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IMPERCEPTIBLE EFFECTS OF CHLORANTHRANIL PROFILE ON THE ECOSYSTEM – A CRITICAL REVIEW

VANDANA NANDAL[1] AND MANU SOLANKI[1*]

Department of Biotechnology, Faculty of Engineering and Technology, Manav Rachna International Institute of Research and Studies, Faridabad, Haryana
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ABSTRACT

Pesticides are in use since the 1900s and their application has increased steadily. This has led to a plethora of adverse effects on the biotic and abiotic components of the ecosystem. The indiscriminate use of pesticides adversely affects the activities of the soil microbiota thus affecting the quality of soils and would therefore have serious ecological consequences. Many emerging pesticides are now in use and have replaced the conventional ones. But they are also being used deliberately and may pose a risk to the environment including humans. This demands that they should be assessed thoroughly for their various effects on the ecosystem. One such recently introduced pesticide is Chloranthranilprole (Coragen) that claims to be quite safe to the environment when applied. But due to its quick mode of action it is being used extensively on vegetable crops and fruits which may pose harmful effects to the environment. This brief review intends to focus the effects of coragen on the ecosystem.

KEY WORDS : Pesticide, Rhizosphere, Micro flora, Chlorantraniliprole (coragen)

INTRODUCTION

The rhizosphere is the zone of soil in which the soil microflora is directly influenced by the plant root secretions (Ahemad and Kibret, 2014). Plants can amend the rhizosphere during their growth by secreting various root exudates that have an intense effect on the rhizospheric microflora, both quatitatively as well as quantitatively. A plant can modify its rhizosphere through various mechanisms that includes uptake of various insoluble and soluble compounds, production of roots exudates, releasing organic compounds and changing the acidity and alkalinity of the rhizosphere.Plant root exudates fuels both beneficial microorganisms and pathogens, and can oxidize many nutrient such as iron, sulphur and manganese. Soil is a home for plethora of different strains of rhizospheric bacteria improves the plant growth by exhibiting multifarious activities. Such bacteria are commonly called as plant growth promoting rhizobacteria (PGPR) (Kundu *et al*., 2006). PGPR are gaining impetus in last few decades as inoculants and biological control agents in sustainable agriculture. (Gouda *et al*., 2018). Soil microorganisms play a key role in the environment through their various activities like organic matter decomposition, nutrient recycling and in maintaining soil fertility (Olanrewaju *et al*., 2017). For sustainable environment a perfect balance between various abiotic and biotic components is required. Several factors leading to the alteration of microbial community structure and composition affects the soil ecosystem. In addition, anthropogenic intervention for the management and treatment of soil with the aim of increasing crop productivity also influence microbial diversity (Nicolopoulou-Stamati *et al*., 2016). The indiscriminate use of pesticides to increase the crop productivity has become a global concern in the last decades. They are found as common contaminants of the environment, where they exert harmful effects on plants, animals, insects and beneficial microorganisms harbouring the soil. They may also affect adversely the non target plants, birds, fishes and human beings.

The effect of pesticides on the soil microflora holds utmost importance since many functions related to microbes are responsible for sustainable agriculture and environment including soil health. Since a healthy soil harbours a variety of microbial communities which obviously gets affected by xenobiotics, their measurement represent indicators of choice for monitoring the impact of pesticides on soil ecosystems. Conventional pesticides have been replaced by newer pesticides which are more selective, show good bioefficacy and exerts low mammalian toxicity. In the past years many such emerging pesticides have been in market. Chloranthanilprole, marketed under the trade name coragen, is one of them which is recommended for several fruit crops and vegetable crops. It belongs to a new class of selective insecticides featuring a novel mode of action. Much work has been documented featuring the excellent profile of safety to beneficial arthropods, pollinators and non target organisms such as earth worms. But the studies relating to the effect of this pesticide on soil microbial community and their activities are scanty. Due to their quick mode of action, they have been indiscriminately used in many vegetable crops posing risks to the consumers. The major concern about increasing use of this pesticide is that it is persistent in soil with half life of about one year and this long half life indicates high potential for accumulation in soil after repeated use. The effect of pesticides on the beneficial microbes and other non targeted biological agents has raised a concern globally that needs to be addressed globally. It becomes imperative to assess carefully the effect of these pesticides and any other xenobiotic compound since the disturbances imposed by such agents could alter the microbial communities and may potentially affect the soil fertility and sustainable agricultural productivity. With this background the present review focuses the toxic manifestations of chloranthranilprole which is claimed to be highly safe to be used.

