New pesticide molecules, formulation technology and uses: Present status and future challenges

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ABSTRACT

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Mankind has a history of using crop protection products from non-selective, naturally occurring compounds to highly specific synthetic and biological materials for assured food production and protection of environment since long time. There is a sequential rise in the production and consumption of pesticides in India during the last three decades. Researches are going on to develop safer molecules which could undergo photo-degradation, microbial degradation as well as chemical degradation leaving very less amount of residues in the environment. Conventional pesticide formulations like WP, EC etc are endangering human health and polluting environment. Newly developed modern formulations like water emulsifiable gel, floating granules, drift less dust, macro and micro encapsulated suspension, hollow fibers, monolithic matrix, laminated structures etc can avoid these problems. The prime motto for these developments is to give protection to the crops along with safety to the natural enemies of different pests as a whole safety to environment.

Introduction

Since the dawn of time mankind has had two primary goals obtaining enough food to survive and improving the quality of life. The single most important task facing a society is the production of food to feed its population. A country or society has to feed its people before it can devote resources to education, arts, technology or recreation. In some areas of the world this remains the primary focus of the entire population, producing or accessing food to feed its people. In these countries food can account for over 60% of annual income needs. Today, more than 60% of our population is involved in agriculture, producing enough food for not only our population, but for others around the world. A basic reason for our ability to increase our productivity is our ability to control pests - weeds, insects and pathogens using crop protection products.

Many in our society feel that we have only been using pesticides over the last few decades. In fact, mankind has a history of using crop protection products in the production of our food supply and protection of our environment.

History of pesticide use

Throughout history we have seen the evolution of pest control products from non-selective, naturally occurring compounds

to highly specific synthetic and biological materials that control only specific pests.

Early use patterns showed that most pest control products were naturally occurring and basic poisons. They were non-selective in nature, persistent and toxic to many forms of life. Insecticides included arsenic, lead and fluoride. Herbicides included ashes, salts, and smelter sludges. Fungicides included chalk, woodash and sulphur.

During 1800 century Insecticides included botanicals, nicotine, rotenone and pyrethrums. These products were more specific in terms of control, but not very stable for use in agriculture given rapid breakdown in the environment. It was the century where disease control using sulfur and copper compounds became common on fruits, vegetables and ornamental plants.

The modern era of synthetic organic pesticides began in the 1930's. The research behind medical (including antibiotics) and military uses funded research that led to the discovery of many pesticide families that are still in use today. A real breakthrough in weed control occurred with the introduction of 2, 4-D in the 1940's for broad-spectrum broadleaf weed control in corn and cereal crops. The early twentieth century

brought the introduction of organo-mercurials for disease control and organo-chlorines, such as DDT for insect control. These products were very persistent and efficacious with good properties for agriculture and for public health, but not desirable after control was achieved. The introduction of organophosphates brought a new class of insecticides with reduced persistence and lower risks to both users and the environment.

The evolution of materials continued with new chemical families discovered that offered reduced persistence and environmental concerns along with attractive and valued benefits to producers and end-users. This period saw the introduction of soil residual herbicides such as triazine. The triazine herbicide atrazine evolving to the introduction of nonresidual products like glyphosate in the 1970's. Several broadspectrum fungicide families with active ingredients like chlorothalonil were introduced followed by the introduction of highly selective systemic fungicides that worked on specific metabolic processes in specific diseases. It was also the period of introduction for synthetic pyrethroid insecticides. The discovery and use of systemic and single mode of activity pesticides also created resistance concerns and the introduction of resistance management strategies to keep these products viable tools for producers. (Source: http://oregonstate.edu/ ~muirp/pesthist.htm)

The evolution of scientific procedures for evaluating the impact of pesticides on users and the environment along with

the introduction of newer classes of reduced risk products led to the removal of many older classes of chemistries that were persistent with negative impacts on the environment.

The close of the twentieth century brought the evolution to newer classes of highly specific, low-toxicity and low use rate insecticides and fungicides. These products were used at the rates of milliliters or grams per hectare. Insecticides were registered that controlled only certain stages of the lifecycle without harming beneficial species in crops like apples. Likewise fungicides were introduced that featured both upward and downward systemic activity to control diseases like apple scab in apples. This period also saw the refinement of natural products in terms of use patterns with the introduction of newer and more user-friendly and environmentally safe formulations.

