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Review Article

NANOTECHNOLOGY FOR INSECT PEST CONTROL

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Abstract: Nanotechnology is a promising field of interdisciplinary research. It opens up a wide array of opportunities in various fields like insecticides, pharmaceuticals, electronics and agriculture. The potential uses and benefits of nanotechnology are enormous. These include management of insect pests through the formulations of nanomaterials-based insecticides. Traditional strategies like integrated pest management used in agriculture are insufficient, and application of chemical pesticides have adverse effects on animals and human beings apart from the decline in soil fertility. Therefore, nanotechnology would provide green and efficient alternatives for the management of insect pests in agriculture without harming the nature. This art is focused on traditional strategies used for the management of insect pests and potential of nanomaterials in insect pest control as modern approaches of nanotechnology.

The advances in science and technology in the last decades were made in several areas of insecticide usage. It includes either development of more effective and non-persistent pesticides and new ways of application, which includes controlled release formulation (CRF). The endeavors are direct towards the successful application of those compounds on crops and their efficacy and availability improvement and reduction of environmental contamination and workers exposure (Savary *et al*., 2006). In that line, new types of formulation were developed. One of the most promising is the use of micro and nanotechnology to promote a more efficient assembly of the active compound in a matrix in order to protect core materials from adverse reactions due to factors like air or light. An outcry is exhibited against the use of pesticides due to their hazardous effects on human as well as environment (Sparks *et al*., 2012). There is a great concern regarding the nonmaterial which have potential to exert hazardous effects on human and the environment and when we have a nano-pesticide, it becomes a double edged weapon. Nanomaterials need to be evaluated, so that this novel technology does not meet the same apprehensions and bottle-neck as faced by genetically modified crops (Gopal *et al*. 2012).

Keywords: Nanotechnology**,** insect control, nanopesticides, formulation.

Insect pest and their control

Insects are one of the biggest animal populations with a very successful evaluative history, once they can be found chiefly in all possible environments all over the world, and the number of species and individuals. Their success can be attributed to several important evolutionary aspects like wings, malleable exoskeleton, high reproductive potential, habits diversification, desiccation-resistant eggs and metamorphosis, just to name a few. On the

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other hand, many insects are vectors of many diseases, and many others damages crop plantations or wood structures, causing serious health and economic issues. In order to combat the numerous losses that are caused by insects on agriculture, several chemicals have been used to kill them or inhibit their reproduction and feeding habits. (Mogul *et al*. 1996).

Nanotechnology

According to Bhattacharyyal *et al.* (2010) the word "Nano" is developed from the Greek word meaning "dwarf". In more technical terms, the word "nano" means 10^{-9}, or one billionth of something. For example, a virus is roughly 100 nm in size. Naturally, the word nanotechnology evolved due to use of nanometer size particles (size of 1 to 100 nm). The potential uses and benefits of nanotechnology are enormous. These include agricultural productivity enhancement involving nanoporous zeolites for slow release and efficient dosage of water and fertilizer, nanocapsules for herbicide delivery and vector and pest management and nanosensors for pest detection. The atom by atom arrangement allows the manipulation of nanoparticles thus influencing their size, shape and orientation for reaction with the targeted tissues. It is now known that many insects possess ferromagnetic materials in the head, thorax and abdomen, which act as geomagnetic sensors. In this paper, our discussion is focused on nanoparticles in insects and their potential for use in insect pest management.

Leiderer and Dekorsy (2008) found that targeted nanoparticles often exhibit novel characteristics like extra ordinary strength, more chemical reactivity and possess a high electrical conductivity. Thus, nanotechnology has become one of the most promising new technologies in the recent decade. Nanoparticles possess distinct physical, biological and chemical properties associated with their atomic strength.

Nanoscale Materials and Their Application

In nature, living organisms from bacteria to beetles rely on nanometer-shaped protein machines that perform everything from whipping of flagella to flexing of muscles. Nanometer-sized carbon (carbon black) that improves the mechanical properties of tires, nanometer silver particles that initiate photographic film development, and nanometer particles that are the basis of catalysts critical to the petrochemical industry have contributed to commercial products for many years (Huck, 2008). Nanotechnology has already shown great potential for application in environmental protection (Nowack, 2009).

