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ABSTRACT: Neonicotinoids insecticides are neurotoxic systematic insecticides used in agricultural field for the crop protection. Neonicotinoids kills not only the insects also kills the pests and had a great threat to the pollinators. These includes acetamiprid, thiacloprid, nitenpyram, imidacloprid, dinotefuran, thiamethoxam and clothianidin. Most of the neonicotinoids are persistent and have high leaching runoff potential in soil. Because of these characteristics, neonicotinoids leads to affects the surface water, ground water, flora and also less effects on the fauna and human beings. This review suggests the toxicity amount of neonicotinoids and also the acute and the chronic effects. The above and below limits of concentration of these insecticides in soil and water may causes the acute and the chronic effects respectively. These are mainly detected with the help of HPLC or else LC-MS. Neonicotinoids are not easily biodegradable, the variety of bacterial community are used to reduce the concentration of neonicotinoids in step by step process. Due to these ill effects, most of the country restricts to use these insecticides and created many law to use their limits. These review are informative to the risk assessment of neonicotinoids in the soil and water in agricultural fields.

Keywords: Biodegradation, Neonicotinoids, Pollinators, Soil, Toxicity and water

1 Introduction

Credentials of Neonicotinoids

Neonicotinoids concentration are high in soil and water but are very less in the sediments. The assessment of neonicotinoids are acute impacts to the insecticides and chronic impacts to the aquatic environment. Imidaclopride impacts in soil are spread over up to 1km from the applied and these are most poisonous insecticides all over the world (Jean Marc bonmatin et al., 2019). The types of crop and concentration of neonicotinoids are assessed by the

statistical analysis method. The distribution of neonicotinoids to the fields are having varies methods. Due to the persistent and runoff nature, the concentration of neonicotinoids high in soil. The occurrence and distribution of neonicotinoids insecticides in surface water at different seasons are analyzed (John Struger et al., 2017). Neonicotinoids are neurotoxic insecticides that are mostly affects the insects than the invertebrates. Due to their toxic nature, it causes the acute and the chronic diseases. (Kathryn L. Klarich et al., 2017).

Neonicotinoids concentration are detected inside and outside the fields throughout the sampling periods. The quantification of usage of neonicotinoids are determined by the software Analyst 1.4.1. This study resulted the concentration of neonicotinoids in soil and water by using LC-MS method (Schaafsma et al., 2015). The insecticides concentration in leachate

was assessed for the six consecutive months from the month of distribution of neonicotinoids. The ground water contains the neonicotinoids are reused back onto the crop fields through the high capacity irrigation wells and it creates continues effects on the surrounding ecosystem (Anders et al., 2014). The detection and quantification of five different types of neonicotinoids were determined and measured by LC-MS. In the limit of detection was at the lowest concentration which can be detected with an acceptable accuracy and precision manner (Damian Pietrzak et al., 2019).

Properties and Environmental Fate

Neonicotinoids are long persistence in soil and easily soluble in water. Due to this properties, the residues of neonicotinoids tends to leach through the soil, soluble to the storm runoff water and percolates into the soil reach the ground water (Jean Marc bonmatin et al., 2019). Neonicotinoids are rarely detected in precipitation, most of the detection are only during the period of distribution. These insecticides not only kill the invertebrates but also destroys the pollinators. (John Struger et al., 2017). The exposures of neonicotinoids to the living being are through inhalation, injection and drinking of contaminated water. These may causes the health effects to the humans and mammals. Due to this effects human being are highly infected by carcinogenic diseases (Damian pietrzak et al., 2019).

The distribution of neonicotinoids to the vegetations are by spraying method. By these method

of distribution these insecticides are deposited on the surface of the fruits, vegetables and leaves. After the consumption of these contaminated fruits and vegetables may causes the severe effects (Sarfraz Hussain et al., 2016).The usage of these insecticides is against the bees, cockroaches, termites and larvae in maize and sugarcane fields. These may also causes the potential risks to the humans and animals. It also changes the properties of the soil, ground water and surface water (Gabriel Rodriguez Castillo et al., 2018).

1.2. Toxicity of Neonicotinoids

The samples collected from the different types of the crop fields, about 75% of the samples are contain the higher value of imidacloprid (230ng/lit). These maximum concentration of imidacloprid in the fields affects the characters of the soil nature (John Struger et al., 2017).The major contaminants of neonicotinoids in the maize field surface water and the soil are imidacloprid and thiamethoxam. The toxicity concentration of imidacloprid and thiamethoxam are 43ng/l and 16ng/l. These causes the major impacts to surface water and the soil in maize field (Schaafsma et al., 2015).

The residues of neonicotinoids such as imidacloprid, clothiadinin and thiamethoxam are present in most of the soil and deep wells in the potato cultivation areas. The toxicity concentration 41ng/l, 23ng/l and 18ng/l (Anders et al., 2014).The toxicity concentration of acetamiprid, imidacloprid and clothiaindin in the fruits at the region are 0.058mg/l, 0.095mg/l and 0.12mg/l. Due to the consumption of these contaminated fruits affects the diseases to the humans and animals (Carol J.Hartley et al., 2019).

2 Acute and Chronic Impacts

The acute effects of neonicotinoids on mammal, generally reported as less when compared with other insecticides like carbamate and organophosphate. However the bee population faces the great threat because of neonicotinoids and it may not severely affect the aquatic invertebrates (Jean Marc bonmatin et al., 2019). According to the sensitivity characteristics of the aquatic arthropods to the neonicotinoids the acute and chronic effects changes. The imidacloprid causes feeding inhabitation in many flies if their LC_{50} concentration is $\geq 1\mu\text{g/L}$. These may causes the nervous disorder to the invertebrates (Gabriel Rodriguez Castillo et al., 2018).

