CROP PRODUCTION

Research review

Present status and scope of further work in India on degradation of pesticides applied to crops

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ABSTRACT

On degradation of pesticides in plants and soil under semi-tropical and tropical conditions, most of the studies have been carried out on insecticides, neglecting fungicides, herbicides and nematicides. The researches conducted so far deal mainly with persistence of the parent compound recovered from the plants. No information has been generated on metabolites, conjugates and bound residues formed during the post-application period. These conjugates and bound residues need to be characterized and their bio-availability has to be evaluated. Monitoring of pesticide residues has widespread contamination of environment with them, particularly with residues of hexachlorocyclohexane (HCH) and 1, 1, 1-trichloro-2,2-bis (*p*-chlorophenyl)-ethane (DDT). Micro-organisms in nature are able to degrade a large quantity of many of these compounds. Methods have to be developed to decontaminate the environment from pesticide residues. The pesticidal-degradation character of several microbes has been located on small fragment of extrachromosomal deoxyribonucleic acid (the plasmid). Though some bacterial strains, viz *Flavobacterium* sp ATCC 27551 and *Pseudomonas* sp, capable of degrading toxic pesticides have been isolated, they need to be tested in field.

Pesticides constitute an integral part of the modern crop-management practices for increasing the agricultural production. Change in cropping pattern and large-scale introduction of new high-yielding varieties with increased nitrogen input have inadvertently led to the build-up of prevalent major pests or erstwhile minor pests such as brown planthopper (*Nilaparvata lugens* Stål.) in rice (*Oryza sativa* L.) (Kulshrestha *et al.* 1974). Further,

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warm and moist conditions in the tropical countries favour the build-up of a variety of pests harmful to man and agricultural crops. Accordingly, there has been a steady increase in the use of pesticides, especially insecticides, in most of the tropical countries. In India the use of pesticides steadily increased from a meagre 4 000 tonnes of technical-grade material in 1960 to more than 82 000 tonnes in 1991, out of which 68 000 tonnes are insecticides (SPPL, Bombay 1992). Among the insecticides, hexachlorocyclohexane (HCH) and 1,1,1-trichloro-2,2-bis (*p*-chlorophenyl)-ethane (DDT) alone constitute 70%. In addition, 700 tonnes of aldrin and heptachlor are

used. These organochlorines have a tendency to persist in the environment, and due to their high fat solubility accumulate and magnify in various organisms. This can lead to the transfer of these toxic compounds to human-beings (Siddiqui *et al.* 1981, Kaphalia and Seth 1983, Ahmad *et al.* 1988, Bhatnagar *et al.* 1992). On the contrary, organophosphorous and carbamate group of pesticides, being biodegradable, do not accumulate in the environment. However, most of these are highly toxic and can cause acute toxicity on consumption of contaminated food containing these pesticides. For the last 2 decades considerable literature has accumulated on residues of parent pesticides in crop plants and their dissipation in soil. These studies show widespread contamination of our food commodities and environment (Agnihothrudu and Mithyantha 1978, Agnihotri and Chattopadhyay 1992).

PERSISTENCE OF PESTICIDES ON CROPS

The residues of parent pesticides have been monitored in many crop plants after their application at recommended levels and intervals under various agro-climatic conditions (Agnihothrudu and Mithyantha 1978, Agnihotri *et al.* 1980). As the insecticides are the prominent group of pesticides used in India, most of the studies on persistence have been carried out on them, whereas herbicides and fungicides have been grossly neglected. Since most of the fungicides are used on fruit and vegetable crops, which form an important constituent of diet, studies on fungicides deserve priority, particularly in the fruits eaten raw. The presence of herbicide residues left from their application to the previous crop can be phytotoxic, adversely affecting the yield of the succeeding crop, depending on the edaphic factors and climate. Despite many instances of herbicidal phytotoxicity, no

serious efforts have been made to study their persistence and degradation under different agro-climatic conditions prevailing in India. Although the use of nematicides is limited to some areas in India, their rates of application are much higher compared with those of the insecticides, necessitating study on persistence in view of their toxic residues. Some of the studies carried out with nematicides show their high persistence in soil as well as plant (Meher *et al.* 1989, Meher and Sethi 1992).