Natural Nanoparticles in Several Insects

Although naturally occurring nano-structures are being neglected, they are a potentially rich source of products that meet certain specifications (Watson and Watson, 2004). The emerging industries based on nanotechnology have so far made little use of 'free' technology available in nature (Ehrlich *et al*., 2008). A good example is the ordered hexagonal packed array of structures in the wings of cicada for instance, *Psaltoda claripennis* Ashton and termite for example, family Rhinotermitidae (Zhang and Liu, 2006). Studies have shown that the size of the nanoparticles may vary from 200 to 1000 nm. The structures tend to have a rounded shape at the apex and protrude some 150-350 nm out from the surface plane. These wing nanoparticles help in the aerodynamic efficiency of the insect. Isolated nanoparticles of insects have diameters of about 12 and 11 nm in abdomen with petiole and head with antennae, respectively. Nanostructure components are also present in compound eyes of insects. Wings of butterflies possess bright color components and these color components are nothing but nanoparticles. Recently, a novel photodegradable insecticide involving nanoparticles has been prepared (Guan *et al*., 2008).

Nanopesticides

Nanopesticides defines as any formulation that intentionally includes elements in the nm size range and/or claims novel properties associated with these small size range, it would appear that some nanopesticides have already been on the market for several years. Nanopesticides encompass a great variety of products and cannot be considered as a single category. Nanopesticides can consist of organic ingredients (e.g., a.i., polymers) and/or inorganic ingredients (e.g., metal oxides) in various forms (e.g., particles and micelles). The aims of nanoformulations are generally common to other pesticide formulations and consist in:

1- Increasing the apparent solubility of poorly soluble active ingredient

2- Releasing the active ingredient in a slow/targeted manner and/or protecting the active ingredient against premature degradation.

Nanoformulation are expected to

1- Have significant impacts on the fate of active ingredient

2- Introduce new ingredients whose environmental fate is still poorly understood (e.g. nanosilver).

3- The current level of knowledge does not appear to allow a fair assessment of the advantages and disadvantages that will result from the use of some nanopesticides.

It is clear that a great deal of work will be required to successfully combine analytical techniques that can detect, characterize (e.g., through size, size range, shape or nature, surface properties), and quantify the active ingredient and adjuvants emanating from nanoformulations, and also to understand how their characteristics evolve with time, under realistic conditions.

Polymers

Adak *et al*. (2012) recorded that amphiphilic copolymers, synthesized from poly (ethylene glycols) and various aliphatic diacids, which self assemble into nano-micellar aggregates in aqueous media, were used to develop controlled release (CR) formulations of imidacloprid [1-(6 chloro-3-pyridinyl methyl)-N-nitro imidazolidin-2-ylideneamine] using encapsulation technique. High solubilization power and low critical micelle concentration (CMC) of these amphiphilic polymers may increase the efficacy of formulations. Formulations were characterised by Infrared (IR) spectroscopy, Dynamic Light Scattering (DLS) and Transmission Electron Microscope (TEM). Encapsulation efficiency, loading capacity and stability after accelerated storage test of the developed formulations were checked. The kinetics of imidacloprid release in water from the different formulations was studied. Release from the commercial formulation was faster than the CR formulations. The diffusion exponent (n value) of imidacloprid, in water ranged from 0.22 to 0.37 in the tested formulations. While the time taken for release of 50 % of imidacloprid ranged from 2.32 to 9.31 days for the CR formulations. The developed CR formulations can be used for efficient pest management in different crops. When a commercial formulation for a practical field application is desired, it is very important to employ materials that are compatible with the proposed applications: environment friendly, readily biodegradable, not generating toxic degradation by products and low-cost. The use of several biopolymers, i.e., polymers that are produced by natural sources, which at the same time have good physical and chemical properties and still present mild biodegradation conditions, are an interesting approach to avoid the use of petrochemical derivatives that might be another source of environmental contamination. The common polymers (synthetic and natural ones) used in CRFs for insecticides application are listed in Table 1.

Table 1. Several examples of polymers often used in the nanoparticle production.