Fate of Pesticides in Soil and Affecting Factors

Pesticides are the chemicals that kill pests. Pests are any agents that damage the field crops and include include fungi, bacteria insects, worms, and nematodes etc. Wide scale application of pesticides has become a common practice to augment crop yield which can lead to imbalance of rhizospheric microbial communities, environmental pollution and health hazards. Ideally a pesticide should have the ability to degrade non-toxic substance and to destroy the target pest as quickly as possible. Since soil is the ultimate sink of the pesticides and other chemicals applied in agriculture, it acts as a scavenger of harmful substances. (Li *et al*., 2004; Rodríguez *et al.,* 2006; González-Delgado *et al.,* 2015). Different soil factors determine the extent upto which it is adsorbed. A pesticide may get adsorbed to the soil particles, the extent of which depends both upon the properties of the pesticides and soil physicochemical properties. The pesticides which are less water soluble tend to be adsorbed more to the soil whereas chances of leaching from the soil to groundwater are more with highly soluble pesticides. Moreover a highly volatile pesticide most likely finds its way to the atmosphere. The soil properties that affect the sorption of pesticides to the soil include soil texture, soil permeability, soil pH and organic matter content. Soils having a fine texture tend to retain pesticides A pesticide tends to get in contact with fine textured soils for more time due to the greater surface area and lower permeability. The soils with high clay content tend to hold water and dissolved chemicals longer as have very small pore size and a large surface for adsorption. Moreover due to hydrophilic nature, the pesticides tend to be adsorbed to the external surfaces of clay particles (Lagaly, 2001). Another factor that influences the solubility of pesticides is soil pH. Acidic soil tends to increase the solubility of the pesticides and hence decreases the adsorption onto the soil particles. Another sorbent in the soil is organic matter having very heterogenous composition majorly contributed by crop residues, microbial biomass and organic amendments. (Sadegh-Zadeh *et al*., 2017). The water holding capacity can be increased by amendments like addition of organic matter (Eden *et al*. 2017). One such amendment include application of biochars to soil that is reported to affect the environmental fate of pesticides and can be used to adsorb organic contaminants including and thus finds its potential use as a filter material to prevent point source pollution in agriculture (Beesley *et al*., 2010; Herath *et al*., 2016; Mandal *et al*., 2017). In a recent study the adsorption and desorption of the pesticides bentazone, chlorpyrifos, diuron, glyphosate and (4-chloro-2-methylphenoxy) acetic acid (MCPA to the biochar were tested and the adsorption affinity of the native biochar was found to vary considerably amongst the tested pesticides (Cederlund *et al*., 2016). Adsorption of a pesticide is also influenced by the water content of the soil (Roy *et al.,* 2000). The adsorption of pesticides increases with water content since it aids the diffusion of pesticides to sorption sites. This holds well with the hydrophilic pesticides; for hydrophobic pesticides, the adsorption decreases with increase in the soil water content increases since hydration of the surfaces of adsorbents leads to decreased accessibility to adsorption sites (Swann and Behrens, 1972). Adsorption of pesticides in soil is also reported to be influenced by temperature (Racke *et al.,* 1997. "At elevated temperature, decrease in the adsorption of pesticides has been reported (Ten Hulscher and Cornelissen, 1996). Moreover increase in temperature favours the growth of a certain groups that tends to dominate and also affects the adsorption of pesticides (Perucci *et al*., 1999).

Pesticide tends to move to water bodies like rivers, lakes, wells, sewers and groundwater through runoff and leaching besides being adsorbed "Excessive application of pesticides and too much rainwater or irrigation water often leads to runoff and leaching. Further, pesticides mixed in water bound to eroding soil can be carried by runoff. The pesticides which have a greater solubility in water have the greatest potential for movement as compared to those that are relatively persistent, and readily absorbed by soil particles (Kookana *et al*.,1995). Recently efforts are being diverted in minimizing the leaching of applied pesticides. "A novel composite gel composed of carboxymethyl-chitosan (CM-chit) and bentonite was used as the carrier for encapsulating atrazine and imidacloprid to control their release in water and retard their leaching in soil (Li *et al*. 2012)."