FATE OF PESTICIDES APPLIED TO CROPS

Pesticides applied directly to a crop canopy as a spray or wettable powder ultimately penetrate the cells, wherein phytotoxic and bio-transformation reactions occur. Plants metabolize xenabiotic compounds through a series of intermediates, ultimately leaving insoluble residues. The chemical nature and quantity of intermediate metabolites and insoluble residues in a plant are influenced by the site of absorption of the pesticide, translocation and time they remain in the plant (Shimabukuro and Walsh 1979). Since plants lack an excretory mechanism, they metabolize pesticides to water-soluble conjugates and insoluble terminal residues, which remain in the plant during its life (Kaufman *et al.* 1976) or until eventual detachment of the organ containing the residues from the plant due to senescence.

Sufficient attention has not been paid on the metabolic transformation of pesticides recovered from plants without information about their metabolites for terminal residues. Marshall and Dorough (1977) using radio-isotopes reported that 30–70% of the applied pesticides could end up as conjugate or bound (non-extractable) residues in plant. In a recent study on metabolism of deltamethrin on cotton (*Gossypium* spp) and gram (*Cicer arietinum* L.), plants showed deposition of

28.3 and 31.2 ppm residues after 30 days of application (Mathew 1992). The residues comprised 15.7% deltamethrin, 13.1% metabolites, 46.0% conjugates and 25.2% bound residues on cotton, and 16.1% deltamethrin, 27.0% metabolites, 32.6% conjugates and 24.3% bound residues on gram.

Information on bio-availability of plant-bound residues is very limited. The bioactivity and toxicological significance of bound residues of DDT and HCH in wheat (*Triticum aestivum* L. emend. Fiori & Paol.) grains fed to rat (*Rattus rattus* L.) appeared minimal (Verma and Pillai 1991).

PERSISTENCE OF PESTICIDES IN TROPICAL SOILS

Soil is the major sink for the bulk of pesticides applied directly to the soil as granules or eventually reaching the soil after foliar application. Though exhaustive information is available on the behaviour of pesticides in temperate soils, scientific data on the fate of pesticides in tropical soil environments are scarce. However, available information indicates that under hot and humid conditions of the tropics and subtropics, several pesticides reaching the soil dissipate much faster than in temperate soils. Thus Singh *et al.* (1989) observed that the degradation flux of different isomers of HCH in flooded soil under the cover of rice crop continued to increase for 60 days and then decreased. Also 99.4% lindane, 96.3% aldrin, 94.4% dieldrin and 80.4% heptachlor were lost from an agricultural soil of Delhi in 180 days (Agnihotri *et al.* 1977). In a sandy-loam soil of Delhi during the monsoon, winter and summer seasons in field, both ^{14}C-*pp*-DDT and ^{14}C-HCH dissipated most rapidly during the initial 60 days (Samuel *et al.* 1988). In an intensive study, the half-lives of DDT, aldrin and lindane in an agricultural field in Delhi were found to vary from 26.9 to

102.7, 10.7 to 26.7 and 6.3 to 28.4 days, respectively, depending on the season, method of application (soil-incorporated or surface applied) and soil-moisture conditions (Gajbhiye 1989).

The dissipation of biodegradable pesticides belonging to organophosphorous and carbamate groups was also faster in our tropical conditions, though most of our soil are low in organic matter (Agnihotri *et al.* 1981, Meher *et al.* 1985, 1989). Residues of some of the organophosphorous insecticides like chlorpyriphos, fensulfothion and chorfenvinphos persisted in the soil for 4–6 months when applied at normal rate (@ 1.5 kg/ha). Similarly, residues of synthetic pyrethroids persist in the soil for a long time, particularly when incorporated into the soil (Kumar and Agnihotri 1991). This result clearly shows that data generated from temperate region of the world cannot be directly applicable for use under tropical conditions.

BOUND RESIDUES OF PESTICIDES IN SOIL AND THEIR SIGNIFICANCE

Studies using radio-labelled compounds show that 20–80% of the applied pesticides could end up as bound residues in soil (Khan 1982, Calderbank 1989). Bound residues are formed with all classes of pesticides as parent compounds and their degradation products. Recently efforts have been made in India to determine the bound residues of some pesticides in soils and their availability to plants (Kumar 1989, Verma and Pillai 1990, 1991, Barooah 1991). The persistent organochlorine insecticides (DDT, HCH) form comparatively less bound residues in soil than the non-persistent organophosphorous and other class of pesticides (Khan 1982).

