The rapid developments in nanopesticide research over the last two years have motivated a number of international organizations to consider potential issues relating to the use of nanotechnology for crop protection. This analysis of the latest research trends provides a useful basis for identifying research gaps and future priorities. Polymer-based formulations have received the greatest attention over the last two years, followed by formulations containing inorganic nanoparticles (e.g., silica, titanium dioxide) and nanoemulsions. Investigations have addressed the lack of information on the efficacy of nanopesticides and a number of products have been demonstrated to have greater efficacy than their commercial counterparts. However, the mechanisms involved remain largely unknown and further research is required before any generalizations can be made. There is now increased motivation to develop nanopesticides that are less harmful to the environment than conventional formulations, and future investigations will need to assess whether any promising products developed are able to compete with existing formulations, in terms of both cost and performance. Investigations into the environmental fate of nanopesticides remain scarce, and the current state of knowledge does not appear to be sufficient for a reliable assessment to be made of their associated benefits and risks. A great deal of research will therefore be required over the coming years, and will need to include (i) the development of experimental protocols to generate reliable fate properties, (ii) investigations into the bioavailability and durability of nanopesticides, and (iii) evaluation of current environmental risk assessment approaches, and their refinement where appropriate.

© 2013 Elsevier Ltd. All rights reserved.

**Contents**

1. Introduction .............................................................. 225
2. Definition and scope .......................................................... 225
3. General trends ............................................................. 225
4. Latest research by type of nanopesticide ............................................................. 226
   4.1. Nanoemulsions ............................................................. 226
   4.2. Polymer-based nanopesticides ............................................................. 227
       4.2.1. Release and efficacy ............................................................. 228
       4.2.2. Towards “greener” nanopesticides? ............................................................. 228
   4.3. Hybrid nanoformulations ............................................................. 229
   4.4. Inorganic nanoparticles associated with an organic active ingredient ............................................................. 229
   4.5. Inorganic nanoparticles as active ingredients ............................................................. 229
       4.5.1. Silica ............................................................. 229
       4.5.2. Titanium dioxide ............................................................. 229
       4.5.3. Silver ............................................................. 229
       4.5.4. Copper ............................................................. 230
       4.5.5. Aluminum ............................................................. 230
5. Considerations concerning environmental fate ............................................................. 230
   5.1. Facilitated transport ............................................................. 230
   5.2. Bioavailability ............................................................. 231
   5.3. Release profile ............................................................. 231
       5.3.1. Release mechanisms ............................................................. 231
       5.3.2. Models used for nanopesticide release ............................................................. 232

* Corresponding authors.
E-mail addresses: melanie.kah@univie.ac.at (M. Kah), thilo.hofmann@univie.ac.at (T. Hofmann).

0160-4120/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.envint.2013.11.015
1. Introduction

Research into nanotechnology applications for use in agriculture has become increasingly popular over the past decade. The development of novel plant-protection products has received greater attention than other applications, such as those related to nanosensors or fertilizers.

Two complementary literature reviews have previously been published, presenting the knowledge available up to the end of 2011. Kah et al. (2013) integrated information from more than 3000 patents and 100 peer-reviewed publications and reports to provide an overview of the different types of nanopesticides that had been proposed. Possible fate and environmental impacts of nanopesticides were discussed in order to analyze the suitability of current regulatory exposure assessment. A complementary analysis focusing mainly on inorganic nanopesticides and fertilizers (based on 36 publications and 33 patents) has been presented by Gogos et al. (2012).

There has been a considerable amount of subsequent research in this field, and this paper aims to provide an update on the latest research presented in peer-reviewed publications since October 2011 (more than 40 papers in total, not included in previous literature reviews).

A number of issues relating to the definition of nanopesticides are first discussed, in order to define the scope of our analysis. General trends in the most recent research are then presented, followed by more detailed discussions on each specific category of products. The closing sections of the paper discuss a number of key aspects relating to environmental risk assessment for nanopesticides, and that have not been included in any previous literature reviews. The processes discussed are particularly relevant to polymer-based nanopesticides that have received a great deal of attention in recent years.

2. Definition and scope

It is important to distinguish the different ways in which the term “nanopesticide” is used within regulatory, scientific, public, and commercial frameworks, as the criteria that are applied in these different contexts typically vary with regard to, for example, particle size, activity, and the perceptions of novelty or risk. Issues relating to the definition of nanoparticle and how the criteria proposed to date could apply to nanopesticides have been previously discussed by Kah et al. (2013).

A definition based on size alone (i.e., most often 100 nm as upper size boundary, for instance in EU, 2011) is probably too simplistic as on one hand, a 100 nm upper size limit would exclude many recent nanoformulations, and on the other hand, microemulsions—which have been on the market since the beginning of the 1990s—would be included under such a definition when many would argue that microemulsions are unlikely to exhibit any significant nano-behavior.

The need for a regulatory definition of nanopesticides is becoming increasingly recognized. The recurrent question of whether nanopesticides are already on the market cannot be answered until a clear definition has been agreed. The US EPA is often considered to be the first regulatory authority to have recognized the issue of nanopesticides. The FIFRA Scientific Advisory Panel was consulted by the EPA concerning the evaluation of nanometal pesticide products (FIFRA-SAP, 2009), and in 2011 the EPA granted a conditional registration for the first nanosilvers pesticide (US-EPA, 2011). It is important to note, however, that the product registered is an antimicrobial agent designed for use in clothing, and not intended for application to crops.

A number of national and international organizations have recently considered potential issues relating to the application of nanotechnologies in the agriculture sector. The Food and Agriculture Organization of the United Nations, for example, recently published a report with the World Health Organization on nanotechnologies in the food and agriculture sectors (FAO/WHO, 2013). Nanopesticides were also on the agenda of the European Union’s Standing Committee on the Food Chain and Animal Health, under the section entitled “Phytopharmaceuticals – Plant Protection Products – Legislation” (SANCO, 2013). The International Union of Pure and Applied Chemistry has also been looking into generating some guiding principles to facilitate a harmonized ecological risk assessment framework for nanopesticides (IUPAC, 2013).

For this review we have decided to embrace a rather broad definition of nanopesticides in order to provide an overview of all the various products currently being discussed in scientific literature. It is envisaged that the information collected will provide useful support, if required, for any subsequent decision on a more restrictive definition of nanopesticides for regulatory purposes. We have herein considered nanopesticides to be all plant-protection products that (i) intentionally include entities in the nm size range (up to 1000 nm), (ii) are designated with a “nano” prefix (e.g., nanohybrid, nanocomposite), and/or (iii) are claimed to exhibit novel properties associated with the small size of their components. An overview of potential applications of nanotechnology within the pesticide of formulation sector, as well as definitions and illustrations for the different nanopesticide types (e.g., microemulsion, nanoeumulsions, nanodispersion) can be found in Kah et al. (2013).

