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Chapter- 8

An Overview of Clothianidin, Dinotefuran and Thiacloprid on Aquatic Communities: Evaluating the Impacts of Environmental Risks Posed by Neonicotinoids

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Keywords: Neonicotinoids, Aquatic Environment, Impact on Animal.

Abstract:

Effective pest management is one of the potential methods to boost crop output because pest infestations account for more than 45% of the annual loss in food production. In order to combat pests and diseases spread by vectors, a wide range of pesticides must be applied to crop plants. Currently, India is the largest producer of pesticides in Asia and ranks twelfth in the world for the use of pesticides. Numerous factors, including chemical classes, functional groups, modes of action, and toxicity, can be used to categories pesticides. Insecticides stand out because they are made to be poisonous to the organisms they are intended to kill. They may be hazardous to non-target creatures, such as fish, because many of their targets are substantially conserved across many taxa. The majority of insecticides used worldwide now are neonicotinoid pesticides, which make up 26% of the insecticide marketed globally. Neonicotinoid insecticides have historically been seen as the best alternatives to some insecticides (such as organophosphates and carbamates), in part because they were thought to have little environmental or non-target organism danger. They are nicotinic acetylcholine receptor agonists, which bind tightly to the nicotinic acetylcholine receptors (nAChRs) in the central nervous systems of insects. At low concentrations, they stimulate the nervous system; at higher concentrations, they block the receptors, cause paralysis, and cause death. Neonicotinoids are specifically more harmful to insects because they bind to insect nAChRs more strongly than they do to vertebrate nAChRs.

Introduction:

Growing enough food to feed the world's increasing population is a challenge, and the changing food habits of an expanding middle class across Asia have made it necessary to manage a wide range of insect pests in order to increase agricultural productivity and quality (Sparks, 2013; Ivanišová et al., 2022). In addition to its role in agriculture, insecticides are widely used in industry, households, and military to control insect pests that are disease vectors, suggesting its essential role in human life (Xiao et al., 2017; De et al., 2019; Saha et al., 2022). Several types of newly developing illnesses that pose a hazard to public health are spread by

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arthropod vectors, including ticks (like Lyme disease), sandflies (leishmaniasis), mosquitoes (malaria, dengue fever, yellow fever, encephalitis, filariasis, West Nile fever, and chikungunya) etc. The World Health Organization (WHO), as well as other scientific studies and publications, have provided ample evidence that the application of synthetic pesticides can significantly lower the incidence of insect-borne illnesses, including malaria (Himeidan et al., 2012).

Neonicotinoid sales have increased due to its high activity and persistent control qualities (Wakita et al., 2004). Neonicotinoids, when compared to other insecticides, are extremely soluble and thus absorbed by the plant due to their systemic nature. After prolonged exposure to sublethal dosages, they cause delayed mortality in arthropods, however they are not particularly hazardous to vertebrates (Sanchez-Bayo, 2014). Beyond their use in agriculture, neonicotinoids are used to control human and animal parasites such as bed bugs and fleas (Bass et al., 2018). Imidacloprid, acetamiprid, dinotefuran, thiamethoxam, and clothianidin are among the neonicotinoid pesticides. Due to their extensive usage against a wide range of sucking and certain chewing pests, neonicotinoid insecticides have seen the quickest growth in the last ten years in the field of crop protection (Ensly, 2018). Similar to the naturally found alkaloid (S)-(−)-nicotine, all neonicotinoids function as agonists of the molecular target site, the post-synaptic nicotinic acetylcholine receptors (nAChRs), on the insect central nervous system (CNS) in a selective manner (Jeschke et al., 2008).