The release and potential availability of bound pesticide residues to plants has been demonstrated by several studies (Fuhremann

and Lichtenstein 1978, Khan 1980, Calder-bank 1989). In general, only a small fraction (< 1%) of the activity is translocated into the plant. When gram (*Cicer arietinum* L.), maize (*Zea mays* L.) and rice were grown in the soil containing bound residues of ^{14}C-DDT or ^{14}C-HCH, gram and maize in 144 days and rice in 20 days accumulated 0.61, 0.13 and 0.05% of the initially added bound residues from DDT and 0.95, 0.11 and 0.04% from HCH (Verma and Pillai 1991). In a similar study, Barooah (1991) reported that 0.89–6.20% of the bound residues of cypermethrin present in the soil were translocated in wheat plants 15 days after growth. Only 0.02% of deltamethrin-bound residues were absorbed by cowpea [*Vigna unguiculata* (L.) Walp.] plant a month after growth (Kumar 1989). More work is required on other pesticides with different crops to substantiate the relevance of these findings.

Soil-bound residues are not permanently stable; these can be degraded further by soil micro-organisms, though at a much slow rate. Up to 31.5% soil-bound residues of cyper-methrin were mineralized in 6 weeks, as evident by ^{14}CO$_2$ evolution (Barooah 1991), which was rapid in the first week followed by a sharp decline thereafter, indicating that all the residues are not bound with the same strength. Perhaps the nature and strength of binding, which differ with the soil type, govern the release and bioavailability of soil-bound pesticides. The effect of repeated applications of pesticides on formation of bound residues and their long-term effect on micro-organisms need to be investigated.

TRANSFORMATION OF PESTICIDES IN SOIL

A pesticide on reaching the soil is transformed by various physical, chemical and biological forces. Degradation by physico-chemical or chemical means is invariably in-complete and seldom leads to inorganic end-products like CO$_2$ and water.

Volatilization

Volatilization can be a major means of pesticide loss from the site of its application in the hot climate of the tropics. Gajbhiye (1989) and Gajbhiye and Agnihotri (1991, 1992) reported that within 28 days of soil incorporation or surface application of lin-dane, aldrin and DDT @ 10 and 20 kg ai/ha, the volatilization losses accounted for 1.33–9.33, 1.01–3.63 and 0.23–2.51 kg/ha respectively. Maximum volatilization occurred during rainy season, followed by summer and winter, and a reduction in volatilization of all the insecticides by one-half to one-third in soil incorporation than surface application. The air above the field contained up to 3.25 $\mu g/m^3$ lindane, 1.27 $\mu g/m^3$ aldrin and 0.405 $\mu g/m^3$ DDT residues. Kaushik *et al.* (1987) found 160–930 ng/m^3 HCH residues in air around Delhi. Similarly, Ramesh *et al.* (1989) detected 15 ng/m^3 residue of HCH and 0.28 ng/m^3 DDT in the air of Porto Novo (Tamil Nadu), caused mainly by the use of HCH and partly by DDT in flooded rice fields and their subsequent volatilization. Vijaylakshmi (1988) also reported that soil-applied carbofuran is readily absorbed by rice plants, translocated to the foliage and eventually lost through evapo-transpiration.

Most of these studies have been carried out on organochlorine insecticides by drawing air samples from a single point; therefore the gradient that exists in the field could not be established. Relatively, there are no studies on the volatilization losses of other pesticides, particularly from fields under flooded conditions and from surface of water bodies.

