, spray booms to trees, row crops etc. This is one of the more common forms of pesticide application especially in conventional agriculture (Matthew and Thornhill, 1994; O'Sullivan et al, 2010).

4.0. Merits and demerits of different pesticides

4.1 Availability

Biospesticides are readily available to our farmers locally, for instance, the plant "neem" (*Azadiractha indica*) with its pesticidal potentials that is predominant in our environment (Thakore, 2006). A farmer that needs this neem plant extract can easily harvest the leaves and prepare the extract without much trouble unlike the synthetic pesticides that are mostly imported from abroad. The Federal Government of Nigeria recently had placed embargo on importation and use of these pesticides because of their negative effects on the environment thereby making these pesticides unavailable to the rural farmers when they are needed. Yar'adua (2007) stated that botanical pesticides are simple to prepare, locally renewable, user friendly and environmentally safe.

4.2 Efficacy

Several researchers have demonstrated the efficiency and efficacy of botanical extracts or biopesticides on the control of post-harvest rots in plant products (Onyeke and Maduwesi, 2006). Copping (2004) reported that the use of biospesticides usually have slow speed of action due to the characteristics of the biological active ingredients it contains. It usually follows a gradual stepwise action pattern that results in long term effective impacts on the pests.

However the use of synthetic pesticide unlike biopesticide results in rapid action against the pests. This rapid action lures farmers to use synthetic pesticide in pest outbreaks. Cornell University (2007) reported that pesticides sprayed in an effort to control adult

mosquitoes may temporarily depress mosquito population. However, they may or usually results in a large population in the long run by damaging the natural controlling factors. These secondary pest outbreaks or pest resurgence result in repeated control measures, thus, increasing input cost, high labour requirement, reduced yield etc. Muckenfuss *et al.* (2009) also reported that in a study comparing biological pest control and use of pyrethroid insecticide for diamond back moth, showed that the insecticide application created a rebounded pest population due to loss of insect predators, whereas biocontrol did not show the same effect. Thus, biopesticides are preferred because they are efficacious, retard onset of resistance and thus improve agricultural sustainability. Similarly, the insecticidal and anti-feedant properties of some botanicals have been documented and claimed comparable with conventional insecticides such as DDT, HZI and Carbary and no serious side effect have been reported (Oliver, 1986).

4.3 Affordability

The use of biopesticide is cheap and available to everybody especially our rural farmers who can handle its extraction and application. For instance, farmers can easily harvest the leaves of plants that have pesticide potentials available to them locally and extract them and use it as pesticides. The bio-pesticides provide a long-term protective effect on pests (Yar'dua, 2007; Cheng et al, 2010) and therefore, save the farmers the trouble of repeated application that could increase production costs. Synthetic pesticides on the other hand, are expensive and difficult to handle and also have adverse detrimental effects on environment and human health (Miller, 2004).

The benefits of nanomaterial based formulations are the improvement of efficacy due to higher surface area, higher solubility, induction of systemic activity due to smaller particle size and higher mobility and lower toxicity due to elimination of organic solvents in comparison to conventionally used pesticides and their formulations (Sasson *et al.* 2007; Chaudhari et al, 2011). In case of biopesticides, NPs can play a major role in enhancing the efficacy and stability of whole cells, enzyme and other natural products used.

Currently, there are increasing reports for resistance development to the prevalent groups of insecticides and fungicides that are applied for pest and pathogen control (Smith *et al.* 2008). In addition, the stringency of regulatory bodies like Central Insecticide Board (CIB, India), Food and Drug Administration (FDA, USA) though rightly, has increased for the registration of pesticides (Racke 2003). Other materials such as nano-clays and layered double hydroxides possess good biocompatibility, low toxicity and potential for controlled

release (Choy *et al.*2007). Controlled release for nano-clays was engineered by surface coating with different polymers that manipulated electrostatic interactions between the chemical load and clay particles (Lee and Fu 2003). It has been established that nano-clays protected the agrochemicals against Ultra Violet-degradation (El-Nahhal *et al.* 1999). In the case of hydrophobic chemicals, the arrangement prevented re-crystallization, increased solubility and therefore bioavailability.