Polymer	Active compound	Nanomaterial	Reference
Lignin-polyethylene glycol-ethylcellulose	Imidacloprid	Capsule	Flores-Cespedes *et al.* (2012)
Polyethylene glycol	B-Cyfluthrin	Capsule	Loha *et al.* (2012)
Chitosan	Etofenprox	Capsule	Hwang *et al.* (2011)
Polyethylene	Piperonyl Butoxide And Deltamethrin	Capsule	Frandsen *et al.* (2010)
Polyethylene glycol	Garlic Essential Oil	Capsule	Yang *et al.* (2009)
Poly(acrylic acid)-b-poly(butyl acrylate) Polyvinyl alcohol Polyvinylpyrrolidone	Bifenthrin	Capsule	Liu *et al.* (2008)
Acrylic acid-Buacrylate	Itraconazole	Capsule	Goldshtein *et al.* (2005)
Carboxymethylcellulose	Carbaryl	Capsule	Isiklan (2004)
Alginate-glutaraldehyde	Neen Seed Oil	Capsule	Kulkarni *et al.* (1999)
Alginate-bentonite	Imidacloprid or Cyromazine	Clay	Fernandez-Perez *et al.* (2011)
Polyamide	Pheromones	Fiber	Hellmann *et al.* (2011)
Starch-based polyethylene	Endosulfan	Film	Jana *et al.* (2011)
Methyl methacrylate and methacrylic acid with and without 2-hydroxy ethyl methacrylate crosslinkage	Cypermethrin	Gel	Rudzinski *et al.* (2003)
Lignin	Aldicarb	Gel	Kok *et al.* (1999)
Lignin	Imidacloprid Or Cyromazine	Granules	Fernandez-Perez *et al.* (2011)

N-(octadecanol-1-glycidyl ether)-O-sulfate chitosan-octadecanol glycidyl ether	Rotenone	Micelle	Lao *et al*. (2010)
Polyethyleneglycol-dimethyl esters	Carbofuran	Micelle	Shakil *et al*. (2010)
Carboxymethyl chitosan-ricinoleic acid	Azadirachtin	Particlea	Feng and Peng (2012)
Chitosan-poly(lactide)	Imidacloprid	Particlea	Li *et al.* (2011)
polyvinylchloride	Chlorpyrifos	Particle	Liu *et al*. (2002)
Vinylethylene and vinylacetate	Pheromones	Resin	Wright (1997)
Glyceryl ester of fatty acids	Carbaryl	Spheres	Quaglia *et al*. (2001)
Poly(methyl methacrylate)-poly(ethylene glycol) Polyvinylpyrrolidone	Carbofuran	Suspension	Chin *et al*. (2011)
Anionic surfactants (sodium linear alkyl benzene sulfonate, naphthalene sulfonate condensate sodium salt and sodium dodecyl sulfate)	Novaluron	Powder	Elek *et al*. (2010)

The nanoparticles used in biopesticides controlled release formulations

The most popular shape of nanomaterials (Figure 1) that have been using in CRFs for biocides delivery are:

1- Nanospheres: aggregate in which the active compound is homogeneously distributed into the polymeric matrix

2- Nanocapsules: aggregate in which the active compound is concentrated near the center core, lined by the matrix polymer

3- Nanogels: hydrophilic (generally cross-linked) polymers which can absorb high volumes of water

4- Micelles: aggregate formed in aqueous solutions by molecules containing hydrophilic and hydrophobic moieties.

