A Review on Contamination of Soil and Water by Neonicotinoid Pesticides and Trends in Soil and Water Samples with Chromatographic Analytical Techniques

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ABSTRACT

Pesticides are synthetic chemicals that destroy pests and insects, improving vegetation and damaging the ruling class. Pesticides gain the vegetation; However, the protective use of pesticides goes against the traditional ethics of Integrated Pest Management (IPM), leading to environmental concerns. It has been observed that neonicotinoid pesticides and their metabolites can continue and accumulate in soils. They are freely soluble in water and compulsive, draining into waterways, and more are found in environmental samples, eventually affecting human well-being. Therefore, regional instability, the traditional principles, and anthropogenic versus natural origin of conceivably dangerous title pesticide in soils and water assessment are precariously main to evaluate human impact. This review article mainly focuses on extensive information about the sample preparation methods, discovery methods, and the developed systems to samples from various fields of soils and water to detect the neonicotinoids.

Keywords: Soil contamination, Water contamination, Neonicotinoid pesticides, Anthropogenic, Sample preparation, Chromatographic techniques.

INTRODUCTION

Neonicotinoids are a category of chemicals that are amalgamated from evidently taking place plant compounds with insecticidal properties like nicotine. Neonicotinoid pesticides are categorized into three generations: chloronicotine, thionicotine, and furan nicotine, along with Imidacloprid (IMI), Acetamiprid (ACE), thiamethoxam (THM), furosemide (FSM), fluidoximide (FDM), chlorothiazide (CLO), imipramine, thiaclorop (THA)1. Clothianidin, imidacloprid, thiamethoxam, acetamipride, and thiaclorop neonicotinoid...
compounds are licensed for utilization as pesticides in the UK and EU. Worldwide pesticides collectively with fertilizers play a crucial position in agriculture for a significant increase in food production. The annual worldwide net population growth is eighty million, but this has been kept. The world population is anticipated to be nine billion human beings via means of 2030. Consequently, pesticides are carried out in modern agricultural practices to satisfy the demand for food production. The structure, chemical formula, molecular weight, and year of introduction of neonicotinoid insecticides are shown in Fig. 1. Also, the NEOs’ chemical properties (log Koc, Kow, and Solubility) are shown in Table 1. 

| Analytical compound | Water solubility (mg/L) at 20°C | Lipophilicity (log Kow) | Soil Affinity (log Koc) | Reference |
|---------------------|---------------------------------|-------------------------|------------------------|-----------|
| ACE                 | 2950                            | 0.80                    | 2.3                    | [4]       |
| CLO                 | 340                             | 0.91                    | 2.08                   |           |
| IMI                 | 610                             | 0.57                    | 2.19-2.90              |           |
| THA                 | 184                             | 1.26                    | 3.67                   |           |
| THM                 | 4100                            | -0.13                   | 1.75                   |           |

The neonicotinoids evolved in the 1980s, and the primary neonicotinoid, Imidacloprid, was launched by Bayer Crop Science LLC in the early 1990s. Initially, Imidacloprid was advanced to control agricultural pests, and bugs have been validated to be a completely powerful pediculicide in dogs and cats. Their molecular goal is that neonicotinoids selectively act on insect nicotinic acetylcholine receptors (nAChRs). Therefore, the synthesis of neonicotinoids may be considered a milestone and enables the knowledge of practical residences of the insect nAChRs.