Photo-decomposition

Among the physical factors influencing the residual fate of pesticides in nature, sunlight (particularly ultraviolet) is the most

significant. Such transformations become more significant in tropical countries like India where sunshine is aplenty. Many pesticides undergo degradation by photolytic reactions in air and water and on the surface of soil and plant (Matsumura 1988). In contrast to other degradation processes, photodegradation is more exhaustive and non-specific, leading to several additional degradation products (Dureja et al. 1990). Sometimes these are even more toxic than their parent compounds (Holmstead 1978). Products of photo-degradation depend on factors such as intensity and wavelength of light, duration of irradiation and the state of chemical, pH, presence of water, air and photosensitizers. The presence of photo-sensitizers like chlorophyll plays an important role in the photo-degradation of pesticide on plant surface (Mutsumura 1982). This may be responsible for faster degradation of pesticides on plant leaves than other surfaces. Although much is known about photo-degradation, no efforts have been made to utilize ultraviolet or sunlight for decontamination of pesticide residues from the environment.

Chemical and microbial degradation

Chemical transformation of pesticides in soil is common and widespread (Kearney and Helling 1969). For instance, carbamate (Rajagopal et al. 1984) and organophosphorous (Sethunathan et al. 1977) insecticides undergo rapid hydrolysis under alkaline condition and the products formed depend on the physico-chemical properties of the soil.

Biological degradation plays the most important role in more complete transformation of many pesticides in the soil environment to inorganic end-products. A bio-degradable pesticide seldom remains in the environment for a long period. Therefore for environmental safety, bio-degradation is necessary to metabolize the pesticide by the micro-organisms

after the desired period of its pesticidal action. Sethunathan et al. (1991) reported microbial involvement in the degradation of many pesticides in tropical soils. Aerobic–anaerobic interface in the flooded soil, especially in those growing rice, helps in better mineralization of complex organic pollutants than in exclusively aerobic or anaerobic systems (Reddy and Sethunathan 1983).

Predominantly anaerobic conditions in the soil, generated after flooding and accentuated by organic amendments, hasten the decomposition of HCH isomers from a flooded soil (Drego et al. 1990). Dominant anaerobes such as *Clostridia* are associated in creating instability of HCH isomers in flooded soils and ecologically important anaerobic ecosystems (Sethunathan et al. 1983). Soil suspension from HCH-retreated flooded or non-flooded fields causes exceptionally rapid degradation of gamma- and alpha-HCH under aerobic conditions (Bhuyan et al. 1991). A *Pseudomonas* sp, isolated from HCH-treated rhizosphere soil of sugarcane (*Saccharum officinarum* L.), readily degrades not only gamma- and alpha-isomers of HCH, but also its thermodynamically more stable beta isomer under aerobic conditions (Sahu et al. 1990).

FACTORS AFFECTING PESTICIDE DEGRADATION

Metabolism of pesticides in a complex and dynamic crop–soil ecosystem is influenced by many factors such as soil type, moisture regime, organic matter, temperature and presence of plants etc. The soil type equally influences the persistence of pesticides and their degradation products. Thus phosphorothioate insecticides, viz. parathion, methyl parathion and fenitrothion, were degraded by hydrolysis with concomitant accumulation of respective nitrophenols in selected soils, particularly under non-flooded condition. Under flooded condition, the

degradation products from these pesticides differ, depending on soil type, viz (*i*) only amino-analogue in organic-rich soil, (*ii*) only nitrophenol in laterite and saline alluvial soil, and (*iii*) both amino-analogue and nitrophenol in alluvial soil (Adhya 1990).

Water regime also affects the pathway of degradation. Thus DDT rapidly converts into 2,2-bis (*p*-chlorophenyl)-1,1-dichloroethane (DDD) under flooded condition, whereas into 2,2-bis (*p*-chlorophenyl)-1,1-dichloroethane (DDE) and DDD under non-flooded conditions is seldom detected (Mitra and Raghu 1988). Likewise, parathion and related organophosphorous insecticides undergo hydrolysis under non-flooded condition, and nitro-group reduction under flooded condition (Adhya *et al.* 1986).

Organic matter and temperature also affect the persistence of a pesticide in a crop–soil ecosystem. Application of organic matter increases the degradation of all types of pesticides. Even the degradation of recalcitrants like DDT and HCH is increased by addition of organic matter (Ferreira and Raghu 1981, Mitra and Raghu 1988). Very little is known about the effect of temperature on the persistence of pesticides and their degradation products. Increase in the temperature from 25 to 35°C not only increases the rate of degradation of methyl parathion in a flooded soil, but also shifts its pathway from nitro-group reduction to hydrolysis (Sharmila *et al.* 1988).