As well, we entered into an era of genetically engineered pesticides and crops designed or bred to reduce or eliminate the use of pesticides in controlling specific pests. Examples include borer resistant corn or canola resistant to diseases like blackleg. The use of pheromones to disrupt insect mating habits and the use of microorganisms to combat diseases were also introduced and used on a broader scale in specific crops like greenhouse vegetables, or fruit crops like apples. The latter half of the 1990's saw the introduction of herbicide tolerant crops including soybeans, corn, canola and cotton using both traditional and transgenic breeding techniques, and the introduction of varieties of corn and cotton resistant to corn borer and boll weevil respectively. These introductions

$$H$$
 N
 N
 CH_2
 CH_3
 CH_3
 CH_3
 CH_3

$$H_3C \longrightarrow O$$
 $H_3C \longrightarrow O$
 $H_3C \longrightarrow O$
 $H_3C \longrightarrow O$
 $H_3C \longrightarrow O$
 $H_3C \longrightarrow C$
 $CH_3 \longrightarrow C$

revolutionized pest control and dramatically reduced the volumes of pesticides used on these crops by either eliminating the need or switching use patterns to more environment friendly or broad-spectrum products like glyphosate or glufosinate-ammonium.

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Trends in pesticide use

As with fertilizers, application rates for chemical pesticides

are highest in industrialized countries, reflecting the low cost of farm inputs in relation to farm incomes. Application rates in Vietnam, for example, are around 1.0 kg/ha (a.i.), compared to 11.8 kg/ha in South Korea and 19.4 kg/ha in Japan. In India the application rate is only 450 g a.i./ha. Application rates in Taiwan ROC are even higher than in Japan.

| Table 1 | |
|--|---|
| Consumption of pesticides (group-wise) in MT during 1995-96 to 2004-05 | į |

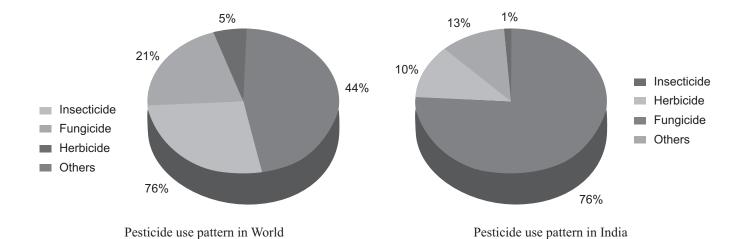
| Pesticide Group | 1995-96 | 1996-97 | 1997-98 | 1998-99 | 1999-2000 | 2000-01 | 2001-02 | 2002-03 | 2003-04 | 2004-05 |
|-----------------|---------|---------|---------|---------|-----------|---------|---------|---------|---------|---------|
| Insecticide | 38,788 | 34,665 | 33,379 | 30,469 | 28,926 | 26,756 | 29839 | 28197 | 25627 | 25929 |
| Fungicide | 10,563 | 9,969 | 10,054 | 10,428 | 8,435 | 8,307 | 9222 | 10712 | 9087 | 6397.4 |
| Herbicide | 6,040 | 7,060 | 7,103 | 7,292 | 7,369 | 7,299 | 6979 | 7857 | 5610 | 7364 |
| Others | 5,869 | 4,420 | 1,703 | 968 | 1,465 | 1,222 | 1308 | 1398 | 438 | 1660 |
| Total | 61,260 | 56,114 | 52,239 | 49,157 | 46,195 | 43,584 | 47348 | 48146 | 40762 | 41350.4 |

(Source: http://www.ncipm.org.in/asps/pesticides)