3. General trends

Analysis of all relevant peer-reviewed literature published between 2000 and 2013 (about 90 peer-reviewed papers) revealed that the majority of publications originated from Asia (mainly from China and India, representing 28% and 20% of the total number of publications, respectively), followed by the United States (20%). About half (i.e., 55%) of the nanopesticides investigated were insecticides, followed by fungicides (30%) and herbicides (15%).

The high proportion of nanoformulations for insecticidal purposes can be at least partially explained by the fact that the active ingredients (AI) of many conventional insecticides have limited water solubility and thus require a delivery system for their application in the field.

Another clearly emerging motivation for insecticide-related research is the possibility of using alternative insecticide AIs that are less harmful to non-target organisms and may potentially reduce the development of resistances. Many of these alternative AIs are unstable and require protection against premature degradation, which can be achieved by nanoformulations. Target substances for use as AIs are mainly essential oils, including neem oil (Anjali et al., 2012; Jerobin et al., 2012; Xu et al., 2010), garlic essential oil (Yang et al., 2009), Artemisia arborescens L essential oil (Lai et al., 2006), and Lippia sidoides oil (Abreu et al., 2012). Nanodelivery systems for pheromones (Bhagat et al., 2013; Hellmann et al., 2011) and various plant extracts have also been proposed (e.g., capsaicin from chili peppers, Bohua and Ziyong, 2011; Lansiumamid B extract from the seeds of Clausena lanzium, Yin et al., 2012).

The motivation to develop nanotechnological formulations that are less harmful to the environment is also apparent from the types of nanocarriers used, with an increasing interest in biodegradable polymers of natural origins, as discussed further in Section 4.2.2.

With regard to the types of nanoformulation, the majority of papers (both overall and over the last two years) presented polymer-
based formulations, followed by nanometals (used alone as AI) and nanoemulsions (Fig. 1). Since some research groups have been particularly active and published whole series of papers on similar products, any trends based on the number of papers published should be interpreted cautiously as they may actually reflect the activities of only a small section of the research community.

During the last two years some authors have also suggested combining several strategies in order to develop hybrid formulations of increasing complexity such as the encapsulation of nanoemulsions (Jerobin et al., 2012) or liposome coating (Hwang et al., 2011; Kang et al., 2012). In view of the associated increased production costs that can be anticipated for such formulations they will need to exhibit significantly enhanced properties compared to other formulations, but this has yet to be demonstrated.

Overall, polymer-based nanoformulations seem to have the greatest potential for further development and practical application, judging by the number of related publications (from a wide variety of research groups) and their greater efficacy compared to commercial formulations. Polymer-based nanoformulations allow a wide range of objectives to be achieved, and also combined (e.g., slow release, protection against degradation, and low solubility of the AI), which makes them suitable for a large number of different applications.

Over the last two years, efficacy tests have emerged that include both field trials and comparisons with commercial formulations, providing valuable information for possible future developments. Attempts have also been made to characterize the products and evaluate their environmental fate. Data on fate and efficacy are summarized in Tables 1 and 2, and are further discussed for each category of products in the following section.

4. Latest research by type of nanopesticide

4.1. Nanoemulsions

The aim of nanoemulsions is generally to increase the apparent solubility of poorly soluble AIs, while keeping the concentration of surfactants lower than that in microemulsions (typically 5–10% of surfactant, compared to 20% in microemulsions).

Fig. 1. Number of peer-reviewed papers for each type of nanoformulation, published by October 2011 (in light gray, reviewed in Kah et al., 2013) and between October 2011 and October 2013 (dark gray, discussed herein).

Table 1

<table>
<thead>
<tr>
<th>Type and AI</th>
<th>Fate of the nanoformulation compared to that of a commercial formulation or the pure AI</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene glycol</td>
<td>Slower release in water than commercial formulation (e.g., for β-cyfluthrin, time for 50% release was 1.4–20.5 d and 4–5 d, respectively)</td>
<td>Adak et al. (2012); Kaushik et al. (2013); Loha et al. (2011, 2012); Pankaj et al. (2012); Sarkar et al. (2012)</td>
</tr>
<tr>
<td>Imidacloprid</td>
<td>More rapid release with increasing PEG molecular weight</td>
<td></td>
</tr>
<tr>
<td>Thiamethoxam</td>
<td>Slower release in soils compared to commercial formulation (time for 50% release was 3.5–6 d and 1.3 d, respectively)</td>
<td>Sarkar et al. (2012)</td>
</tr>
<tr>
<td>Carboburan</td>
<td>Enhanced photostability compared to commercial formulation (half-life of about 6 and 1 d, respectively)</td>
<td>Qing et al. (2013)</td>
</tr>
<tr>
<td>Thiram</td>
<td>Enhanced photostability compared to pure AI</td>
<td>Yin et al. (2012)</td>
</tr>
<tr>
<td>Beta-cyfluthrin</td>
<td>Weaker sorption than pure AI</td>
<td>Silva et al. (2011)</td>
</tr>
<tr>
<td>Thiamethoxan</td>
<td>Reduced volatilization compared to pure AI (prolonging activity from 3 to up to 33 weeks)</td>
<td>Bhagat et al. (2013)</td>
</tr>
<tr>
<td>Other polymers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Emamectin</td>
<td>Enhanced photostability compared to commercial formulation</td>
<td></td>
</tr>
<tr>
<td>Lansiumamide B</td>
<td>Enhanced photostability compared to pure AI</td>
<td></td>
</tr>
<tr>
<td>Paragquat</td>
<td>Weaker sorption than pure AI</td>
<td></td>
</tr>
<tr>
<td>Pheromones</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solid lipid nanoparticles</td>
<td>Decreased direct and indirect photodegradation compared to pure AI (relatively high losses still observed for the nanoformulation)</td>
<td>Nguyen et al. (2012a,b)</td>
</tr>
</tbody>
</table>

AI: active ingredient.
Nanoemulsions have received a great deal of attention from the pharmaceutical sector, for example as potential vehicles for transdermal delivery of hydrophobic drugs (Shakeel et al., 2012). Nanoemulsions of pesticidal AIs have often been suggested to increase the uptake of the AIs, but supporting data in the context of plant-protection products remains scarce. However, results from two recent studies support the hypothesis of enhanced uptake. In the first of these studies, experiments on a series of nanoemulsions of neem oil showed that the LC50 (the concentration required to achieve 50% mortality) (Kumar et al., 2013) decreased with droplet size, which was interpreted as indicating an increased uptake of the nanoformulated AI (Kumar et al., 2013). However, the authors acknowledged that additional adjuvants may be required to limit losses and increase adhesion to leaves under a range of weather conditions.