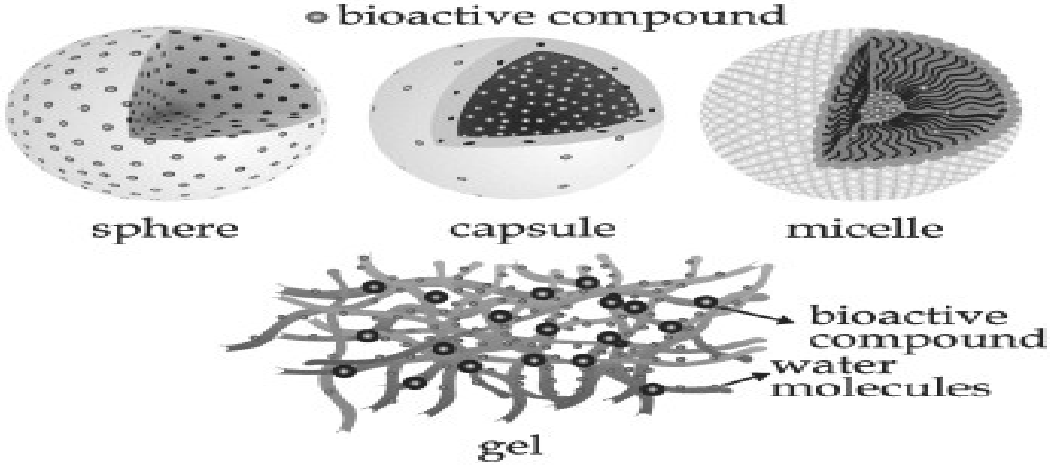

Figure 1. Morphological representation of different nanoparticles

Methods for Preparation of Nanomaterials Based on Controlled-Release Formulations (CRFs) For Biocides Application

According to Wilkins (2004) the methods for CRF (Controlled Release Formulations) preparation can be separated in chemical or physical ones (Figures 2 and 3, respectively). The chemical methods are based on a chemical bond (usually a covalent one) formed between the active compound and the coating matrix**,** such as a polymer. This bound can be placed in two different sites: in the main polymeric chain or in a side chain. In the first one, the new "macromolecule" is also called a pro-biocide, because the compound will get its properties in fact when it is released. In the second one, the insecticide molecule can bind initially to the side-chain of one monomer and then the polymerization reaction takes place or the polymerization occurs first and only after that, the biocide binds to the side chain.

There is still a third way, based on the intermolecular interactions. In this case, the biocide is "immobilized" in the net produced by the cross-linkages in the polymer. The physical methods can also be split in two distinct categories. In the first, a mixture of biocide and polymer is made.