5.0 Effects on the environment

Pesticides are the only group of chemicals that are purposely applied to the environment with the aim to suppress plant and animal pests and to protect agricultural and industrial products (Bocquene and Franco, 2005). However the majority of synthetic pesticides are not specifically targeting the pests only, rather during their application, they also affect non-target plants, animals and impact generally on the environment (Miller, 2004). The environmental impact of synthetic pesticides consists of the effects on non-target species. Many synthetic pesticides are not easily degradable, they persist in the soil, leach to groundwater and surface water and contaminate the environment. Repeated application leads to loss of biodiversity and increase pest resistance (Jiang et al, 2009). Depending on their chemical properties, synthetic pesticides can enter an organism, bioaccumulate in food chains and consequently influence human health (Fantke et al, 2012).

Public concern over the undesirable environmental effects of synthetic pesticides arose in the early 1960's with the publication of Rachel Carson, an American courageous woman and scientist. Her book, 'Silent Spring' was a landmark that pointed out the sudden dying of birds caused by indiscriminate spraying of synthetic pesticides (DDT). This changed the existing view on pesticides and stimulated public concern on their impact on health and the environment (Shegunova et al, 2007). Data on synthetic pesticide usage remain scattered and/or not publicly available especially in the rural areas and the common practice of incident registration in the western world is grossly inadequate in the rural areas for understanding the entirety of effects (Schefer et al, 2007). Some of these synthetic pesticides are characterised by a high persistence in the environment (depending on their chemical properties, their half life ranges from 7 to 30 years). They have low water solubility and thereby has the potential to accumulate in fatty tissue of living organisms including humans (Hildebrandt et al, 2009). However, the use of bio-pesticides unlike synthetic pesticide does not have any acknowledged effects or impact on the environment (Horrigan et al, 2002). This is likely, because of its natural state (nature doesn't affect nature) for God had created them in a way to

co-interact and influence each other positively, not otherwise. It also doesn't leave harmful residues for they are biodegradable unlike synthetic pesticides found persisting for long and leading to bioconcentration of organochlorine insecticide through terrestrial food chains, thus, affecting the biota along the food chain (Toan et al, 2007). The use of bio-pesticide unlike synthetic pesticides help to build up soil quality and high water retention in soils. This is probably because they are biodegradable without leaving harmful residues on the ecosystem (Hole et al, 2005). These bio-pesticides are ecologically friendly since they are materials that are sometimes even consumed directly as food.

The future of nanotechnology is uncertain due to many reasons, such as lack of public awareness, initial negative reaction of the public towards novel breakthroughs, lack of many of the requisite skills in public agricultural research organizations for this type of research and ill-equipped and somewhat hesitant regulatory structures to deal with these new technologies. Over 60 percent of the public feels that the food supply has become less safe in recent years. There is need to create sensible nanotechnology oversight policies that will help ensure the safe and sustainable application of nanotechnologies to climate change, food security, water purification, health care, and other pressing global problems. Given that the development of nanotechnology involves numerous scientific disciplines, it is clear that nanoscale products have been and will be used in agriculture for purposes of controlling disease vectors and urban pests control prior to a complete evaluation of exposure and risk. There is need for public awareness with this rapidly progressing technology to inform the public at large about the advantages of the nanotechnology. This will result in a tremendous increase in interest and discovery of new applications in all the domains. Choy (2007) predicated that by 2014, a projected \$2.6 trillion in global manufactured goods will incorporate nanotech, and this would usher in new industrial revolution. It has been reported that Nanotechnology enabled delivery of agriculture chemicals (fertilizers, pesticides, herbicides, plant growth regulators, etc.) with many nanoscale carriers, including encapsulation and entrapment, polymers and dendrimers, surface ionic and weak bond attachments and other mechanisms used to store, protect, deliver and release by control of intended payloads in crop production processes (Johnston, 2010). According to the researcher, one of the advantages of nanoscale delivery vehicles in agronomic applications is its improved stability of the payloads against degradation in the environment, thereby increasing its effectiveness while reducing the amount applied. This reduction helps address agricultural chemicals run-off and alleviate the environmental consequence. The nanoscale