Nanoemulsions of permethrin (presented in Anjali et al., 2010) additionally decreased effects on non-target organisms (soil bacteria and plants), which was interpreted as indicating an increased uptake of smaller droplets. In the second study, the efficacy of nanoemulsions of neem oil showed that the LC50 (24 h) were 2.1 and 19.4 mg/L, respectively.

Nanoemulsions have been previously published. Papers in the second category explore polymer-based nanopesticides that may be required to limit losses and increase adhesion to leaves in order to ensure efficacy under a range of weather conditions.

Nanoemulsions of permethrin (presented in Anjali et al., 2010) were increased uptake of smaller droplets. In the second study, the efficacy of nanoemulsions of neem oil showed that the LC50 (24 h) were 0.006 and 0.022 mg/L, respectively.

Nanoemulsions of neem oil Cytotoxicity (human lymphocyte): alginate- starch-polyethylene glycol-formulations Jerobin et al. (2012)

Nanoemulsions have been previously published. Papers in the second category explore polymer-based nanopesticides that may be required to limit losses and increase adhesion to leaves in order to ensure efficacy under a range of weather conditions.

Nanoemulsions have been previously published. Papers in the second category explore polymer-based nanopesticides that may be required to limit losses and increase adhesion to leaves in order to ensure efficacy under a range of weather conditions.

Nanoemulsions have been previously published. Papers in the second category explore polymer-based nanopesticides that may be required to limit losses and increase adhesion to leaves in order to ensure efficacy under a range of weather conditions.

Nanoemulsions have been previously published. Papers in the second category explore polymer-based nanopesticides that may be required to limit losses and increase adhesion to leaves in order to ensure efficacy under a range of weather conditions.

Nanoemulsions have been previously published. Papers in the second category explore polymer-based nanopesticides that may be required to limit losses and increase adhesion to leaves in order to ensure efficacy under a range of weather conditions.

Nanoemulsions have been previously published. Papers in the second category explore polymer-based nanopesticides that may be required to limit losses and increase adhesion to leaves in order to ensure efficacy under a range of weather conditions.

Nanoemulsions have been previously published. Papers in the second category explore polymer-based nanopesticides that may be required to limit losses and increase adhesion to leaves in order to ensure efficacy under a range of weather conditions.

Nanoemulsions have been previously published. Papers in the second category explore polymer-based nanopesticides that may be required to limit losses and increase adhesion to leaves in order to ensure efficacy under a range of weather conditions.

Nanoemulsions have been previously published. Papers in the second category explore polymer-based nanopesticides that may be required to limit losses and increase adhesion to leaves in order to ensure efficacy under a range of weather conditions.

Nanoemulsions have been previously published. Papers in the second category explore polymer-based nanopesticides that may be required to limit losses and increase adhesion to leaves in order to ensure efficacy under a range of weather conditions.

Nanoemulsions have been previously published. Papers in the second category explore polymer-based nanopesticides that may be required to limit losses and increase adhesion to leaves in order to ensure efficacy under a range of weather conditions.

Nanoemulsions have been previously published. Papers in the second category explore polymer-based nanopesticides that may be required to limit losses and increase adhesion to leaves in order to ensure efficacy under a range of weather conditions.

Nanoemulsions have been previously published. Papers in the second category explore polymer-based nanopesticides that may be required to limit losses and increase adhesion to leaves in order to ensure efficacy under a range of weather conditions.

Nanoemulsions have been previously published. Papers in the second category explore polymer-based nanopesticides that may be required to limit losses and increase adhesion to leaves in order to ensure efficacy under a range of weather conditions.

Nanoemulsions have been previously published. Papers in the second category explore polymer-based nanopesticides that may be required to limit losses and increase adhesion to leaves in order to ensure efficacy under a range of weather conditions.

Nanoemulsions have been previously published. Papers in the second category explore polymer-based nanopesticides that may be required to limit losses and increase adhesion to leaves in order to ensure efficacy under a range of weather conditions.

Nanoemulsions have been previously published. Papers in the second category explore polymer-based nanopesticides that may be required to limit losses and increase adhesion to leaves in order to ensure efficacy under a range of weather conditions.

Nanoemulsions have been previously published. Papers in the second category explore polymer-based nanopesticides that may be required to limit losses and increase adhesion to leaves in order to ensure efficacy under a range of weather conditions.

Nanoemulsions have been previously published. Papers in the second category explore polymer-based nanopesticides that may be required to limit losses and increase adhesion to leaves in order to ensure efficacy under a range of weather conditions.

Nanoemulsions have been previously published. Papers in the second category explore polymer-based nanopesticides that may be required to limit losses and increase adhesion to leaves in order to ensure efficacy under a range of weather conditions.

Nanoemulsions have been previously published. Papers in the second category explore polymer-based nanopesticides that may be required to limit losses and increase adhesion to leaves in order to ensure efficacy under a range of weather conditions.
4.2.1. Release and efficacy

A group of researchers based in New Delhi (India), has been very active in developing and testing a series of insecticide formulations with polyethylene glycol (PEG) based amphiphilic copolymers (previously described in Shakil et al., 2010). Release of the AIs in water was significantly slower than from commercial formulations (and followed first order kinetics) for a variety of AIs including imidacloprid (Adak et al., 2012), thiamethoxam (Sarkar et al., 2012), carbofuran (Pankaj et al., 2012), thiram (Kaushik et al., 2013) and β-cyfluthrin (Loha et al., 2011). The release rates increased with increasing PEG molecular weight, potentially allowing the availability to be tuned to the optimum period. For instance, the release of β-cyfluthrin from the nanoformulation occurred over a period that ranged from 1 to 20 days (Loha et al., 2011), whereas release from a commercial formulation occurred within a period of 4–5 days (Loha et al., 2012).

Some of these PEG-based formulations have been demonstrated to perform more effectively than commercial products. For example, insect mortality bioassays by Loha et al. (2012) recorded an LC50 of 30–45 mg/L for the β-cyfluthrin nanoformulation and 125 mg/L for a commercial formulation. Similar results were also observed using carbofuran against root-knot nematodes, both in pots and in field trials (Pankaj et al., 2012). It is important to note that the greater efficacy of the nanoformulations relative to the commercial formulations was generally only noticeable over a relatively long time period (i.e., 30 days). The greater efficacy was thus probably mainly due to the slower release of the AIs, rather than to an increased uptake of the nanoformulated AIs by the target organisms.