Regulation on pesticides

The Government of India has taken steps to ensure the safe use of pesticides. The Insecticides Act, promulgated in 1968 and enforced on 1st August, 1971, envisages to regulate the import, manufacture, sale, transport, distribution, and use of insecticides, with a view to prevention of risks to human beings or animals, and for matters connected therewith. Prior to this, four insecticides mainly used in the public health programmes were being controlled under the Drugs and Cosmetics Act, 1940. It was desirable as a prerequisite to the enforcement of the Insecticides Act, to evaluate the magnitude of pesticide pollution in the country and related health hazards to ensure

their safe use for the benefit of the society. ICMR's National Institute of Occupational Health (NIOH), Ahmedabad, and several other national laboratories, Agricultural universities and other R&D organizations have been engaged in toxicological evaluation of pesticides, synthesis of safer molecules and evaluation of environmental contamination due to pesticides. Currently, there are 217 pesticides registered for use in India (up to 18.02.2009). There is a sequential rise in the production and consumption of pesticides in India during the last three decades. However, the consumption pattern of these chemicals in India differs that in the rest of the world. (http://www.cibrc.nic.in/reg_products.htm).



Pesticide formulations

Pesticide formulation consists of one or more active pesticide ingredients plus other ingredients which have no pesticidal action i.e. inert ingredients. Inert ingredients generally include fillers, talc, petroleum distillate, solvents, wetting agents, extenders, emulsifiers, adjuvants etc.

Types of formulations

Depending upon the intended use of pesticides there are different types of formulations

microconsumers, such as bacteria, lacked enzymes capable of degrading - basically they hadn't evolved to use it as an energy source, as well as from other features of its chemistry.)

The **indirect toxicity** related to two principles:

(i) **Bioconcentration** - the tendency for a compound to accumulate in an organism's tissues (especially in fatty tissues for fat soluble organochlorines such as DDT)

| Solids | Liquids | Gases | |
|--|---|-------------------------------------|--|
| Dust or powders, Granules, Pellets, Tablets Particulates or Baits, Dry flowables, Wettable powders, Ear tag/ Vapour strips, Seed treatment WDGs | Suspensions Concentrate (Flowables), Solutions, Emulsifiable concentrates, Gels, Aerosol, Ultralow volume concentrates, Microemulsions, Suspoemulsions | Fumigants sold as liquids or solids | |

There are many problems we are facing in using the conventional pesticide formulations. High concentration of pesticides in WP formulation endangering human health and contaminating environment, organic solvents used in EC formulation are inflammable and enhance per-cutaneous toxicity by dermal penetration. To avoid these problems some of the newly developed modern formulations are Water Emulsifiable gel, Floating granules, drift less dust, macro and micro encapsulated suspension, hollow fibers, monolithic matrix, laminated structures etc.

Pesticides, non-target organisms and our environment:

Regarding effect on non target organisms, the most important publication was Rachel Carson's best-selling book "**Silent Spring**," published in 1962. She (a scientist) issued grave warnings about pesticides, and predicted massive destruction of the planet's fragile ecosystems unless more was done to halt what she called the "**rain of chemicals**." In retrospect, this book really launched the environmental movement.

She was focusing on the chlorinated hydrocarbons, such as DDT, and pointed to evidence linking them to death of non target creatures (organisms other than those that the pesticide is intended to kill), such as birds. She argued that the death of non targets occurred via two basic ways:

- (1) **Direct toxicity -** It was discovered that DDT was toxic to fish (especially juveniles) and crabs, not only to insects.
- (2) Indirect toxicity related to its persistence. (Its persistence came in part from its insolubility; from the fact that it was a synthetic, recently introduced compound that

(ii) Biomagnification - an increase in concentration up the food chain (These terms are sloppily used; sometimes "bioaccumulation" is also used to mean for both the terms) (Source: http://oregonstate.edu/~muirp/ pesthist.htm)

(Source: "The Fate of Pesticides in the Environment and Groundwater Protection," by C.L. Brown and W.K. Hock. Agrichemical Factsheet#8, Penn State Cooperative Extension. 1990.)

Improvisation in pesticide use

Many of the harmful effects from applying chemical pesticides are observed not so much from pesticide use but from pesticide misuse. This includes over application, repeated application of the same pesticide, poor application technology, and even the use of pesticides to catch fish. It was suggested that rather than focus on new technologies such as biological control and IPM, it might be more effective to make sure that pesticides are used properly.