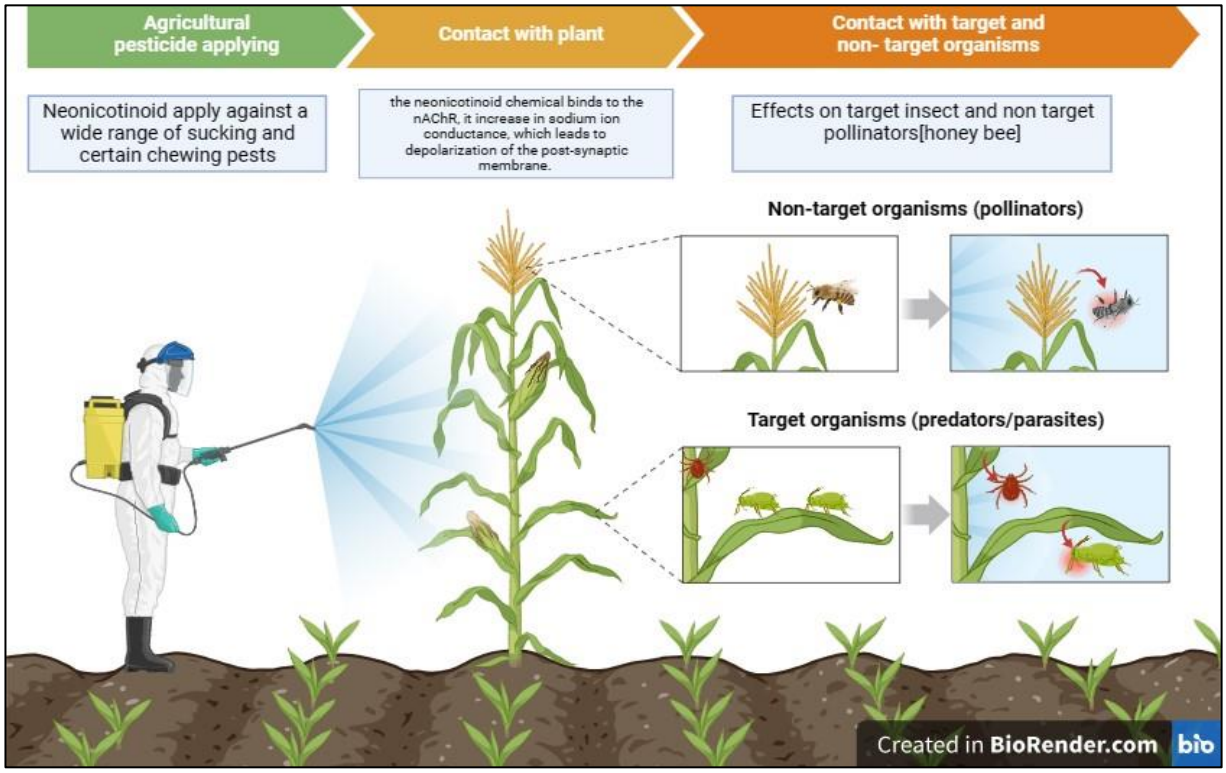


Figure 1. Neonicotinoid on Insects in Agriculture

Neonicotinoids are now well known to a large number of individuals due to media and online publications concerning bee reductions. Numerous studies have been conducted on this subject in recent years, and the data indicates that neonicotinoids' effects on bees and other pollinators are too significant to be disregarded (Osborne, 2012). In recent years, there has been much discussion about the potential cause of colony collapse disorder, with neonicotinoid insecticides receiving particular attention. The extent of the harm produced by these pesticides is debatable, though; some investigations indicate that bees are harmed by neonicotinoids in amounts commonly used in crops, while other papers state that the data is inconclusive (Guzman-Novoa, 2016).

Few people are aware of neonicotinoids' effects on aquatic environments since the discussion over them has been centered on bees. However, when we consider the implications for the greater aquatic ecosystem, they provide challenges to this ecosystem that may be more subtle in nature but more widespread in reach. In the present review, we have selected dinotefuran, clothianidin and thiacloprid owing to their distinct chemical features, in order to throw light on their effects in aquatic environment. The main ways that materials get into aquatic ecosystems are through surface runoff from rainy events, soluble or insoluble fractions carried by snowmelt, leaching into groundwater and subsequent subsurface discharge into wetlands and other surface waters, dust from talc and graphite from seeding drills, decomposition of effectively treated plants in lakes and streams, and deposition of treated seeds, soil, or spray drift into holes in the ground. Most surface water pollution is anticipated to occur from runoff following significant precipitation occurrences (Morrissey et al., 2015; Rangamani et al., 2023).

Chemical residues found in water are a continual threat to aquatic life since they are unable to escape it. The internal concentration of the insecticide, which in turn depends on its external concentration, the dynamics of each species, and its detoxifying capacity, determine how long it takes an organism to reach its death threshold (Hong et al., 2018). Fish inhabit almost all aquatic habitats and are extensively spread. Fish are a great model for environmental toxicological research in aquatic systems and chemical safety evaluation because they are a bio-indicator that is sensitive enough to changes in the aquatic environment (Dutta et al., 2014; Sarkar & Madhu, 2016; Sanchez-Bayo et al., 2016).