Another formulation based on PEG (with acetophen as AI, Choudhury et al., 2012) was shown to have both a greater efficacy against target organisms and a lower toxicity to non-target organisms than its commercial counterpart (Pradhan et al., 2013). The greater efficacy could be explained by a slower rate of release and consequent protection of the relative halide AI, but as with the nanoemulsions (discussed in Section 4.1), the reasons for the lower toxicity to non-target organisms have yet to be elucidated.

4.2.2. Towards “greener” nanopesticides?

Many recent papers presenting new polymer-based nanoformulations have shared the common objective of developing less harmful plant-protection products through the use of biodegradable polymers and/or AIs of natural origin.

The types of polymers considered for nanopesticides are similar to those used in the pharmaceutical or cosmetic sectors, consisting mainly of polysaccharides (e.g., chitosan, alginites and starch), polyelectrolytes (e.g., poly-ε-caprolactone, and polyethylene glycol). During the last two years there has been an increase in the use of biodegradable materials of biological origin such as beeswax, corn oil, or lecithin (Nguyen et al., 2012a,b), or cashew gum (Abreu et al., 2012). In addition to being viewed as more eco-friendly, it is conceivable that such matrix materials, when associated with AIs of natural origin, could be considered for use in organic crop production. Many natural substances are known to exhibit pesticidal properties but they are generally rather unstable and require protection against premature degradation. A number of polymer-based nanoformulations in the form of nanospheres, nanogels, or nanofibers, have recently been proposed for this purpose.

4.2.2.1. Nanospheres. The pesticidal properties of lansiumamide B, a molecule extracted from kernels of C. lansium, have recently been discussed by Han et al. (2013), but the compound is difficult to dissolve in water and unstable in the environment. Yin et al. (2012) presented a polymer-based nanoformulation of lansiumamide B whose nematicidal activity was increased relative to that of the nonformulated compound. It remains unclear, however, whether the potential toxicity of the formulation ingredients (i.e., sodium dodecyl sulfate, N-amyl alcohol, petroleum ether and chloroform) was fully accounted for. Nevertheless, on the basis of disease progression and average numbers of rot knots, the performance of lansiumamide B (both formulated and nonformulated) exceeded that of a synthetic nematicide (ethophos, pure AI, Yin et al., 2012), demonstrating the potential usefulness of lansiumamide B.

4.2.2.2. Nanogels. Nanogels may be superior to nanospheres (or microspheres) because (i) they are insoluble in water and thus less prone to swelling or shrinking with changes in humidity (Bhagat et al., 2013), and (ii) they can significantly improve the loading and release profiles (limited the occurrence of bursts or potential leaks, Paula et al., 2011). Over the last two years, nanogels have been proposed for use in plant-protection products as a possible way to meet organic farming standards, with pheromones, essential oils, or copper as the AIs.

Pheromones are considered to be highly specific and eco-friendly biological control agents, but their deployment requires slow-release and protection from decomposition under ambient conditions. Bhagat et al. (2013) proposed the immobilization of pheromones within a nanogel (without using any potentially toxic chemicals such as crosslinkers or antioxidants). Evaporation of the pheromones in the nanogel was significantly reduced compared to the evaporation of the pure AI, extending their effectiveness for up to 33 weeks compared to only three weeks for the pure AI. Bhagat et al. (2013) also demonstrated the efficacy of the nanoformulation in an open orchard during an adverse season.

The efficacy of a nanogel formulation of essential oil extracted from L. sidoides (known to have fungicidal, bactericidal and larvicidal properties) was also shown to be superior to that of the free oil. Finally, Brunel et al. (2013) proposed the use of pure chitosan nanogels to improve the performance of antifungal treatments based on copper. Potential advantages of using a nanogel rather than a solution include easier handling, an improved distribution on the leaves, and the long-term release of copper onto leaves or into the soil with no loss of antifungal properties. Formation of the copper(II)–chitosan complex is pH dependent, and since most fungi tend to reduce the pH of their surrounding environment, Brunel et al. (2013) also suggested that the release of copper(II) may be triggered by the growth of the pathogen. When testing the formulations (over 7 days, in 96 well plate tests) a strong synergistic effect was observed between chitosan and copper in inhibiting the growth of Fusarium graminearum (Brunel et al., 2013). This effect is difficult to explain because the mechanisms involved in the antifungal activities of chitosan remain only poorly understood (Brunel et al., 2013).

4.2.2.3. Electrospun nanofibers. Electrospinning technology shows potential for scaling-up and for fulfilling the requirements of industrial production (Persano et al., 2013), and nanofibers obtained by electrospinning have recently been investigated for plant-protection applications. The potential advantage of such nanofibers over spheres or capsules lies in their ability to avoid the release bursts that occur when the AI is not homogeneously distributed within the polymer matrix (Xiang et al., 2013).

Hellman et al. (2011) demonstrated the possibility of efficiently incorporating pheromones into nanofibers made of polyamide or cellulose acetate (about 30 wt%), and of achieving an almost linear release over several weeks. The authors proposed that nanofiber webs could be distributed across the fields to be protected (quite similar to spider webs) in order to allow a uniform release of pheromones. A similar nanofiber network composed of poly(lactic acid) and cellulose nanocrystals has been presented by Xiang et al. (2013). The fibers loaded with thiamethoxam were efficient against whitefly over a 9 day period in a glass house experiment, at 50% of the recommended dosage for the pure AI (Xiang et al., 2013). Unfortunately, no comparisons with commercial formulations or with the pure AI were performed and it is therefore not possible to draw any conclusions on possible reductions in application rates.
4.3. Hybrid nanoformulations

Nanoformulations developed in the pharmaceutical sector have inspired researchers to explore the potential of more complex nanoformulations for the delivery of pesticides. Two examples using solid lipid nanoparticles and coated liposomes are presented below.

Solid lipid nanoparticles are increasingly being proposed as an alternative to polymeric nanoparticles for the formulation of pharmaceuticals (Pardeshi et al., 2012). Applications in the agrochemical sector remain limited, however, and only two formulations had been presented by 2011. A second-generation of lipid nanoparticles has recently been developed, incorporating liquid lipids into the solid matrix of solid lipid nanoparticles in order to increase the payload and avoid rapid leakage of the AI. Two papers have recently been published on the potential of such formulations to protect deltamethrin from photodegradation (Nguyen et al., 2012a,b). Both direct and indirect photodegradation were reduced for the formulated AI relative to the pure AI, but relatively high losses were still observed (e.g., after 24 h UV irradiation of deltamethrin in dry form, about 30–40% of the formulated deltamethrin remained compared to about 15% of the pure deltamethrin, Nguyen et al., 2012b).