delivery vehicles may be designed to “anchor” to plant roots or the surrounding soil structures and organic matter if molecular or conformational affinity between the delivery nanoscale structure and targeted structures and matters in soil could be utilized. Controlled release mechanisms allow the active ingredients to be slowly taken up, hence, avoiding temporal overdose, reducing the amount of agricultural chemicals used, and minimizing the input and waste. Under this arrangement, environmental consideration including precision farming can reduce pollution to a minimum.

6.0 Conclusion

Considering the advantages of bio pesticides over the synthetic pesticides in the control of pests and the detrimental effects of synthetic pesticides on human health and its environment, it is strongly recommended that the development of technologies for effective application of bio-pesticides in place of synthetic pesticides is likely to pave way for effective food security and safety. Consequently, nanomaterial based formulations have the benefits of improvement in efficacy due to higher surface area, higher solubility, induction of systemic activity due to smaller particle size and higher mobility and lower toxicity due to elimination of organic solvents in comparison to conventionally used pesticides and their formulations

Promising results and applications are already being developed in the areas of delivery of pesticides and plant genetic transformation. In an era of high demand for blemish-free food and high cost inputs, sustainable agriculture has only a slim margin to make profits while guaranteeing food supply to a growing population. Nanotechnology has the potential to revolutionize the existing technologies used in various sectors including agriculture in the near future. Its products can be used in a number of ways to reduce disease levels and prevent the development and spread of pathogen, thus promoting crop yield and quality of crop produce. As with any other technology, controversy surrounding nanotechnology is no exception in a heterogeneous society. Several concerns need to be addressed on different issues like food safety and beneficiaries of the technology. All people require food, and the policy makers have the responsibility to make the correct decisions for its adequate implementation and delivery. Therefore, it is high time that we strengthen research in this direction to gain long term benefits from nanotechnology. And more also, governments agencies should make a complex decision about the suitability of existing regulatory systems and determine whether new measures are needed for nanoparticles to be adopted into the market. Increasing agricultural productivity is necessary, but keeping in mind the damage to the ecosystem, therefore new approaches need to be considered. The use of nanomaterials for

delivery of synthetic and bio-pesticides is expected to reduce the dosage and ensure controlled slow delivery. Application of nanoparticles is anticipated to stabilize biocontrol preparations that will go a long way in reducing the environmental hazard. Nanotechnology, by exploiting the unique properties of nanomaterials, has developed nanosensors capable of detecting pathogens at levels as low as parts per billion