In insects, those receptors are positioned totally in the central nervous system. Mammalian tissue additionally carries more than one nAChRs subtypes, and those are shaped through combos of 9α, 4β, γ, and ε subunits differently. Fipronil and neonicotinoids have an excessive vapour pressure, values starting from \(2.8 \times 10^{-8}\) and \(0.002\) mPa at 25°C. The low ability for volatilization of those materials means during spray applications and will be found in the only gaseous form for a short period. Even though desorption was reduced at low temperatures and low pesticide concentrations, Imidacloprid sorption was favourably related to the soil's natural matter and mineral clay content material. The solubility of neonicotinoids in water is determined by the temperature & pH of the water, the pH of water, and the physical state of pesticides used. For example, at 20°C and pH 7, thiacloprid and nitenpyram have solubility's ranging from 184 mg/L (moderate) to 590.0 mg/L (high). The physiochemical traits of neonicotinoids, in terms of water solubility, \(P_{ka}\), and \(k_{ow}\) confer systemic characteristics enabling them to be absorbed and translocated within all plant tissues and are continual and neurotoxin. As per the Environmental Protection Agency (EPA) guidelines, neonicotinoids are categorized as II and III magnificence toxicity agents. Generally, at fieldsensensible ranges of pollution, neonicotinoids and fipronil have a poor impact on a wide variety of non-target invertebrates physiology and survival in terrestrial, aquatic, marine, and benthic habitats. Neonicotinoids are used to treat seed, so NIN's taken by plants that are attractive to pollinators, including Oil Seed Rape (OSR), maize, and sunflowers. In the field, thiamethoxam is metabolized to clothianidin. Some bees have very catholic tastes and are not likely to feed most effectively on vegetation treated with neonicotinoids. Hence, the risk to be populations from neonicotinoids noticed.
However, neonicotinoid pesticides are very functional agents for improving food production rates. Still, the non-targeted pests, aquatic animals, and birds are affected by the residue of neonicotinoids in soil and environmental samples. Various studies reported that the plant's average absorption of active ingredients of insecticides is about 20% depending on plant type and size; subsequently, the remaining 80% of bulk ingredient is speeded over the environment\textsuperscript{15}.

Imidacloprid neonicotinoids display the impact on white-tailed deer and fawns with noticeably excessive concentration of Imidacloprid in spleen and genital organs additionally tended to be smaller and much less healthy\textsuperscript{16}. The higher toxicity of neonicotinoid insecticides, such as N-(6-chloropyridin-3-ylmethyl)-2-nitro imino imidazolidine (Imidacloprid), to bugs than to mammals is owing in part to target site selectivity on the nicotinic acetylcholine receptors (nAChRs) identified\textsuperscript{17–19}. Imidacloprid is a neonicotinoid insecticide that focuses on the nervous system by blocking acetylcholine receptors. It is considered non-poisonous to humans, however unintended inhalational exposure to Imidacloprid can cause severe gastrointestinal symptoms as well as breathing problems\textsuperscript{20}.

**Contamination of soil by neonicotinoids**

For more than a decade, it was observed that neonicotinoids have been linked to environmental and food contamination. Literature reveals that NEOs have been found in soil, surface water, dust, pollen, vegetable plants, fruits, tea, human hair, honey, and other places\textsuperscript{21–27}. In addition, neonicotinoids are being used as insecticides to replace organo phosphorus and carbonate insecticides, and their use is likely to rise internationally\textsuperscript{7}.

Pesticide residues of several pesticides were found in 83 percent of the tested agricultural soil, and 58 percent carried multiple residues, indicating that soil is contaminated with pesticides and their metabolites. Multiple pesticide residues in the agricultural soil environment appear to be the rule rather than the exception\textsuperscript{21}.

However, the amount of neonicotinoid pesticide residue is not the same for the longest time, and this was dependent on several factors like the type of soil, type and quantity of the compound, organic matter content, sunlight, temperature, and groundwater circulation shown in Figure 2\textsuperscript{15}.

![Fig. 2. Factors affecting the amount of NEOs in the soil (Reconstructed from\textsuperscript{15})](image)

In a recent European Union research, three hundred seventeen agricultural topsoil samples were tested for 76 pesticide residues. The only neonicotinoid studied, imidacloprid, was discovered in 7% of EU topsoil samples, with a maximum concentration of 0.06 mg/kg\textsuperscript{21}. An investigation reported that the accumulation of NEOs in the soil profile rose with the age plants' cultivation. This age had a significant role in regulating the overall amount of NEOs in the soil profile. In a large-scale field research conducted across the whole Swiss lowland agricultural area, it was discovered that practically all soils are contaminated by NEO insecticides, primarily IMI NEO\textsuperscript{28}. During the investigation of soils of five areas in Tianjin, China, six NEOs were identified, with ACE, IMI, and THX being the most commonly detected NEOs\textsuperscript{29}.