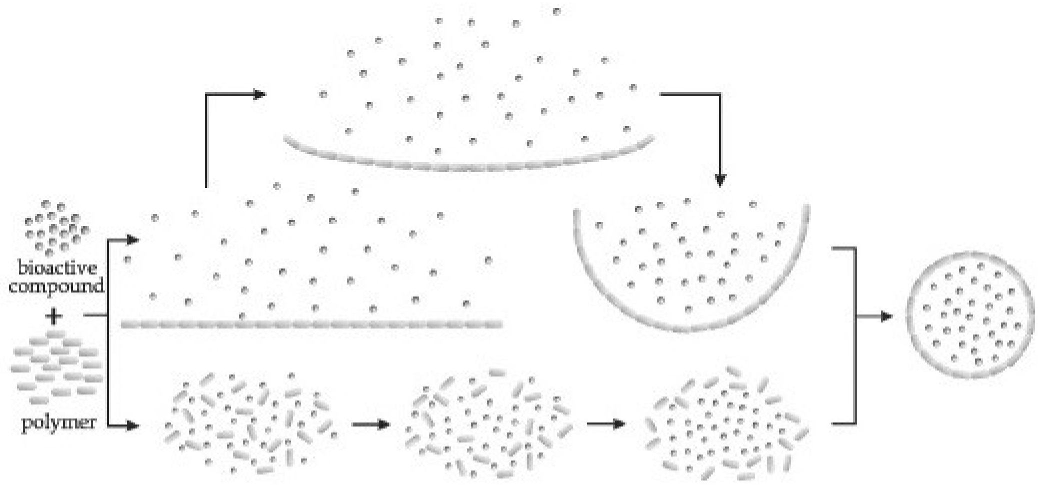

Figure 2. Physical methods for CRF preparation

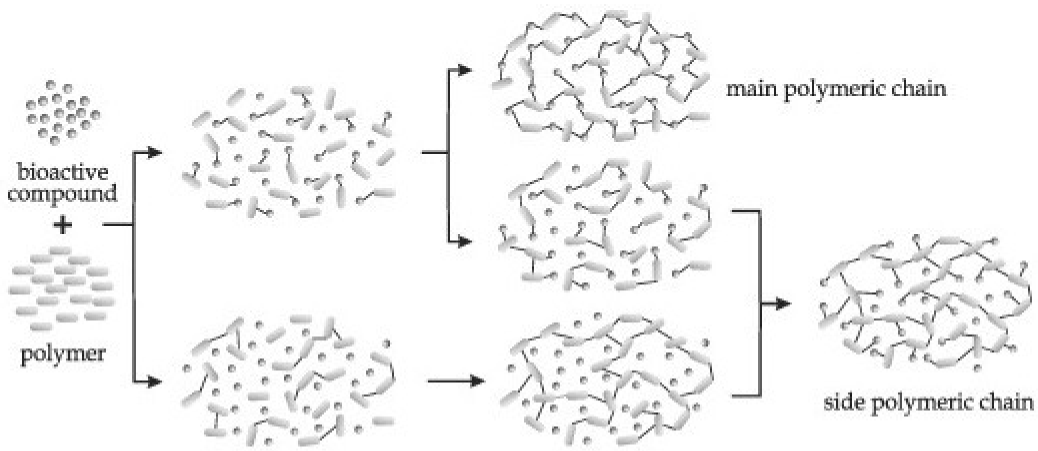

Figure 3. Physical methods for CRF preparation

In the other one, the polymeric chain forms a "membrane" isolating the bioactive compound from the external environment. This is the method which will produce the nanocapsules themselves. Although there are some different kinds of nanomaterials that can be used in CR formulations, the micro- and nanocapsules are by far the most widely used for controlled release of biocides.

Developing New Nanopesticides

Many attempts have been made to manage plague insects, for example, using biological control, which is very time consuming. Controlled release systems dawn in this scenario as a very attractive alternative in this battle field. Controlled release formulations (CRFs) associate the active compound with inert materials. The last ones are responsible for protecting and managing the rate of compound release into the target site in a defined period of time. The main purpose of controlled release systems is ruling the (bio) availability of the active compound after the application (Wilkins, 2004). Most of those controlled release biopesticides applications were and still are successfully made due to the advances in nanotechnology area. Nanomaterials-based formulations are known for some decades. The first microcapsule-based formulation became commercially available in the 1970s (Fanger, 1974). Nanocapsules have been widely used in medicinal area as drug carrier in treatment of diverse diseases (Radhika *et al.,* 2011), from tropical ones (Kuntworbe *et al*., 2012) up to cancer (Joshi *et al*., 2012). Microencapsulation has been used as a versatile tool for hydrophobic pesticides, enhancing their dispersion in aqueous media and allowing a controlled release of the active compound. As smart delivery systems, they confer more selectivity, without hindering in the bioactive compounds towards the target pathogen (Peteu *et al*., 2010). Other advantages of the use of nanoparticle insecticides are the possibility of preparing formulations which contain insoluble compounds that can be more readily dispersed in solution. It reduces the problems associated with drifting and leaching, due to its solid nature, and leads to a more effective interaction with the target insect. These features enable the use of smaller amount of active compound per area, as long as the formulation may provide an optimal concentration delivery for the target insecticide for longer times. Since there is no need for re-applications, they also decrease the costs), reduce the irritation of the human mucous-membrane, the phytotoxicity, and the environmental damage to other untargeted organisms and even the crops themselves (Margulis-Goshen and Magdassi, 2012). In a few words, nanotechnology can be applied in several ways in order to enhance efficacy of insecticides in crops.

Nanoencapsulation

Nanoencapsulation is a process through which a chemical is slowly but efficiently released to the particular host for insect pests control. Release mechanisms include dissolution, biodegradation, diffusion and osmotic pressure with specific pH (Vidyalakshmi *et al*., 2009). Encapsulated citronella oil nano-emulsion is prepared by high-pressure homogenization of 2.5% surfactant and 100% glycerol, to create stable droplets that increase the retention of the oil and slow release. The release rate depends upon the protection time; consequently a decrease in release rate can prolong mosquito protection time (Sakulk *et al*., 2009). Nanopesticides, nanofungicides and nanoherbicides are being used efficiently in agriculture (Owolade *et al*., 2008). Bhagat *et al.* (2013) stated that environment-friendly management of fruit flies involving pheromones is useful in reducing the undesirable pest populations responsible for decreasing the yield and the crop quality. Ananogel has been prepared from a pheromone, methyl eugenol (ME) using a low-molecular mass gelator. This was very stable at open ambient conditions and slowed down the evaporation of pheromone significantly. This enabled its easy handling and transportation without refrigeration, and reduction in the frequency of pheromone recharging in the orchard. Notably the involvement of the nano-gelled pheromone brought about an effective management of oriental fruit fly, *Bactrocera dorsalis*, a prevalent harmful pest for a number of fruits including guava.