The toxicity concentration of acetamiprid, imidacloprid and clothiaindin are comparatively less in fruits at the region are 0.058mg/l, 0.095mg/l and 0.12mg/l. Due to the consumption of these contaminated fruits affects the long term of chronic diseases to the humans and animals (Damian

Pietrzak et al., 2019).*Daphnia magma* is the only species considered as the global industry invertebrates species for most of the chemicals test. Several reviewers reported that *Daphnia magma* is the far least sensitive test species for acute and chronic impacts of neonicotinoids studies (Sarfraz Hussain et al., 2016).The toxicity concentration of acetamiprid, imidacloprid and clothiaindin are comparatively less in fruits at the region are 0.058mg/l, 0.095mg/l and 0.12mg/l. Due to the consumption of these contaminated fruits affects the long term of chronic diseases to the humans and animals (Carol J.Hartley et al., 2019).

3 Analysis of Neonicotinoids

The collected samples from the different regions are conducted for the detection and analysis of concentration of neonicotinoids by using LC-MS test. The limit of detection (LOD) and limit of quantification (LOQ) are the theoretical methods used for the detection and quantification of neonicotinoids in the samples are calculated. The chromatographic analysis was performed using a gradient program with a binary mobile phase consists of A and B (John Struger et al., 2017).The neonicotinoids were extracted from the original collected soil samples by using the following procedures, the soil samples were sieved through 0.5mm mesh and oven for 2-3 days at 40°C and grinded into a powder form with a mortar. 1g of powdered sample were weighed and mixed with 9ml of pure H₂O and 20ml of acetonitrile 125ml of ethyl acetate were centrifuged at 4000rpm for 5 min and the supernatant was formed. The supernatant was mixed with 2g of magnesium sulphate, 0.5g of sodium chloride, 0.5g of trisodium citrate and 0.25g of sodium hydrogen citrate were shaken well and centrifuged at 4000rpm for 5 min. The epiphase were formed and collected for further analysis in LC-MS or UHPLC (Jean Marc bonmatin et al., 2019).

The analysis of five neonicotinoids was done by using ultra high performance liquid chromatography (UHPLC), where UPLC system was coupled to a TQ-S triple quadrupole mass spectrometer in the case of water. The mobile phase A consist of H₂O + 0.05% formic acid + NH₄FA and mobile phase B of acetonitrile + 0.05% formic acid. The positive electrospray ionization using multiple reaction monitoring mode (MRM) was performed to detect MS/MS (Michelle L.Haldik et al., 2017).The software ANALYST 1.4.1 were used to find out the data acquisition, processing, peak area integration, final quantification and linear regression. The linear regression analysis of the peak area ratios of analyst/IS versus analytic concentration were used to from linearity calibration curve (Damian Pietrzak et al., 2019).

4 Treatability Methods

To reduce the neonicotinoids residues by different physiochemical approaches such as absorption, granular activated carbon, direct photolysis, incineration and advanced oxidation process. The recent studies suggest the biodegradation and biotransformation methods to reduce the concentration of neonicotinoids (Damian Pietrzak et al., 2019). The concentration of neonicotinoids in the drinking water samples were quantified and the suitable treatment methods were adopted. The Granular Activated Carbon filtration method were used to reduce the concentration of neonicotinoids in the drinking water. GAC method rapidly and near completely remove the neonicotinoids in the drinking water (Jean Marc bonmatin et al., 2019).

Biopurification systems (BPS) is a biotechnological method used to reduce the point source contamination of insecticides from on farm practices. Biomixture is the active core in the Biopurification systems, the biomixture contains coconut fiber, compost and pre exposed soil at different volumetric compositions (50:25:25). The biomixture were moistened 75% and stored at 25°C for 1 month when prior to use (Gabriel Rodriguez Castillo et al., 2018). Biodegradation are classified into two different methods such as pure bacterial culture biodegradation and microbial consortia biodegradation. Bacterial biodegradation may be catabolic or cometabolic. The neonicotinoid contain the rich content of carbon and nitrogen, these content are highly used for the growth of bacteria in catabolic bacterial biodegradation (Sarfranz Hussain et al., 2016).

5. Conclusion

We conclude that, the solubility and persistent nature of neonicotinoids are disrupting both the food chain and biogeochemical cycles. Many interacting factors of neonicotinoids are debated to cause the honey bees and also affects the parasites, diseases to mammals, habitat loss and climatic changes. The neonicotinoids insecticides are more sustainable in the soil than the water. The residues of neonicotinoids are more bonded to the soil components and they are not easily biodegradable. The toxicity concentration may depends on the seasonal variations at the crop fields. During the summer season the concentration of residues are high due to the average distribution of water from wells, rivers and the less runoff water. Due to the high level of toxicity of these insecticides causes the colony collapse disorder to the bees and the diseases to the invertebrates. The concentration of imidacloprid and thiamethoxam in the honey bees are 3.7ng/l and 5ng/l respectively.

The limit of detection (LOD) and limit of quantification (LOQ) are the theoretical methods used for the detection and quantification of neonicotinoids in the samples are calculated. The analysis of neonicotinoids was done by using LC-MS, HPLC and ultrahigh performance liquid chromatography (UHPLC). The software ANALYST 1.4.1 were used to find out the data acquisition, processing, peak area integration, final quantification and linear regression. To reduce the neonicotinoids residues by different physiochemical approaches such as absorption, granular activated carbon, direct photolysis, incineration and advanced oxidation process. The recent studies suggest the biodegradation and biotransformation methods to reduce the concentration of neonicotinoids. Biomixture is the active core in the Biopurification systems and Biodegradation are classified into two different methods such as pure bacterial culture biodegradation and microbial consortia biodegradation.

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