Wind erosion from contaminated soil may cause neonicotinoids to drift off target. These provide information on non-target species risk analysis models in maize agro ecosystems\textsuperscript{22}. In diverse soil types, the movement of neonicotinoid pesticides (clothianidin and thiamethoxam) applied as a maize seed dressing or pre-emergence spray application was studied. Guttation liquid measurements were used to characterize uptake of these in plants sprouting from coated seeds\textsuperscript{23}.

Only 5% of the neonicotinoid active
ingredient in insecticides is taken up by agricultural plants, with the rest dispersing into the environment. The European Food Safety Authority (EFSA) was involved with assessing the risks of clothianidin, imidacloprid, and thiamethoxam and their influence on bees. B. Kumari et al., claimed that 80% of soil and groundwater samples collected from paddy-cotton, sugarcane fields, and tube wells in fields surrounding Hisar, Haryana, India, contained neonicotinoid residues beyond regulatory limits. Based on projected half-lives >150 days, neonicotinoid insecticides may be persistent in the soils examined. In general, one of the physical characteristics that determine the low-sorption co-efficient of neonicotinoids in the soil is soil organic carbon.

Two systemic neonicotinoid pesticides transfer from the soil into the pollen and nectar of squash flowers. In nectar, the concentration range is 13-17 ppb, while pollen has a concentration range of 21-22 ppb. Vertebrates are less vulnerable than arthropods; in birds and mammals, a modest number of prepared seeds can cause direct fatality. The capacity of active substances to elute in sandy soil was associated with their water solubility, demonstrating that thiamethoxam eluted 30 percent faster than clothianidin.

Contamination of water by neonicotinoids

Because neonicotinoids have such a long half-life within soils and are water-soluble, they can deposit and flow into surface and groundwater. So there’s a link between bird losses and the presence of neonicotinoids in water, and they also damage fisheries, lowering yields dramatically. The structure and function of aquatic ecosystems are being impacted by the collapse of many invertebrate populations, mostly due to the ubiquitous presence of waterborne residues and the severe chronic toxicity of neonicotinoids.

The finding of neonicotinoid residues in surface water systems up to 225 g/L, is cause for concern because aquatic invertebrates are important members of many fresh water bodies, and some species are highly vulnerable to neonicotinoids.

Neonicotinoids are toxic to aquatic and grassland invertebrates and disrupt local ecosystems at very low levels in the environment.

Methods for the determination of neonicotinoids in soil and water

For the evaluation and quantification of neonicotinoids in title samples, several procedures have been developed. The analytical method chosen has a significant impact on the quality and accuracy of the results. Regardless of the method utilised, there are three main phases that must be completed before evaluation: extraction, separation, and detection, and it is shown in Figure 3.

Sample preparation

The sample preparation stage is critical to the entire process, yet it is also the most time-consuming and labor-intensive phase. Furthermore, most errors occur during this stage, endangering the results. The primary purpose of sample preparation is to maximize solvent extraction and enrichment of target analytes while reducing interferences during analysis. Sample preparation and enrichment of the target chemicals are crucial because numerous contaminants are found in title samples at low amounts. The initial stage is to extract substances using a variety of organic solvents, either alone or in combination.

In addition, some processes incorporate a clean-up step after extraction to eliminate interfering species before moving on to the analysis. The type of separation will influence sample preparation and the quantitative procedures used. Table 2 summarise the various extraction and detection techniques for the estimation of NEOs in soil and water samples.
Solid Phase Extraction (SPE)

Herbicides were extracted using the SPE technique. The principle of SPE is to retain selected substances on sorbents before eluting them with appropriate solvents. The extraction and clean-up operations are merged into a single step, resulting in clean extracts and lower solvent usage than the liquid-liquid extraction method; they are evaluated directly by Liquid Chromatographic technique. In the analysis of complicated matrices, the relative speed, simplicity, resilience, and consumption of a low volume solvent alternative. For neonicotinoid pesticides, this method was chosen by many researchers.