Neonicotinoids can be ingested by people who are not in close touch with them by means of fruits and vegetables that have been harvested from farm-land that has been treated with neonicotinoids. Neonicotinoids were found in 29 samples of fruits and vegetables, in 72% of the fruits and 45% of the vegetables (Borsuah et al., 2020). It has been discovered that neonics have effects on mammalian nAChRs that resemble those of nicotine. The operation of the human brain depends critically on these receptors, particularly throughout development and for memory, cognition, and behaviour. The capacity to bind to the most common subtype of nAChRs in mammals, the α4β2, which is concentrated in the thalamus, is one unique feature of neonic toxicity. Changes in this neuroreceptor subtype's density have been linked to a number

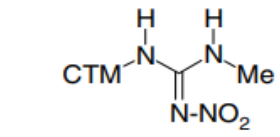
of illnesses affecting the central nervous system, such as depression, schizophrenia, Parkinson's disease, and Alzheimer's disease (Cimino et al., 2017; Haloi et al., 2023).

Structure of Neonicotinoids

Neonicotinoids synthesized in the past few decades have four chemical structures: an aromatic heterocyclic group; elastic bonds; hydro heterocyclic groups, often known as guanidine/amidine groups; and an electron-withdrawing group. Furthermore, by altering the structures of the aforementioned compounds to substitute a sulfonamide functional group or its cyclical equivalent for a cyano- or nitroguanidine/amidine group, new neonicotinoid derivatives are constantly being produced (sulfonamide neonicotinoids, e.g., sulfoxaflor) (Buszewski et al., 2019).

Clothianidin

Clothianidin, also known as (E)-1-(2-chloro-1,3-thiazol-5-yl-methyl)-3-methyl2-nitroguanidine, is a novel nicotinic insecticide with outstanding efficiency, safety, and selectivity. Its impact was comparable to that of the nicotinic acetylcholine receptor, causing shock, gastrointestinal toxicity, and internal absorption (Panget et al., 2020). Clothianidin is mostly used in rice, vegetables, fruit trees, and other crops to control hemipteran, coleopteran, dipteran, and some lepidopteron pests. For a wide range of pest species belonging to the groups Orthoptera, Isoptera, Diptera, Lepidoptera, Homoptera, and Heteroptera, clothianidin shows good control efficacies in modest doses. The vast insecticidal spectrum, strong activity at low dosage, long-term control impact, outstanding systemic action, numerous treatment options, and high crop safety may be summed up as the biological qualities of clothianidin. In insect nicotinic receptors, clothianidin binds with a high affinity (Wakita, 2011).

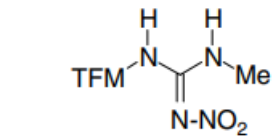


Clothianidin (TI-435, 2002)[a]
(H, Me)

Structure 1. Clothianidin

Dinotefuran

Mitsui Chemicals Agro created dinotefuran, also known as (RS)-1-methyl-2-nitro-3-(tetrahydro-3-furylmethyl) guanidine, a neonicotinoid pesticide. Furthermore, dinotefuran was a chiral insecticide that has two isomers: R-dinotefuran and S-dinotefuran (Wakita et al., 2003). The LC_{50} values of R-dinotefuran and S-dinotefuran in soil were found to be 8.786 and 3.286 mg/kg, respectively, while the toxicities of S-dinotefuran and R-dinotefuran to earthworms differed by 2.67-fold. Different from other neonicotinoids, dinotefuran offers a tetrahydrofuran (THF) moiety that contains a chloropyridine or chlorothiazole ring, which is thought to be



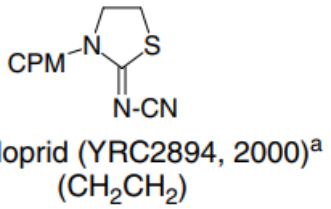
Dinotefuran (MTI-446, 2002)[a]
(H, Me)

Structure 2. Dinotefuran

a crucial structural component for the neonicotinoid activity. With the use of the cholinergic ester moiety as a lead structure, a successful molecular design technique, dinotefuran with the cyclic ether THF functional group has been discovered (Zhang et al., 2022).

Thiacloprid

Thiacloprid is a neonicotinoid pesticide used to protect vegetables, orchards, tea, maize, and oilseed rape seeds (Uneme, 2011). Thiacloprid was created to be used on agricultural crops to control insects, particularly aphids and small flies. It is a product used to protect oilseed rape, fruit trees, vines, vegetables, potatoes, and ornamental woods against animal and insect pests and flies. Thiacloprid molecules are polar, and its white powder is soluble in water as well as organic solvents such as acetone, dichloromethane, dimethyl sulfoxide, and ethanol. Because Thiacloprid is stable throughout the pH range 4-9, pH has no effect on solubility. The low partition coefficient (log P = 1.26) suggests that it is poorly soluble in fat and has poor absorption and distribution in the body (Verebova et al., 2021).