REFERENCES

- [1] Alam, G (1994). *Biotechnology and Sustainable Agriculture. Lessons from India.* Technical paper 103. Paris 1994; OECD Development Center.
- [2] Badawy, M.E.I, Rabea E.I, Rogge TM, Stevens C, Steurbaut W, Höfte M, Smagghe, G. (2005). Fungicidal and insecticidal activity of *O*-acyl chitosan derivatives. *Polymer Bull.* 54, 279–289.
- [3] Baruah S, Dutta J. (2009). Nanotechnology applications in pollution sensing and degradation in agriculture: a review. *Environ Chem Lett* ;7:161–204.
- [4] Bateman, R.P. (2003). Rational Pesticide Use: spatially and temporally targeted application of specific products. In: *Optimising Pesticide Use* Ed. M. Wilson. John Wiley & Sons Ltd, Chichester, UK. pp. 129-157.
- [5] Bowman D.M, Hodge G. A (2007). A small matter of regulation: an international review of nanotechnology regulation. *Columbia Sci. Technol. Law Rev.*, 8 (2007), pp. 1–32
- [6] Chaudhari Q, Castle L (2011). Food applications of nanotechnologies: an overview of opportunities and challenges for developing countries. *Trends Food Sci. Technol.*, 22, pp. 595–603
- [7] Cheng X.L, Liu C.J, Yao J.W (2010). The Current Status, Development Trend and Strategy of the Bio-pesticide Industry in China. *Hubei Agric. Sci.* 49: 2287-2290.
- [8] Choy J.H, Choi S.J, Oh J.M, Park T (2007). Clay minerals and layered double hydroxides for novel biological applications. *Appl Clay Sci*;36:122–32.
- [9] Cooper J, Dobson H (2007). The benefits of pesticides to mankind and the environment. *Crop Protection* 26: 1337-1348., Retrieved on February 25, 2011.
- [10] Copping L.G. (2004). *The manual of Biocontrol Agents*, 3rd Edition. British Crop Production Council (BCPC), Farnham, Surrey UK.
- [11] Cornell University (2007). *Toxicity of Pesticides. Pesticide Fact Sheets and Tutorial, Module 4. Pesticide Safety Education Program* (2007).
- [12] Council on Scientific Affairs (1997). *Education and Information Strategies to Reduce Pesticide Risks.* American Medical Association

- [13] Daly H, Doyen J.T, Purcell A'H (1998). Introduction to insect biology and diversity. 2nd edition. Oxford University Press, New York.
- [14] Ecobichon D.J (1996). Toxic effects of pesticides in Waasen, C.D. (ed): Cassrett and Doull's Toxicology. The basic science of poisons 5th ed. New York, Macmillan: pp. 643-689.
- [15] El-Nahhal Y, Nir S, Margulies L, Rubin B (1999). Reduction of photodegradation and volatilization of herbicides in organo-clay formulations. *Appl Clay Sci*; 14:105–19.
- [16] Environmental Protection Agency (2008). Pesticide Health and Safety. National Assessment of the Worker Protection Workshop, EPA The EPA and Food Security 2007; available at <http://www.epa.gov/pesticides/food/ipm.htm>
- [17] Fantke P, Friedrich R, Jolliet O (2012). Health impact and damage cost assessment of pesticides in Europe. *Environ Int* 49: 9–17.
doi:10.1016/j.envint.2012.08.001 PMID 22940502.
- [18] FAO (2008). Climate change: Implications for food safety. (available at <http://www.fao.org>)
- [19] Food and Agriculture Organization of the United Nations (2002). International Code of Conduct on the Distribution and Use of Pesticides. Retrieved on 2007-10-25.
- [20] Frost J, Sullivan Y (2009). The North American and Western European Biopesticides Markets Will Grow Strong Thanks to Chemical-free Crops, Date Published: 18th Nov. London.
- [21] Gao S.H (2006). Advent of nano-bio-pesticides. *Pesticides Market News*, pp. 2-3.
- [22] Gilden R.C, Huffling K, Sattler B (2010). Pesticides and health risks. *J Obstet Gynecol Neonatal Nurs* 39 (1): 103–10. doi:10.1111/j.1552-6909.2009.01092.x. PMID 20409108.
- [23] Graeme M (2005). Resistance Management Pesticide Rotation. Ontario Ministry of Agriculture, Food and Rural Affairs.
- [24] Johnston C.T (2010). Probing the nanoscale architecture of clay minerals. *Clay Minerals*, 45, 245-279.
- [25] Koirala P.S, Dhakal. PD Tamrakar A.S (2009). Pesticide application and food safety issue in Nepal.
- [26] Kuniuki S (2001). Effects of organic fertilization and pesticide application on growth and yield of field-grown rice for 10 years". *Japanese Journal of Crop Science* 70 (4): 530–540.