The preparation of coated liposomes for the slow-release of insecticide was first described by Bang et al. (2009). Two studies have since tested the insecticidal efficacy of such formulations and demonstrated the prolonged or delayed activity of the nanoformulations relative to that of the pure AIs (Hwang et al., 2011; Kang et al., 2012). For instance, pure pyriproxyfen had its best lethal efficiency 2 days after treatment whereas for the nanoformulation it was 14 days after treatment (Kang et al., 2012). The authors suggested that simultaneous application of conventional and nanoformulated AIs (for immediate and delayed release, respectively) could reduce the required application frequency, and hence the labor costs. Further research is however required to evaluate whether large scale preparation methods can be cost effective for plant protection.

4.4. Inorganic nanoparticles associated with an organic active ingredient

Until recently, formulations in this category involved (i) using mesoporous silica as a carrier for slow release, or (ii) incorporating TiO₂ in a polymer matrix to catalyze the photodegradation of the organic AIs (Kah et al., 2013). Three new formulations have recently been proposed involving the use of silica (Mingming et al., 2013; Song et al., 2012) or calcium carbonate (Qian et al., 2011) nanoparticles as carriers, for the slow release of an organic AI.

All three of these nanoformulations were shown to increase the activity of the AIs, but no generalizations are yet possible due to the very different natures of the AIs investigated (i.e., an insecticide, a growth promoter, and a fungicide).

Both laboratory and field tests demonstrated that the insecticidal activity of chlorfenapyr associated with silica nanoparticles was twice as high as that of chlorfenapyr associated with microparticles (Song et al., 2012), but this observation may relate to the insecticidal properties inherent in the silica nanoparticles themselves (see Section 4.5.1 on silica).

Formulations with silica nanoparticles were also shown to improve the performance of a plant growth regulator when compared to results obtained using the pure AI. The mechanism involved is, however, different from that for the insecticide formulation described above and is probably related to the slow release (i.e., over 10–20 weeks) of an AI that is toxic when applied at high concentrations (Mingming et al., 2013).

Similarly, the prolonged activity of validamycin when formulated with calcium carbonate nanoparticles can be explained by the sustained release of the AI over 14 days (Qian et al., 2011).

4.5. Inorganic nanoparticles as active ingredients

4.5.1. Silica

Silicon has long been known to enhance plant tolerance of various abiotic and biotic stresses and silica nanoparticles have therefore naturally been suggested as potential candidates for increasing the control over a range of agricultural pests (Barik et al., 2008). Supporting experimental data remains limited but two papers have recently reported on the potential of nanosilica to control insects during grain storage. Deb Nath et al. (2011) observed higher insect mortality from treatment with silica nanoparticles (15–30 nm) than with bulk silica (100–400 nm). The similar efficacy of nanoparticles with different coatings (i.e., with no coating or with hydrophobic, hydrophilic, or lipophilic coatings) indicated a mechanical mode of action that could be enhanced for smaller particles. A second study, however, indicated that silica nanoparticles coated with 3-mercaptopropyltrimethoxysilane were more efficient than those coated with hexamethyldisilazane (Debnath et al., 2012), and in this case the effect was not related to size since the former nanoparticles (29–37 nm) were larger than the latter (15–20 nm). Further research is therefore required to elucidate the mode of action involved. The application rates were generally comparable with those recommended for commercially available diatomaceous forms (0.5–2 g/kg, Debnath et al., 2011), and hence the additional costs involved in engineering nanoparticles may not be justified by the slight (if any) increase in efficacy.

4.5.2. Titanium dioxide

The antimicrobial activity of titanium dioxide is well recognized and several studies have suggested that applying titanium dioxide to crops can suppress bacterial and fungal pathogens (e.g., Norman and Chen, 2011, and references therein). The antibacterial potential of photocatalytic nanoscale titanium dioxide has recently been tested. Nanoscale titanium dioxide was used, either alone or doped with silver or zinc, against the causal agent for bacterial spot disease in tomatoes (Paret et al., 2013b) and roses (Paret et al., 2013a). Greenhouse (Paret et al., 2013b) and field (Paret et al., 2013a) trials showed that using titanium dioxide/zinc could result in significantly reduced bacterial spot severity compared to using untreated controls. The overall efficacy was better than, or on a par with, the standard treatments for management of the diseases. Leaf phytotoxicity (affecting 5% to 10% leaf area) was observed after repeated applications, but this may be avoided by using electrostatic instead of conventional sprayers (Paret et al., 2013b). The main advantage of the titanium dioxide/zinc formulation presented is its potential to lower ecological and toxicological risks, compared to currently used copper-based treatments (at the application rates investigated).

4.5.3. Silver

Silver has long been known for its antimicrobial properties and several in vitro studies have demonstrated that nanosilver can significantly inhibit the growth of plant pathogens in a dose-dependent manner. The most recent study was by Kim et al. (2012) who demonstrated the in vitro activity of nanosilver against 18 plant pathogens.

While possible uses as coatings for fruit bags (Chun et al., 2010) or as treatments for cut flowers (Liu et al., 2009; Solgi et al., 2009) are conceivable, the application of nanosilver to crops that are likely to enter the food chain (on ryegrass, Jo et al., 2009; green onions, Jung et al., 2010; and green squash plants, Park et al., 2006) is more questionable.

Possible benefits of nanosilver over synthetic fungicides have been suggested (e.g., reductions in human toxicity, in plant protection related costs, and in pollution, Jo et al., 2009; Jung et al., 2010), but none have yet been demonstrated. It is important to note that the nanosilver pesticide that received conditional registration from the US-EPAs (2011) was designed for use in clothing, and therefore falls out of the scope of the present analysis on plant protection products.

In view of the cost of nanosilver, the uncertainties associated with its toxicity, the latest regulatory developments, and public perceptions, it is
unlikely that formulations of nanosilver for open field application will be developed any further. This conclusion is corroborated by the lack of recent publications on the subject.

4.5.4. Copper

Mondal and Mani (2012) reported that a nanoformulation of copper could suppress the growth of bacterial blight on pomegranate at concentrations of 0.2 mg/L, four orders of magnitude lower than that usually recommended for copper oxochloride (2500–3000 mg/L). This result can be compared to the only other nanocopper formulation discussed to date in peer-reviewed literature (a patent in Gogos et al., 2012), which exhibited an 8% increase in efficiency compared to a formulation of copper hydroxides salts currently in use. The tests by Mondal and Mani (2012) were carried out in vitro and no details of the formulation were provided. This comparison therefore highlights the importance of testing nanoformulations under a range of conditions that are as realistic as possible, and of providing the characteristics of the nanoformulations so that further comparisons can be made.