FUTURE SCOPE OF RESEARCH

The potential hazard of the entry of pesticides and their metabolites into the food-chain can be real and serious even in tropical countries. For instance, in India and other tropical countries where HCH continues to be used on a large scale, problem of its entry into the food-chain through accumulation in rice straw, a major cattle feed, causes concern due to eventual accumulation of HCH residues in milk (Kalra and Chawla 1983). The common practice of exposing straw to the sun in tropical countries may minimize the residues, but it needs confirmation. Fat-soluble pesticides may accumulate in cellular lipids and oil-rich fractions of plants like rice bran or oilseeds like groundnut (*Arachis hypogaea* L.). There is scope for minimizing the residues in the crop produce through post-harvest practices like refining of oils and parboiling in rice. Contamination of water resources through surface run-off, sedimentary transport and leaching to ground-water of pesticide residues also deserves attention. Since the soil near the river bank is highly porous, even the most insoluble pesticides such as DDT, HCH and aldrin get leached into the ground-water and carried to the nearby river system under the influence of moving underwater current.

Continued production and consumption of toxic pesticides, while important for increased agricultural productivity, have also led to pollution problems of great magnitude because of the persistence of many such chemicals in the environment. Micro-organisms in nature, in response to the release of large quantities of such compounds, have evolved the ability to degrade many of these compounds. Attempts to isolate bacterial strains capable of degrading and even metabolize such toxic chemicals have occasionally been successful. In fact, from tropical soils, especially flooded rice soils, several micro-organisms capable of degrading such pesticides have been isolated. For instance, a *Flavobacterium* sp ATCC 27551, isolated from diazinon-treated rice field (Sethunathan and Yoshida 1973), decreased the efficiency of diazinon in rice (Sethunathan and Pathak 1972). It is probably the most potential micro-organism for developing biotechnology for large-scale decontamination of environment heavily polluted with organophosphorous insecticides with a *O*-alkyle phosphate linkage. Karns

et al. (1990) found that *Pseudomonas* sp isolated from the rhizosphere of HCH-treated sugarcane plants, degraded the HCH-isomers including beta-isomer with great ease under aerobic conditions. This bacterium provides new possibility of the aerobic clean-up of HCH-polluted environment in India, since HCH alone accounts for 45% of the total pesticides used here. Aerobic clean-up would be more suitable than the currently suggested anaerobic clean-up of HCH-polluted environment.

Bio-degradation of a pesticide, however, may not always be beneficial. Disappearance of a pesticide before elimination of target pests due to accelerated bio-degradation in acclimatized soils may decrease its efficacy, as noticed with diazinon after its regular use in tropical flooded rice fields (Sethunathan and Pathak 1972). This problem can be common and widespread in areas of intensive use of the pesticide for some years, as in irrigated rice culture or in cotton (*Gossypium* sp) fields. Systematic study is essential on the accelerated microbial degradation of pesticides in acclimatized soils to devise a suitable approach to tackle or prevent such problems.

Biotechnology has brightened the prospects for providing exciting and cost-efficient approaches in solving ecological problems of pesticide residues. The pesticide-degradation character of several microbes has been located on small fragments of extrachromosomal deoxyribonucleic acid, the plasmids. With techniques, such as site-directed mutagenesis, it may be possible to expand the substrate range of the existing enzymes, so that new classes of agricultural chemicals can be more readily degraded. But accelerated degradation of pesticides can be a major agricultural problem after its multiple applications. It is possible to study genetic basis of such accelerated microbial degradation in field. Cloning of the degradative genes

is also possible, especially that of herbicide-degradation genes, in crop plants for developing herbicide-resistant lines (Miller 1991). The need for herbicide resistance is not limited to the crop alone but is applicable also to the nitrogen-fixing cyanobacteria associated with rice ecosystem. Thus much work is to be done in this area and the potential rewards are enormous.

So far isolated attempts have been made to determine the individual role of chemical, physical and biological agents in the degradation of pesticides in the tropical environment. There is need to develop systems approach to determine the combined role of individual components of the total ecosystem using microcosms or in actual field situations, especially in the tropics.

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