This includes the improvement of application technology and sprayers, especially for low-income farmers. The condition and quality of the sprayer, and especially the nozzle, are very important. Under the best of circumstances, it is not easy for farmers to apply a fixed volume of chemical spray evenly over a fixed area. If the application technology is poor, farmers tend to apply far too much pesticide.

For high mammalian toxicity and fatal behaviors in the environment, scientific community made approaches towards the developments of newer molecules which could be easily biodegradable, target-specific with very low mammalian toxicity. A distinct division in scientific opinion was made to decide whether to go for bio-based products or for using synthetic chemicals for protecting the crops. Therefore, a new horizon of analytical chemistry was evolved as pesticide residue analysis to judge the residue level of these harmful chemicals in food grains. Researches were carried out to develop safer molecules which could undergo photodegradation, microbial degradation as well as chemical degradation leaving very less amount of residues in the environment. The prime motto for this development is to give protection to the crops along with safety to the natural enemies of different pests as a whole safety to environment.

Monitoring for pesticide residues

An efficient monitoring system which regularly tests food items for pesticide residues is a strong incentive for farmers to use chemicals wisely. Indeed, unless contaminated shipments can be identified, farmers may not know or care whether the produce they are selling contains pesticide residues. However, the facilities needed for chemical testing are expensive, while there is some controversy over the accuracy of the cheaper bioassay procedure. One promising approach is HACCP - Hazard Analysis at Critical Control Points. This looks at the whole chain of pesticide distribution and use, and selects the particular points where action is feasible and will make an impact.

Future challenges

To develop more and more new molecules having-

- i) Low mammalian toxicity
- ii) Less soluble in water
- iii) Leaching potential shall be less or absent
- iv) New new chemistry
- Molecular weight of new molecules shall be ranged from 200-450
- vi) More discoveries in macromolecular pesticides
- vii) More innovations required for new new neo-nicotinoids
- viii) More biotechnological innovations to be directed in transgenic plants etc.
- ix) More innovative technology to be developed in application of pesticides, a special care shall be given on the nozzles, sprayer or applicator with an intention to minimize the loss of applied pesticide or target organisms
- x) Minimization of residue load in ecosystem
- xi) More emphasis shall be given in bio-control agents
- xii) Research emphasis shall be given in innovations of more plant derived biopesticides.

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New products registered in India since 2006

| Sl. No. | Name of the pesticides | Sl. No. | Name of the pesticides |
|---------|--|---------|------------------------|
| 1 | Azoxystrobin | 21 | Fipronil |
| 2 | Beta Cyfluthrin | 22 | Flubendiamide |
| 3 | Bifenthrin | 23 | Flufenacet |
| 4 | Bitertanol | 24 | Flufenoxuron |
| 5 | Buprofezin | 25 | Flusilazole |
| 6 | Carfentrazone Ethyl | 26 | Imidacloprid |
| 7 | Cartap Hydrochloride | 27 | Indoxacarb |
| 8 | Chlorfenapyr | 28 | Lambda-Cyhalothrin |
| 9 | Clodinafop-propargyl (Pyroxofop-propargyl) | 29 | Lufenuron |
| | | 30 | Milbemectin |
| 10 | Chlothianidin | 31 | Novaluron |
| 11 | Cyfluthrin | 32 | Oxadiargyl |
| 12 | Cyhalofop-butyl | 33 | Pencycuron |
| 13 | Cyphenothrin | 34 | Propiconazole |
| 14 | Difenthiuron | 35 | Propineb |
| 15 | Emamectin Benzoate | 36 | Pyridalyl |
| 16 | Ethofenprox (Etofenprox) | 37 | Rynoxapyr |
| 17 | Fenazaquin | 38 | Spinosad |
| 18 | Fenoxaprop-p-Ethyl | 39 | Sulfosulfuron |
| 19 | Fenpropathrin | 40 | Tebuconazole |
| 20 | Fenpyroximate | 41 | Thifluzamide |

 $(\textbf{Source:} \ http://www.cibrc.nic.in/reg_products.htm)$