4.5.5. Aluminum

The application of nanostructured alumina dusts has been proposed to protect stored grains. Preliminary experiments showed insecticidal activity at rates comparable to those recommended for commercially available insecticidal dusts (Stadler et al., 2010). Stadler et al. (2012) further compared the activity of nanoalumina to that of the most effective diatomaceous earth formulation on the market. Results obtained for two insect species and at three humidity levels showed that nanoalumina was equally effective as, or more effective than the commercial formulation (Stadler et al., 2012). Nanoalumina may thus be a good alternative (or complement) to products based on diatomaceous earth. However, the mode of action of nanoalumina has yet to be elucidated and further research will be required to optimize the product in terms of the mineral composition of the dust and the type of formulation, in order to ensure efficacy for a range of insect species and under a range of environmental conditions.

5. Considerations concerning environmental fate

The effects that a nanoformulation has on the fate of an AI may be multiple and depend on the product under consideration. The objective of many of the nanoformulations presented in published literature is to achieve the slow release of an organic AI and/or to protect it from premature degradation. The data summarized in Table 1 show that a number of products have achieved this objective. Such nanoformulations are therefore expected to have a direct impact on the persistence of the AIs.

The possible effects of a nanoformulation on other environmental fate processes have rarely been considered. Determining the extent to which a nanoformulation will affect processes such as the transport, relocation, or bioavailability of an AI is critical to the development of a robust environmental risk assessment for nanopesticides.

Below we discuss a number of important processes and identify priorities for research on the basis of the current state of knowledge. A great deal of research has been carried out over the past decade into inorganic (mainly metallic) engineered nanoparticles, and the state of knowledge with regard to their fate and risk assessments have been regularly reviewed (e.g., Klaine et al., 2008, 2012). In contrast, we have focused on issues specific to organic nanocarriers, which have so far been relatively rarely considered. Polymer-based nanopesticides have received the most attention to date and can serve as a useful model with which to illustrate the issues discussed in the sections below. We thus consider a nanocarrier (NC) that is loaded with an AI (referred to below as “NC-AI”) and releases the free AI over time.

5.1. Facilitated transport

Sorption is a key process affecting the transport of pesticide AIs following their application. The only test that has been presented for sorption in soil was for a nanoformulation of paraquat, whose release in water occurred within 8 h (Silva et al., 2011). Batch tests were carried out on very small quantities of soil (0.01–0.05 g) over a period of 3 h. The sorption of the nanoformulated paraquat remained low relative to that of the pure AI, even after increasing the organic matter content and/or the quantity of soil. The authors concluded that the nanoformulation could greatly improve the availability of the herbicide during use, since sorption and degradation processes were reduced. This assumes that the NC-AI can be taken up directly, which has yet to be demonstrated (see Section 5.2 on bioavailability). The potential for enhanced transport into surface water and ground water also needs to be assessed.

One possible deleterious effect of an NC is that it may facilitate the transport of AIs that would otherwise be considered to be immobile (Fig. 2). The extent to which an NC can affect the transport of an AI can be assessed on the basis of concepts previously developed to evaluate the potential of particle-facilitated transport of contaminants (Hofmann and Wendelborn, 2007; Kretzschmar et al., 1999), and later applied to engineered nanoparticles (Hofmann and von der Kammer, 2009).

The desorption kinetics of the contaminant from the colloid (equivalent to the release of the AI from the NC) can be compared to the transport time scales by calculating the Damköhler number (Da) from $\text{Da} = \frac{\lambda \tau}{\text{Re} \cdot \text{Sc}}$, where $\lambda$ is a first-order rate constant for reaction (s$^{-1}$), and $\tau$ (s) is the mean residence time in the system (Jennings and Kirkner, 1984). It is generally accepted (Bold et al., 2003) that:

• for $\text{Da} > 100$, desorption (or release) occurs rapidly relative to the transport time scale. Conditions are said to be in equilibrium and facilitated transport can be neglected (Kretzschmar et al., 1999; Roy and Dzombak, 1998). The transport of nanopesticides in this category should be well described by classical solute transport models.

• for $\text{Da} < 0.01$, desorption occurs so slowly that the transport of the colloid (in this case, the NC) and contaminant (in this case, the AI) are said to be “decoupled”, meaning that two independent pools with different fate properties need to be considered: the dissolved pool (based on the properties of the AI properties and solute transport) and the attached pool (based on the NC properties and the colloid transport). Differences between solute and colloid modeling approaches and their applications within a regulatory context have been discussed previously in the context of nanopesticides (Kah et al., 2013).

• $0.01 < \text{Da} < 100$ implies kinetic conditions, for which desorption (or release) kinetics are needed to evaluate the transfer from the attached to the dissolved pools and consequent changes in behavior over the transport time scale.

Determining whether equilibrium, decoupled, or kinetic conditions apply is thus the first step in identifying situations in which facilitated transport of the AI by the NC can be ignored (equilibrium conditions), and in determining which modeling approach to adopt in other situations. When assessing the transport of nanopesticides following their application, the first step should therefore be to characterize the release profiles that are likely to occur under field conditions. Release mechanisms, methods, and models available are discussed further Section 5.3.

The reasoning used (based on the release kinetics) can also be applied to other fate processes. For instance, if the complete release of the AI from the NC occurs much more rapidly than the degradation processes, the impact of the nanoformulation on degradation is likely to be negligible. In contrast, if release and degradation proceed over similar time scales, the overall persistency of the AI will depend on the release rate, the persistency of the released AI, and the persistence
of the AI in the NC-AI form. The assumption that the NC-AI is not bioavailable or subject to any degradation processes has yet to be demonstrated.

5.2. Bioavailability

Polymer formulations are known from extensive research on pharmaceutical drugs to be able to increase the bioavailability of an AI (Vrignaud et al., 2011) by, for instance, enhanced permeation through the skin (e.g., for chitosan-based formulations, Ammala, 2013).

A number of nanoformulations have been shown to be more effective than either the pure AI or commercial formulations (see Table 2). This could possibly be the result of a higher bioavailability and increased uptake of the NC-AI, compared to the AI. While an increased uptake by the target organisms is desirable, it needs to be achieved without increasing the risk to non-target organisms (including handlers and bystanders).

The bioavailability of the NC-AI certainly depends on the carrier properties and cells/organisms considered. In view of the relatively large sizes of many of the NC-AIs reported to date, direct uptake is, in most cases, unlikely to occur. Studies that reported increasing efficacy or toxicity subsequent to the release of the AI have also suggested that the NC-AI has a limited bioavailability.