- [27] Makhluף S, Dror R, Nitzan Y, Abramovich Y, Jelnek R, Gedanken A (2005). Microwave-assisted synthesis of nano crystalline MgO and its use as a bactericide. *Advanced . Functional Mater*; 15:1708 15.
- [28] Matthews G.A, Thornhill EW (1994). *Pesticide Application Equipment for use in Agriculture*. FAO, Rome
- [29] Miller G.T (2002). *Living in the Environment (12th Ed.)* Belmont: Wadsworth/Thomson Learning.
- [30] Miller, G.T (2004). *Sustaining the Earth, 6th Edition*. Wadsworth/Thomson Learning.
- [31] Muckenfuss AE, Sheppard, BM, Ferrer ER 2009. Natural mortality of diamond back moth in coastal South Carolina Clemson University Coastal Research and Education Center.
- [32] Nair R, Varghese SH, Nair BG, Maekawa T, Yoshida Y, Kumar D.S (2010). Nanoparticulate material delivery to plants. *Plant Sci.*, 179, pp. 154–163.
- [33] National Park Services US Department of the Interior (2006). *Sequoia and kings Canyon National Park: Air Quality Airborne Synthetic Chemicals*.
- [34] Nwachukwu E.O, Umechuruba C.I (2000). Anti-fungal activities of some leaf extracts on seed borne fungi of Africa yam bean seeds, seed germination and seedling emergence. *Appl. Sci. and Enviro, Manage* 5(1): 29-32.
- [35] O’Sullivan C.M, Tuck C.R, Butler Ellis M.C, Miller P.C.H, Bateman R (2010). An alternative surfactant to nonyl phenol ethoxylates for spray application research. *Aspects of Applied Biology*, 99: 311-316.
- [36] Oerke E.C (2006). *Crop losses to pests. Journal of Agricultural Science*, 144: 31-43. Cambridge University Press
- [37] Oliver B.B (1986). *Medicinal plants of tropical West Africa*. Cambridge University Press. London p.325.
- [38] Onyeke C.C, Maduewesi J.N.C (2006). Evaluation of some plant extracts for the control of post-harvest fungal diseases of banana fruit in south-eastern Nigeria. *J. Phytopathology* 148: 351-355.
- [39] Prakash A, Rao J (1996). *Botanical pesticide in agriculture*. CRC Press New Delhi, Indian.
- [40] Racke KD (2003). Development and registration of pesticides with reduced risk characteristics. In: Voss G, Ramos G, editors. *Weinheim, Germany: Wiley-VCH*; p. 322–33.
- [41] Sasson Y, Levy-Ruso G, Toledano O, Ishaaya I (2007). Nanosuspensions: emerging novel agrochemical formulations. In: Ishaaya I, Nauen R, Horowitz AR, eds. *Insecticides*

design using advanced technologies Netherlands: Springer-Verlag; p. 1–32.

[42] Schillhorn TW (1999). *Agricultural Pest Management at a Crossroads: New Opportunities and New Risks*. The World Bank 1818 H Street N.W. Washington D.C. 1999; 20433, USA

[43] Smith K, Evans D.A, El-Hiti G.A (2008). Role of modern chemistry in sustainable arable crop protection. *Phil. Trans. R. Soc. B*;363:623–37.

[44] Thakore Y (2006) The Biopesticide Market for Global Agricultural Use. *Ind. Biotechnol.* 23: 192-208.

[45] US Environmental Protection Agency (2007). What is a pesticide? epa.gov. Retrieved on September 15, 2007.

[46] Weselak M, Arbuckle TE, Foster W (2007). Pesticide exposures and developmental outcomes: the epidemiological evidence. *J Toxicol Environ Health B Crit Rev* 10 (1-2): 41–80. doi:10.1080/10937400601034571. PMID 18074304.

[47] Yar'adua, A.A (2007). Potentials of biopesticides from neem tree (*Azadiracta indica* A. Juss). In sustainable pest and disease management in Nigeria. In *Medicinal Plants in Agriculture*. Proc. Akure-HumbottKellog 3rd SAAT Annual Conference 2007.

[48] Zhu C.H.X (2009). The Current Status and Development Trend of the Bio-pesticide Industry in China. *Bio-technol. Ind.* 3: 42-47.