Structure 3. Thiacloprid

Interaction and selectivity mechanism of Neonicotinoids Insecticides Dinotefuran, Clothianidin and thiacloprid:

Neonicotinoids are nicotinic acetylcholine receptor (nAChR) agonists found in insect nerve synapses. They disturb invertebrate brain activity by binding to post-synaptic nAChRs and functionally interfering with normal neural activity. When the neonicotinoid chemical binds to the nAChR, it produces an increase in sodium ion conductance, which leads to depolarization of the post-synaptic membrane. Unlike acetylcholine, neonicotinoids' action is not restricted by acetylcholinesterase; as a result, neonicotinoids cause extended neuronal activation, which leads to hyper-excitation of the insect nervous system, followed by convulsions, paralysis, and death. The binding of neonicotinoids to nAChRs is thought to be mostly irreversible and cumulative over time. Invertebrates can be harmed by even modest dosages over time, causing stunted growth and development, changed behaviour, restricted mobility, diminished adult emergence, and reduced eating. Furthermore, because of the conserved nature of insect neurophysiology, neonicotinoids impact both pest and non-target species, albeit to varied degrees (Cavallaro et al., 2017). There are several subtypes of nicotinic receptors found in mammalian tissue. The various subtypes are made up of various combinations of subunits. Nicotinic receptors are found in animals' autonomic ganglia, skeletal muscle, spinal cord, and several brain areas. Because of the differing binding qualities of the various receptor subtypes, neonicotinoids have substantially lower action in vertebrates than in insects (Ensley, 2018).

Toxicity of dinotefuran, clothianidin and thiacloprid towards the aquatic environment:

Insecticides, particularly neonicotinoids, have caused surface and ground water contamination in water bodies near high agricultural zones where neonicotinoids are often employed in recent years. Neonicotinoids applied to soil decompose between 25.4% to 80.9%; however, the proportion varies depending on application rate and soil type. This indicates that between 20% and 75% of neonicotinoids used are accessible for transfer to surface waterways via runoff or leaching into groundwater. Furthermore, following pesticide treatments, sprayer equipment typically holding a combination of the residue may result in offsite runoff and have a harmful impact on the environment if not properly controlled (Madhu et al., 2022). Furthermore, there is rising worry about groundwater contamination caused by pesticides used in agricultural businesses and urban areas (Ensley, 2018).

Dinotefuran

Although dinotefuran has a high environmental safety in water, its high solubility and persistence significantly enhance its risk to aquatic life. Dinotefuran has a solubility of 40 g/L at 20 °C and a maximal half-life of 100 days. As a result, it is critical to assess the possible harm of dinotefuran to aquatic creatures (Pang et al., 2020). Furthermore, dinotefuran has a lengthy half-life in acidic, neutral, and slightly alkaline fluids, with a maximum half-life of more than a year (Verebova et al., 2019).

Clothianidin

Due to its poor soil binding, high water solubility, and persistence in soil, most Clothianidin maintained in soil is more likely to move to groundwater, streams, wetlands, and ponds. The Clothianidin has been found at quite high levels in a variety of aquatic habitats, including groundwater, wastewater treatment plant effluents, and wet land ponds (Yang et al., 2022). Clothianidin exhibited modest toxicity in carp, with a 96-hour LC_{50} greater than 100 mg/L. Clothianidin was also shown to be non-toxic to algae (72 hr EC50: 177 mg/L) and Daphnia magna (48 hr EC_{50}: 40 mg/L). These findings indicate that clothianidin has no effect on aquatic organisms (Velisek et al., 2018).

Thiacloprid

Thiacloprid has high-water solubility (184-186 mg/L) and a relatively low log Kow (1.26) at 20°C. Thiacloprid is stable in anaerobic aquatic conditions with a half-life of over one year and degrades in aerobic aquatic conditions with a half-life of 10-63 days (Stara et al., 2021). Thiacloprid has been shown in experiments to produce a variety of pathological and behavioral abnormalities in aquatic creatures. Significant alterations in antioxidant activity and aggressive behavior in crayfish, as well as reduced weight and length of carp (*Cyprinus carpio*) bodies, were observed (Akter et al., 2023).

Persistence of neonicotinoids in soil, surface water and ground water:

Because neonicotinoids are extremely soluble in water, they can easily migrate downhill and stay in the soil for months to years, depending on formulations, soil texture, organic matter content, management techniques, and climatic conditions. The downward flow often occurs from the topsoil, which is thought to be the zone with the most microbial activity; therefore, neonicotinoid residues may constitute a hazard to soil microorganisms (Pietrzak et al., 2020). Neonicotinoid insecticides are susceptible to a variety of processes before reaching groundwater, including sorption, biodegradation/biotransformation, and chemical transformation, which can slow migration rates and/or lower concentrations and loads (Ramadevi et al., 2022).