There is, however, as yet no information available on any investigations into the bioavailability of nanopesticides. Considering the AI loaded onto the NC to be completely unavailable may be too simplistic, as more subtle processes may be involved. It has, for instance, been shown that chitosan (a polysaccharide frequently used as a polymer carrier for nanopesticides) can change the enantioselective bioavailability of the chiral herbicide dichlorprop (Wen et al., 2010). Qing et al. (2013) has also suggested that protection of the AI against photodegradation is highly dependent on its location/distribution within the polymeric matrix. The bioavailability may likewise depend on the location of the AIs within the polymer matrix. It is, for example, conceivable that soil microorganisms could have access to those AI molecules located at the surface of the NC but not to those located in the core.

Understanding the dependency of bioavailability on the nanoformulation characteristics and on the organisms involved would be extremely useful when attempting to explain the differences in efficacy or toxicity observed to date for different types of nanopesticides and for different organisms (target vs. non-targets, e.g., Kumar et al., 2013; Pradhan et al., 2013).

An improved characterization of the distribution and release of the AI under a range of conditions is a prerequisite to answering the remaining key questions concerning bioavailability.

5.3. Release profile

The above sections on transport (Section 5.1) and bioavailability (Section 5.2) illustrate the importance of determining the release profiles of the AI from the NC. Characterizing the durability of the NC-AI is essential for assessing the environmental fate of nanopesticides, in both scientific and regulatory contexts. We present below a brief overview of the mechanisms and models previously developed in the pharmaceutical sector, and their recent application for, and relevance to, nanopesticides.

5.3.1. Release mechanisms

The published literature on pharmaceutical delivery systems based on biodegradable polymers indicates that the release mechanisms can be controlled by diffusion and/or dissolution (erosion), depending on the polymer properties, the way the AI is distributed, and the AI loading and solubility. Furthermore, for a polymer matrix that is subject to swelling and dissolution (i.e., hydrophilic polymers), the thickness of the gel-layer formed will influence the diffusion pathways and thus alter the release behavior (Kaunisto et al., 2013).

The processes leading to polymer degradation are thus expected to greatly influence the release profiles. In this context, Kim and Pack (2006) distinguished two categories of polymer carriers, these being surface-eroding polymer spheres and bulk-eroding polymer spheres. Surface-eroding polymers are typically hydrophobic, resist water penetration into the polymer bulk, and can degrade rapidly at the polymer/water interface through hydrolysis. Release of the AI therefore occurs...
5.3.2. Models used for nanoparticle release

During the past two years there has been a marked increase in the number of attempts to understand the mechanisms of release, and to determine whether release is governed by desorption from the surface, diffusion through the polymeric matrix, and/or erosion of the polymeric structure. The most common approach has involved fitting release curves using mathematical models previously developed for pharmaceuticals (see reviews by e.g., Delfour, 2012; Kaunisto et al., 2011).

The semi-empirical power model described by Ritger and Peppas (1987) has, for instance, been widely used to identify the types of mechanisms involved in the release of pharmaceuticals from nanocomposite systems, and has recently also been applied to nanopesticides (Abreu et al., 2012; Grillo et al., 2012; Kaushik et al., 2013; Loha et al., 2011). This model is appropriate in situations where more than one mechanism is involved, such as a combination of diffusion (Fickian transport) and Type II (non-Fickian) transport, controlled by relaxation of the polymer chains. The value of the exponent can reflect the type of release mechanism: \( n < 0.43 \) indicates a Fickian diffusion mechanism, and \( n > 0.85 \) indicates that release is governed by relaxation processes. Intermediate values (0.43 < \( n < 0.85 \)) suggest anomalous behavior, with non-Fickian release kinetics and a combination of diffusion and relaxation of the polymeric chains. Model fits of the release profiles for nanopesticides in water have indicated both Fickian (Abreu et al., 2012) and non-Fickian (Grillo et al., 2012; Silva et al., 2011) release mechanisms. Non-Fickian behavior has also been observed for AI releases measured in soils (Sarkar et al., 2012).

Xiang et al. (2013) carried out a series of experiments with nanofibers, specifically aiming to distinguish diffusion and degradation controlled release mechanisms using the Higuchi equation (applicable when polymer swelling and dissolution are negligible). Diffusion-controlled release of the AI was significantly influenced by the hydrophobicity of the nanocomposite and followed Fickian kinetics, whereas the concomitant degradation-controlled mechanism followed zero-order, time independent, Case II kinetics (\( n = 1.0 \)). Increasing the cellulose nanocrystal content in the fibers increased the fiber degradation rate and the AI release rate.

Other models commonly applied include linear models (e.g., Bhagat et al., 2013; Hellmann et al., 2011; Jerobin et al., 2012; Nguyen et al., 2012b), first order kinetic models (e.g., Adak et al., 2012), and second order kinetic models (e.g., Hussein et al., 2009, 2010).

Recently published data indicate that release of the pesticide AI will frequently be driven by a combination of desorption from the surface, diffusion through the polymeric matrix, and/or degradation of the polymeric structure. A large number of factors are thus expected to exert a strong influence on the release profiles, both before and after the application of nanopesticides in the field.

5.3.3. Factors affecting release

A number of polymer characteristics have been shown to influence release profiles, including the length of the polymer chains (Loha et al., 2012; Sarkar et al., 2012), the ratio of gum to chitosan (Abreu et al., 2012), and the cellulose nanocrystal content (Xiang et al., 2013). As the particle size decreases, the surface area to volume ratio of the particle increases and thus the flux is expected to increase (Kim and Pack, 2006). More rapid release with decreasing size has been demonstrated for a number of nanopesticide formulations (e.g., for a nanosilica–naphthylacetic acid formulation, Mingming et al., 2013). This casts doubt on the relevance of designing very small carriers (with more rapid release rates than larger carriers), when the objective of a formulation is to achieve prolonged activity over a period of weeks or months.

Environmental factors such as the chemistry of the soil solution or the presence of soil particles and microorganisms, may also influence release profiles. The pH was suggested to have a strong influence on the nanoformulation presented by Brunel et al. (2013), but no data are yet available for other factors.

Release profiles reported in literature published to date were almost exclusively determined in deionized water using dialysis (Abreu et al., 2012), filtration (Nguyen et al., 2012b), two-compartment models separated by a cellulose membrane (1000 Da, Grillo et al., 2012), and centrifugation (Qian et al., 2011).

Separating nano-scale polymer spheres (whose density is close to that of water) can be challenging and it is essential that the separation methods are properly validated in order to prevent experimental artifacts. This is unfortunately rarely in the case of AI.