Nanoparticles

The pediculocidal and larvicidal activity of synthesized silver nanoparticles using an aqueous leaf extract of *Tinospora cordifolia* showed maximum mortality against the head louse *Pediculus humanus* and fourth instar larvae of *Anopheles subpictus* and *Culex-quinque* fasciatus (Jayaseelan *et al*., 2011). Nanoparticles loaded with garlic essential oil are efficacious against *Tribolium castaneum* Herbst (Yang *et al*., 2009). Nanotube filled with aluminosilicate can stick to plant surfaces, while ingredients of nanotube have the ability to stick to the surface hair of insect pests and ultimately enter the body and influence certain physiological functions (Patil, 2009). Nanoparticles present possibilities for more efficient and effective control of pests, but our relative lack of information on how they act and how they can be contained are giving regulators pause before allowing their release into the environment (Khot *et al.* 2012). Nanopesticides hold promise for reducing the environmental footprint left by conventional pesticides.

Application of insecticides nanoformulations

Nanopesticides prepared according to (Gopal *et al*. 2011) of fungicides and insecticides, and compared their efficacy with the conventional products. Nano-hexaconazole was characterized by SEM, TEM, and FT-IR etc. and it was found to be less than 100 nm in size. Patent application on Nano-hexaconazole has been filed. Nanohexaconazole is five times more effective in controlling pathogens and nanosulfur is ten times more effective for control of mites as compared to its water dispersible powder (WDP) formulations. To ensure the materials, it was evaluated before launching. Casanova *et al*. (2005) evaluated the production of a nicotine carboxylate nanoemulsion using a series of fatty acids (C10 – C18) and surfactant. The oil-in-water nanoemulsion showed a monomodal distribution of size, with mean particle sizes of 100nm. The bioactivity of the insecticide formulations was evaluated against adults of Drosophila melanogaster by assessing the lethal time 50 (LT_{50}). They observed that the encapsulation efficiency decreased with increasing size of the fatty acids tested. The bioactivity followed the same trend, with better bioactivity when the chain length decreased.

Mechanism of nanoformulation Release

In the paper published by Kratz *et al*. (2012) the text begins with the statement: "Nanoparticles only start working after they are placed in a desired location". In other words, an efficient CR formulation must remain inactive until the active compound is released. The way how an inert material, such the nanopolymers, controlss the amount and rate a chemical is released is object of study since the late 1960's (Furmidge *et al*., 1968) and early 1970's (Allan and Neogi, 1972). How the release of the bioactive compound occurs depends basically on the chemical nature of the formulation. In various polymeric nanomaterials, the controlled release proceeds via diffusion. Fernandez-Perez *et al*., (1998) prepared a granule-based CRF constituted by lignin and imidacloprid. They measured the amount of compound released in water under a dynamic flow condition during a defined period of time. Some other polymeric nanomatrixes, especially those formed by a carboxylic acid and a metallic cation, can be disassembled when in contact with water, releasing the bioactive compound (Beasley and Collins, 1970). According to Allan *et al*. (1971) to the release takes place, a chemical interaction must be broken. It usually occurs via a hydrolysis reaction, what affects many polymer-insecticide bounds in a chain reaction. The release control depends on the strength of those chemical bounds, the chemical properties of both molecules and on the size and structure of the macromolecule formed.

Safety of Nanoinsecticides

Presentation was made in April 2010, at the EPA Pesticide Program Dialogue Committee (PPDC) meeting. The April 2010 OPP presentation included the following:

"Why is OPP (Office of Pesticide Programs) Concerned?