Soon after its application, a pesticide undergoes degradation into simpler compounds. This degradation may occur spontaneously in the presence of light or aided by microbes. Degradation of pesticides occurs mostly in the upper layers of soil since microbial activity is optimum here due to suitable temperatures, moisture, and organic matter content. Since the presence of organic matter in the soil favours the growth of the microbes and hence degradation is fast which gradually slows down as the pesticide moves down below the root zone, since the conditions donot favour the growth of the microbes. Many pesticides are also degraded by a process known as hydrolysis the extent of which greatly depends upon temperature. Near the soil surface where temperature isconsiderably high, the process is quite fast while it gradually slows down at the depths below the root zone (Cowart *et al*., 1971).

ECOLOGICAL EFFECTS OF CHLORANTHRANILPROLE

Increasing world population demands an increase in crop productivity which has been achieved by the widespread use of pesticides. Although their use offers great benefits in controlling pathogens, insects and weeds in agricultural systems, they also threaten the environmental quality including air, water and soil. The pesticides may interact with non target soil microorganisms and can lead to adverse effects on soil health. It is therefore imperative to study the impact of any xenobiotic compound that makes its way to the soil, on the microbial community. Several studies have already shown that pesticide application leads to alteration in the soil nutrient status including microbial diversity and functions, which obviously can be altered with certain organic amendments (Pose *et al*., 2017). Pesticides in the soil affect the non-target and beneficial microorganisms and their activities which are essential for maintaining soil fertility (Schuster and Schroder, 1990). While some pesticides stimulate the growth of microorganisms, other exerts deleterious effects on microorganisms. There are some others that has no effect on the soil microbial community For examples, *Azospirillum* population is stimulated by carbofuran, but achlor reduced the population of *Azospirillum* (Johnsen *et al*., 2001; Lo, 2010). Difference response to the insecticides and pesrticides has also been reported. Lo. 2010 reported that microbial growth in the soil was promoted by P containing herbicides and insecticides like glyphosate, methamidophos but another insecticide fenamiphos, belonging to the same class was found to impose a negative effect on the nitrifying bacteria.

Chlorantraniliprole (CAP) is a novel anthranilic diamide insecticide which is highly effective for the control of lepidopteran pests and certain species that belongs to Coleoptera, Diptera and Hemiptera that attack a range of fruit crops and vegetables .It is marketed under trade name coragen. It is a new compound by dupont featuring a novel mode of action (Bassi *et al*., 2009). It acts by causing the uncontrolled release and depletion of internal Ca^{2+} stores upon selective binding wherein it causes the activation of the insect ryanodine receptor present on the sarcoplasmic reticulum of muscles, the endoplasmic reticulum of neurons or other cell. This leads to cessation of feeding, muscle dysfunctioning of the muscles thus paralysing the insect. Moreover it is also found to interfere with the development of the larvae and embryo. Its solubility in water is quite low (0.88 mg l^{-1}), very weak acid and is not pH sensitive It has the ability to leach through certain soil types and contaminate groundwater; it is highly mobile through some soils and its half life may vary 230 to 920 days thus making is highly persistent .