One study compared release rates in artificial soil solutions with those in distilled water and showed that a slightly faster release occurred in the former (Khan et al., 2007). A recent study has also reported the release profile of a nanoformulation in soil (Sarkar et al., 2012). A commercial formulation and nanoformulation of thiamethoxam were wrapped in parchment paper and incubated for 30 days in a sandy loam. Soil samples were regularly extracted with organic solvent to determine the amount of AI transferred to the soil (Sarkar et al., 2012). The release from the nanoformulation was found to be slower than that from the commercial formulation, but no comparison with data obtained in deionised water was available and it is not entirely clear how possible losses were accounted for.

Finally, the possibility that a proportion of the AI may remain associated with the NC for extended periods should also be considered, as has been observed for some pharmaceutical formulations from which the release of a proportion of the AI was triggered by severe degradation of the polymer matrix. However, release curves are usually plotted against the total amount of AI released, which does not allow comparisons to be made with the total amount of AI initially loaded onto the NC. Grillo et al. (2012) showed that large differences could be observed in the release profiles for fairly similar compounds and that, over five days, the release efficiency ranged from 19% to 57% depending on the compound (i.e., ametryn, atrazine, or simazine). Release curves suggested that a plateau was close to being achieved, therefore indicating that some of the AI may be “entrapped” within the polymeric matrices for longer periods.

Characterizing release profiles is critical for assessing the fate of nanopesticides and there is an urgent need to develop robust methodologies for deriving more realistic release profiles.

5.4. Characterization and fate of the carrier

Most of the research to date on the fate and effects of engineered nanoparticles has focused on pristine materials (as manufactured), but the importance of transformation processes and the effects that they have on fate and toxicity are being increasingly recognized (e.g., Hueffer et al., 2013; Liu et al., 2013; Lowry et al., 2012; Zhang et al., 2012).

A number of chemical, physical, and biological transformations are known to have an important influence on the characteristics and behavior of metal engineered nanoparticles. The same processes are
expected to apply to nanopesticides. Characterizing and predicting these changes remain challenging as (i) they depend on the solution conditions (e.g., pH, redox state), (ii) many transformation processes are dynamic but not fully reversible, and (iii) multiple transformations can occur simultaneously (Lowry et al., 2012).

When considering polymer-based NC, investigations into the biodegradation of synthetic polymers in the environment may form a useful basis for identifying transformation processes likely to occur following application (see the reviews by Eubeler et al., 2009; 2010). A number of analytical methods have been developed over the last decade (e.g., liquid chromatography with mass spectrometry, and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry) and data is now available for a wide variety of polymers originating mainly from packaging material (e.g., polyesters). It remains, however, very difficult to predict how fast and by which mechanisms polymer NCs consisting of complex mixtures will be eliminated following their release into the environment.

Most of the materials recently used as NCs are unlikely to lead to serious environmental issues. Much attention has focused on polymeric NCs derived from polysaccharides, lipids, and various natural biodegradable polymers, which are likely to be easily degraded and produce metabolites that are of little concern.

Understanding how the characteristics of an NC evolve with time is, however, necessary in order to assess the fate of the AI when decoupled and kinetic conditions apply (see Section 5.1 on transport). It is also important for real applications in order, for instance, to ensure a practical shelf life or to support the selection of the most suitable NC for field applications. Hellman et al. (2011) discussed the advantages and drawbacks of two possible strategies for the future development of electrosprun nanofibers. The first was to use high strength polymers (e.g., polyamides), which do not decompose during the growth period. For the formulation discussed in Hellman et al. (2011), accumulation on the top soil layer should not be a problem considering the small quantities of polymer required (i.e., 1 g/ha). The second strategy was to use biologically-based (e.g., cellulose derivatives) or biodegradable polymers, with the possible disadvantage of exposing non-target organisms (including human bystanders) to rod-like fiber segment generated by degradation.

Possible changes in the characteristics of NCs following application have only relatively rarely been discussed. Attempts to characterize nanopesticides are becoming more common and recent papers generally report their size distributions, polydispersity indices, and zeta potentials. However, measurements are commonly carried out on the pure nanoformulation (sometimes diluted with deionised water), and thus only provide limited information concerning the relevant characteristics for assessing environmental fate.

Gaining an insight into the characteristics of nanopesticides under environmental conditions involves a number of analytical challenges (Kah et al., 2013). A great deal of research effort will be required to (i) develop and validate suitable analytical methods and experimental protocols prior to (ii) characterizing nanopesticides over time and under a range of conditions. These are essential prerequisites for assessing the benefits and risks resulting from the use of nanopesticides.

6. Conclusions

The rapid developments in nanopesticide research over the last two years have motivated a number of international organizations to consider potential issues relating to the use of nanotechnology for crop protection. This analysis of the latest research trends provides a useful basis for identifying research gaps and future priorities.

• Polymer-based formulations have recently received the greatest attention, while research into the application of more classical engineered nanoparticles (e.g., nano silver) for plant protection purposes has generally slowed down. Polymer-based delivery systems appear to be the most promising for the target release of AI, and are thus expected to receive the most attention in the future.

• Earlier analyses have pointed out the lack of knowledge on the efficacy of nanopesticides. In the last two years, investigations have been carried out to address the knowledge gap, including field trials and comparisons with commercial formulations. A number of nanopesticides have been demonstrated to have greater efficacy than their commercial counterparts, in some cases combined with a lower toxicity to non-target organisms. The mechanisms involved, however, remain largely unknown and further research is required before any generalizations can be made.

• There are now increasing incentives to develop nanopesticides that are less harmful to the environment than conventional formulations. This has been achieved by considering AIs from natural origins (e.g., pheromones, essential oils) and/or potentially safer adjuvants (e.g., the use of biodegradable polymers from natural origins, and the avoidance of surfactants). Most of those promising products are at a very early stage of development. Future investigations will need to assess whether they are able to compete with existing formulations, in terms of both cost and performance.

• Investigations into the environmental fate of nanopesticides remain scarce, and have generally only focused on the particular processes targeted by the formulation (e.g., degradation, in a formulation aiming to protect the AI from premature degradation). Possible unintended changes have generally not been considered. The current state of knowledge does not appear to be sufficient for a reliable assessment to be made of the benefits and risks associated with nanopesticides. A great deal of research will therefore be required over the coming years, and will need to include (i) the development of experimental protocols to generate reliable fate properties, (ii) investigations into the bioavailability and durability of nanopesticides (e.g., release profiles, and aggregation behavior under realistic conditions), and (iii) evaluation of current environmental risk assessment approaches, and refinement where appropriate.

References


Kainu T, Shikal NA. Evaluation of AAPS Phosphoric Acid NaNS-036018. 10.1080/17458080903531013.