Potential Human Health Concerns:

1- Dermal absorption (so small they may pass through cell membranes)

2- Inhalation (go to the deep lung and may translocateto the brain i.e, could cross the blood brain barrier) Potential Environmental Concerns:

3- High durability or reactivity of some nanomaterials raises issues on the fate in environment

4- Lack of information to assess environmental exposure to engineered nanomaterials."

Special considerations for nanotechnology-based pesticides (NBPs) exposures

Alvarez-Roman *et al.* (2004) found that effects of dermal exposure to pesticides may be localized at the immediate area of contact or the pesticide may be absorbed into the bloodstream, depending on a variety of factors, most notably, whether or not the active ingredient or carrier is lipid soluble. After initial skin contact, a key question is whether NBPs would move through the stratum corneum and consequently exert effects on the lower dermal layers. Again, previous NP research can be informative. Multiple dermal exposure studies have focused on titanium dioxide, the results of which could be used for assessing dermal exposure to NBPs, including those that are formulated with functional carriers, such as sunscreens. Hillyer and Albrecht (2001) found that gastrointestinal uptake of nanoparticles has been documented in studies using mice, in which smaller particle size was correlated with higher uptake in the small intestine. Similar to other exposure routes, ingestion of NBPs could be problematic in both occupational and residential settings.

Recommendations to Assess Exposure to Nanotechnology- Based Pesticides

Mittal *et al.* (2010) reported that According to the Government Accountability Office, since 2007 the EPA has received a few applications for registration of various nanosilver pesticide preparations. Some of the applications have disclosed the fact the pesticide included nanomaterials, while in other cases the agency was able to determine the pesticide contained nanomaterials from the manufacturing processes. The EPA has registered at least one pesticide since 2007 without knowing it contained nanomaterials. Stone *et al*. (2010) found that, it is obvious that numerous studies and reviews will be required to address the exposure-related issues highlighted in this article. Fortunately, there are several lines of existing nanotechnology and pesticide research that are directly relevant to NBP exposure. While no single study will address all of the exposure-related concerns outlined above, it is evident that much of the prior research conducted on pesticides and nanomaterials would be applicable to characterize exposure to NBPs. The same authors reported also, some decisions that will likely need to be made include:

1- Whether completely new active ingredients that are synthesized as NBPs are amenable to existing tests and assessment

2- Whether data from conventional active ingredients that may be reformulated into NBPs are suitable for registration purposes

3- Whether NBPs should be regulated under a completely different framework

4- Whether a case-by-case approach that emphasizes a product and not a process should be used.

"EPA regulation of pesticides containing nanoscale materials"

Presentation was made in September 2010, at the meeting of the State Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) Research and Evaluation Group (SFIREG) Pesticide Operations and Management (POM) Committee. The September 2010 OPP presentation included an indication that EPA intends to require that nanoproducts be labeled in some fashion. Stone *et al*. (2010) stated that in the US, the EPA subjects new pesticides to regulation under the authority of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), which includes a review of applicants' physiochemical, efficacy, toxicity, and environmental tests. In addition to initial registration, a prescribed re-registration process occurs at scheduled intervals, intended to account for any new scientific information, use changes, and mitigation measures. Under FIFRA, pesticide registrants must submit data that allow the EPA to determine if the pesticide will be efficacious according to product claims and not pose unreasonable adverse effects on humans or the environment. In addition, when manufacturers become aware of adverse affects, they are required to report these to the EPA. In Europe, the main regulation concerning the use of pesticides is the European Directive 98/8/EC on biocidal Products.

Ethics and Potential Risks of Nanoscience

According to Larrouturou (2005) sense of ethics, reflecting man's desire to enable various generations to live together harmoniously and decently drives us to analyze the moral foundations of discoveries through open debate, turning the scientist back into a concerned citizen. In the field of nanoscience, the perspective of mastering complexity at a tiny scale is used sometimes as a fallacious argument based on fear. Even if ill founded, such negative attitudes must be taken into account: engaging in public debate about ethics is a moral obligation for scientists. A first step in this debate is undoubtedly measuring and recognizing the huge gap between our understanding of a few functions at the nanometric scale and the complexity of life.

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