DEGRADATION OF CHLORANTHRANILPROLE

Degradation of CAP has been extensively studied by Lavitzer *et al*. (2016). Chlorantraniliprole undergoes chemical degradation as well as photochemical degradation in aqueous mileau. CAP is stable in dark in the pure water lacking electrolytes. In the aqueous solution having naturally present bases like hydrogencarbonate it undergoes transformation to compound"(2-(3-bromo-1-(3-chloropyridin-2-yl)-1H-pyrazol-5-yl)-6-chloro-3,8-dimethylquinazolin-4(3H)-one)" . Ultraviolet-A light from sun causes the transformation of chloranthranilprole to a compound which is stable in light and further transforms into another isomeric compound in the presence of alkaline water. This compound is stable in the dark, but undergoes degradation when irradiated. The photolytic degradation and transformation are the important phenomenon contributing the early degradation of chloranthranilprole in the environment. Chloranthraniliprole may accumulate in soil and characterized as persistent and mobile in terrestrial and aquatic environments and extended use is expected to cause accumulation of residues in soil from year to year due to its higher persistence in soil. Studies on the bioremediation as an approach to degrade the pesticide from soil are scanty. A *Pseudomonas* strain from an agricultural soil was reported to remediate coragen and was able to degrade 80.16% of 0.51 millimolar of coragen, for a period of forty hours with CAP as the source of C and energy in minimal nutrient medium. Degradation followed zero order kinetics and toxicity was also reduced (Gupta *et al*., 2016). In a similar study *Pseudomonas* spp has been implicated in the degradation of coragen, albeit at a slower rate with the concomitant decrease in the concentration of residual coragen with the passage of time (Kaur *et al*., 2016).

Ecological Risk Assessment

The consistent and deliberate use of pesticides, can affect the non target organisms which may be beneficial in increasing the soil productivity thus posing a threat for sustainable ecosystem. Chloranthranilprole has been in use widely to control a large number of pests. However several reports present a potential risk of resistance to this pesticide "(Jiang *et al*., 2012; Wang *et al*., 2013; Hu *et al*., 2014; Liu *et al*., 2015; Lu *et al*., 2017; Ribeiro *et al*., 2017; Yao *et al*., 2017; Zhu *et al*., 2017)" which demands the controlled use of this pesticide. Chlorantraniliprole manifests safety towards beneficial organisms and non targeted organism such as earthworm and soil microorganism. In a study nontarget microcrustaceans were found to be sensitive to CAP. However, the transformation products produced either spontaneously or due to photodegadation in water diminish the actual risk imposed by CAP **(**Lavtizar *et al*., 2016**)**. The effects of CAP on *M. pygmaeus* which is found to be beneficial against important pests was evaluated by Zhang *et al*. (2013) and chlorantraniliprole was found to be compatible with *M. pygmaeus*. Further tests at sublethal concentrations reported chlorantraniliprole to manifest behavioral effects mildly. However there are recent reports documenting the hazardous effects of chloranthranilprole. Abbas *et al*. (2016) examined the Chlorantraniliprole treated embryos and reported significantly high percentages of external malformations. "The teratogenic effects of Chlorantraniliprole on chick embryos were assessed at different doses of commercial Chlorantraniliprole (0.1, 0.5, 1.0 and 1.5 µl/1000 µl/egg)". The treated embryos shows significantly high percentages of external malformations as compared to controls at 12th day of development thus indicating that even quite low dosage of CAP could be detrimental for the avian embryos. Further as per a recent study,sublethal concentrations of chlorantraniliprole impair the population growth of *H. axyridis* (Nawaz *et al*., 2017) suggesting that more impetus should be laid down to consider its inclusion in IPM strategies. Another study reports the significant toxic manifestations due to deliberate self harm with Chlorantraniliprole in a 26-year-old female which challenges the claims of being highly selectivity (Mishra *et al*. 2016). The effects of chloranthranilprole on fermentation quality of alfalfa (*Medicago sativa* L.) silage were investigated and chlorantraniliprole has been reported to affect the microbial communities during the fermentation of the alfa alfa silage, especially coliform bacteria and yeast. Wu *et al.* (2017) examined the impact of CAP on soil microbial communities and their activities. The results showed the significant temporal alterations in the soil microbial activities within the first 14 days of the treatment with CAP. Moreover structural differences in the microbial communities were also predominant in the initial period of time of application and negligible differences with the passage of time (50 days) suggesting that CAP does not pose toxicological threats on long term soil health. In a similar study only at high dosage, chloranthranilprole altered the microbial community structure of the soil (Wu *et al*. 2018). However these are the only few studies which were conducted to assess the effect of CAP on soil health and many more long-term laboratory and field studies need to be conducted to advance our understanding on the impact of CAP on soil microflora and proper regulations must be reformulated regarding the use of CAP in soil to minimize ecotoxicity.

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