Because neonicotinoids have such a long half-life in soils and are water-soluble, they can deposit and flow into surface and groundwater. So, there is a correlation between bird losses and the presence of neonicotinoids in water, and they also harm fisheries by drastically cutting yields. The discovery of neonicotinoid residues in surface water systems up to 225 g/L, is cause for worry because aquatic invertebrates are key members of many fresh water bodies, and certain species are especially susceptible to neonicotinoids (Goulson, 2013).

Economic benefits of neonicotinoids:

There is abundant evidence that neonicotinoids can provide effective control of a broad range of insect pests. It is less clear to what extent the widespread adoption of neonicotinoids has contributed to yield increases in farming or whether neonicotinoids offer economic benefits compared to alternatives. Yields per hectare of almost all arable crops have increased markedly over the last 60 years as a result of many changes, including improved crop varieties, widespread use of artificial fertilizers, new agronomic techniques and the development of successive generations of pesticides. However, the pace of yield increases has slowed, and yield increases in the last 20 years in developed countries have been modest, with some crops such as oilseed rape showing no increase coincident with the introduction of neonicotinoids. Where yield gains have occurred in recent years, it is difficult to distinguish the role of neonicotinoids from the effects of other agronomic practices changes (Budge et al, 2015).

Impact on Animal Health:

Oxidative stress

Increased lipid peroxidation, reduced glutathione levels, and altered activity of important antioxidant enzymes (e.g., catalase, superoxide dismutase, and glutathione peroxidase) are all symptoms of neonicotinoid exposure. Thiacloprid raises nitric oxide levels in polymorphonuclear leukocytes and plasma from rats exposed to the drug. Curcumin and vitamin C, for example, can protect tissues against neonicotinoid-induced oxidative damage. Based on the findings, oxidative stress generated by neonicotinoid pesticide exposure has been postulated to have a significant role in their toxicity in non-target species (Wang et al, 2018).

Reproductive Toxicity

Multiple studies have found that neonicotinoids have negative reproductive and developmental consequences in mammals, including greater rates of embryo loss, early delivery, lower pregnancy rates, lower sperm production and function, lower child weight, and stillbirth. Clothianidin substantially raised amounts of thiobarbituric acid-reactive compounds, cholesterol, and palmitic, linoleic, and arachidonic acids in the testis of male rats, but did not promote sperm DNA breakage (Han et al, 2018).

Metabolite toxicity

Metabolites of neonicotinoid chemicals can be more hazardous than the parent compounds. Metabolites generated by the removal of nitro- or cyano-functional groups, in particular, have the potential to be more selective and to bind more strongly to mammalian nAChRs. Desnitro-imidacloprid, for example, exhibits an affinity for mammalian nAChRs equivalent to nicotine. When the neonicotinoid is converted to the desnitro metabolite, the selectivity ratio for insects vs vertebrates decreases from 565 to 0.005. Studies on Mice shown that imidacloprid and desnitro-imidacloprid, like nicotine stimulates the extracellular signal-regulated kinase cascade and cause intracellular calcium mobilization in rat PC12h cells (Wang et al, 2018).

Endocrine Effects

The effects of neonicotinoids on endocrine disruption have been studied in vitro. Thiacloprid inhibits aromatase (CYP19) activity in a fetoplacental steroidogenesis model. Estrone and estradiol production increased, whereas estriol production decreased. Estrogens are vital during pregnancy, and alteration in estrogen production may damage the fetus as well as the mother's health. Evidence suggests that neonicotinoids are metabolized by CYP3A7, which affects the conversion of dehydroepiandrosterone sulphate to estriol and might explain the observed reduction in estriol production. This conclusion is concerning since enhanced estrogen synthesis in tumors has been proven to stimulate cancer cell proliferation, with aromatase playing an important role in this process (Zuscikoa et al, 2023).

Conclusion

The present study will provide the toxicological properties of three individual neonicotinoids: dinotefuran, clothianidin, and thiacloprid. Farmers when suggested to use these pesticides, they must try to use it at safer dose for the protection of aquatic ecosystem. In addition, the pesticide-based method to control insect pest must be replaced by some other eco-friendly and cost-effective approaches. The outcomes of present study suggest reducing the pesticides usage which will help to protect the aquatic biodiversity at their natural habitat.

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