Liquid- liquid extraction

For the measurement of neonicotinoids in samples, liquid-liquid extraction (LLE) is the most commonly employed extraction and purification procedure. Large sample volumes and hazardous solvents are usually used in LLE. The extraction performance varies depending on the solvent and aqueous medium ratios utilised in the extraction technique. When a large amount of solvent is utilised, interferences can co-extract and impair the recovery of the target molecules. For the study of imidacloprid in soil, liquid extraction worked better at greater concentrations than soxhlet extraction. The greatest results were obtained using a mixture of two solvents in the ratio of Acetonitrile to water (20:80, v/v), with no extra clean-up required.

QuEChERS

Study devised the QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) technique with least interference. This might be adopt in any laboratory due of its simplicity. Many difficult analytical procedures being often used in prior procedures are replaced by easier ones in the QuEChERS multiresidue approach. The extraction of target compounds by salting out with magnesium sulphate (MgSO₄), acetonitrile, and sodium chloride (NaCl), as well as dispersive solid-phase extraction (DSPE) with anhydrous magnesium sulphate and primary secondary amine (PSA), is extremely effective for the removal of organic acids from samples. The QuEChERS method's first employed for pesticides in soil. The technique has been used to determine neonicotinoids in title samples in recent years. The modified QuEChERS method was used to determine the properties of the sample and neonicotinoids. For the title samples evaluation and quantification, the QuEChERS technique was utilised by various researchers.

Separation and detection

To separate and quantify neonicotinoids in soil samples, a variety of analytical approaches have been applied. Due to the low concentration of these sample matrix and the complexity of the matrix, analytical procedures with high selectivity and sensitivity are required. SPE, DLLME, liquid-liquid extraction, and QuEChERS extraction are the analytical methodologies and cleanup techniques for determining neonicotinoid pesticides in soil and water at trace level. As published in numerous research papers, Completely chromatographic analytical methods, such as gas chromatography (GC) and high-performance liquid chromatography (HPLC), are the most popular analytical methods for pesticide residues in agricultural and environmental media. Non-volatile and thermally unstable materials should be identified via liquid Chromatography.

Liquid chromatography

Liquid chromatography is a very sensitive and selective method. The most generally used techniques are liquid chromatography with mass spectrometry detector and random MS. However LC with other detectors has also been employed, such as UV and diode array detector (DAD), which have lower sensitivity and selectivity than LC-MS. Neonicotinoids can be detected at low quantities in complicated matrices using liquid chromatography and tandem mass spectrometry. This technique boosts sensitivity, minimise matrix interference, and adds structural data. The ions of interest are exclusively examined by the spectrometer in MS with multiple reactions monitoring (MRM) mode. Quantification of neonicotinoids in soil and water was also done using ultra high-performance liquid chromatography with random mass spectroscopy (UHPLC-MS/MS).
Table 2: Summary of extraction and detection techniques for the estimation of NEOs in soil and water samples

| Target NEOs          | Samples       | Extraction       | Separation/ Detection | Recovery (%) | LOD            | LOQ            | Ref     |
|----------------------|---------------|------------------|------------------------|--------------|----------------|----------------|---------|
| ACM, CLO, THI, THM   | Water         | None             | LC-MS/MS               | 85.2 to 109.3| 4.3 ng/l       | 0.3 to 1.5 ng/l| [15]    |
| 76 pesticides with IMI| Soil          | QuEChERS         | LC                     | None         | None           | None           | [21]    |
| CLO, THM             | Soil & Surface water | SPE & QuEChERS | LC-MS/MS               | 112.9        | 0.02 mg/kg     | 0.06 mg/kg     | [22]    |
| THM                  | Water         | SPE              | LC-MS/MS               | None         | None           | None           | [24]    |
| DIF, THM, CLO       | Cucumber Soil | QuEChERS         | HPLC/DAD               | 100.38       | 0.08µg/g       | 0.24µg/g       | [26]    |
| IMI, ACM, THI, CLO   | Soil          | QuEChERS         | LC-MS/MS               | 72.1 to 100.2| 0.01 to 0.84 ng/g| 0.05 to 2.79 ng/g| [48]    |
| MEF                  | Soil          | QuEChERS / LLE   | LCMS                   | 70 to 110    | None           | None           | [54]    |
| IMI, THI, THM        | Soil & Water  | SPE              | HPLC/UV                | 86 to 110    | 0.04 to 0.1 ng/ml| None           | [58]    |
| ACM, CLO, THM, IMI   | Soil          | QuEChERS         | LC-MS/MS               | 78 to 100.5  | 3.4 ng/g       | 13.3 ng/g      | [55]    |
| ACM, CLO, DIF, IMI, THI, THM | Water | SPE              | LC-MS/MS               | 78 to 107    | None           | None           | [56]    |
| ACM, CLO, DIF, IMI, THI, THM | Water | SPE              | LC-MS/MS               | 70 to 130    | None           | None           | [57]    |
| THM, CLO, THM, IMI   | Soil          | QuEChERS         | LC-MS/MS               | 78 to 100.5  | 3.4 ng/g       | 13.3 ng/g      | [55]    |
| THM, CLO, THI, THM   | Soil          | QuEChERS         | LC-MS/MS               | 78 to 107    | None           | None           | [56]    |
| THM, IMI, ACM, THI   | Water         | SPE              | LC-MS/MS               | 86 to 110    | 0.04 to 0.1 ng/ml| None           | [58]    |
| DIF, NIP, THI, CLO  | Water         | SPE              | LC-DAD                 | 81           | 0.01 to 0.03 mg/kg| None           | [60]    |
| THM, DIF, IMI, THI   | Soil          | QuEChERS         | LC-MS/MS               | None         | 0.012 to 19.3 ng/g| None           | [61]    |
| THM, IMI, CLO, CLO   | Soil          | QuEChERS         | LC-MS/MS               | None         | 0.012 to 19.3 ng/g| None           | [63]    |
| IMI, THI, ACI, CLO   | Soil          | SPEQuEChERS      | LC-MS/MS               | 70 to 120    | 0.025 ppm      | 0.05 ppm       | [64]    |
| DIF, NIP, AC, CLO, IMI| Soil         | DLLME            | HPLC/UV                | None         | 0.8 ng/ml      | 2.1 ng/ml      | [65]    |
| THM & its Metabolites| Soil          | QuEChERS         | LC-MS/MS               | 81.2 to 98.4 | None           | 0.01 mg/kg     | [66]    |
| CLO Metabolites      | Soil          | QuEChERS         | UHPLC-MS/MS            | 84 to 115    | 0.81 to 2.1 μg/g| 0.5 μg/g       | [67]    |
CONCLUSION

The primary and ultimate object of the review article was on trends in neonicotinoid pesticide determination methodologies by different researchers by following standard protocols. The current trend in neonicotinoid insecticide determination is very accurate and sensitive multi-residue analysis by LC technique coupled with MS or MS/MS as a detector. Various pre-treatment and detection approaches are being established, which has tremendously reduction in analysis time, sample size, and interference with respect to sample matrix. However, the extraction and detection technology of choice remains the classic extraction and detection system combined with mass for ultra quantification. These procedures, however, are time-consuming and costly. But, these constraints must be overcome in the near future in order to produce a cost-effective and environmentally acceptable technology that can identify a large number of pesticides in a single run at lower limits than the maximum residual levels. The literature review reveals that numerous extremely sensitive procedures for determination of neonicotinoids and their metabolites in title samples have been developed in recent years which helpful to the upcoming researchers to enhance the quantification methodologies at very low concentrations.

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Conflict of interest

The author declare that we have no conflict of interest.

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