



# Pesticides Analysis In Agricultural Soils Of Eight Different Villages At East Godavari, Andhra Pradesh, India Using Quechers- Dspe Combined Gc-Ms Method.

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## **Abstract:**

The comprehensive application of pesticides in agricultural practices to meet the food demand of growing world population resulted in accumulation of these pesticides into abiotic environment and biotic entities at different hierarchical levels. These toxic chemical substances are highly carcinogenic and a necessary step should be taken to control the application into agricultural practices. In the present study, the soil samples were collected from 8 different agricultural soils (primarily vegetable crops) of East Godavari, Andhra Pradesh, India during post harvesting time and to evaluate multiresidue pesticides qualitatively using QuickEasy Cheap Effective Rugged Safe (QuEChERS)-Dispersive Solid Phase Extraction (dSPE) clean up combined Gas-Chromatography Mass Spectrometry (GC-MS) method. The physiochemical parameter analysis of all soil samples revealed no observed large-scale variation among all study sites. The GC-MS analysis showed presence of 5 major pesticide compounds namely Terbufos (Organophosphate insecticide), Propiconazole (Triazole fungicide), Tebuconazole (Triazole fungicide) Cypermethrin (Pyrethroid insecticide) and Diclofop-methyl (Herbicide). It is evident that the use of restricted pesticides in agricultural operations is still ongoing, and it is essential to regulate this at the fundamental level of agriculture.

**Keywords:** Pesticides, Agricultural Soils, QuEChERS-dSPE cleanup, GC-MS.

## **1. INTRODUCTION:**

Pesticides (insecticides, herbicides and fungicides etc) are organic compounds used in agricultural practices to protect crops from plant and animal pests ultimately to improve crop yield [1,2]. To meet the food demand of growing world population, since last few decades, the use of organic pesticides has been increased intensively [3]. The inappropriate and excessive use of pesticides in agricultural practices causing pollution in various environmental matrices leads to their destruction [1]. These organic pollutants not only toxic, they are also mobile and efficient in bioaccumulation. The application of pesticide class and its quantity largely depend upon crop type and cultivation pattern [4]. Organophosphates, Organochlorines, neonicotinoids,

pyrethroids and carbamates are commonly used pesticide groups in agriculture. Organochlorine compounds are highly toxic, exhibit high solubility and persistence in the soil and water environment. In most cases these compounds exhibit mutagenic and carcinogenic properties. Organophosphates and carbamates are associated with infertility, teratogenic, cytotoxic and genotoxic effects and also inhibits the acetylcholinesterase enzyme in animals [5]. The pesticides in soil environment adsorb highly in clay or organic matter when compared to the sandy soils. Now a days a wide spectrum of pesticide compounds are either applied sequentially or simultaneously in agricultural practices[6]. The unutilised pesticide compounds can be transport to the ground water by percolation and/or surface water runoff through irrigation practices and rainfall. Accumulation of these pesticides in aquatic environment cause adverse effects to aquatic life subsequently to humans through drinking (Homazava et al., 2014; Koura, 2019).It is important to assess the accumulation of these different classes of pesticides with an accurate method. Pesticides are not always applied appropriately, and even in cases where acceptable agricultural procedures are followed, pesticide accumulation can occur during the plant's development period or as a result of post-harvest treatment[8].Because many pesticides persist in agricultural water and soil after cultivation and because the dynamics of these environments are sometimes poorly understood, it is imperative to maintain the agricultural environment safely even when no crops are being cultivated[4].Pesticides of different types can persist in agricultural soils for an extended duration, and research has demonstrated their ability to be transmitted to crops via roots during the growth phase[6].

Soil qualities are highly influential in determining the fate, behaviour, and spread of chemical pesticides, and have become the storage site for pesticides utilized in agriculture. It has the ability to absorb a wide range of pesticides and their breakdown products, potentially impacting several food chains in a detrimental manner. Pesticides have the potential to reach humans ultimately and can undergo bioaccumulation. Pesticides are carried away from soils by the flow of water and subsequently enter water sources. Pesticides can also be released into the atmosphere by volatilization, leading to negative impacts on the quality of air and surface water. Runoff and floods are significant mechanisms for the transportation of pesticides, which can result in unintended dispersion and contamination of non-target areas. This can ultimately have adverse effects on human health. The pesticide content often rises as soil depth increases, leading to elevated amounts in the lower soil layer and perhaps contributing to groundwater pollution[9,10].Monitoring residual pesticides in agricultural soil can help prevent or forecast the migration of these chemicals to crops[11].

Recently, a method called multiresidue pesticide analysis has been developed to monitor pesticide residues. This method allows for the simultaneous detection of numerous pesticides utilising GC–MS/MS and LC–MS/MS. The introduction of the QuEChERS extraction method with the dSPE clean-up method in this multiresidue pesticides analysis aims to decrease the analytical time and reduce the analysis cost. QuEChERS (rapid, easy, cheap, effective, rugged and safe) is a novel technology was developed in 2003 to efficiently extract a diverse array of pesticides from food and consumables. QuEChERS has become increasingly popular in the past decade because of its numerous advantages. In contrast to Pressurized Liquid Extraction (PLE), this technique is cost-effective, does not necessitate specialized equipment, and utilizes a minimal quantity of organic solvent for the extraction process. Furthermore, empirical evidence has consistently shown that

QuEChERS is capable of extracting a diverse array of pesticides from various food matrices with high accuracy[12,13].

The objective of this study is to collect soil samples from agricultural areas growing vegetable crops in 8 villages in Rajamahendravaram, Andhra Pradesh. The samples will be collected during the post-harvesting season. The study will then assess the analysis of multi residue pesticides using the QuEChERS extraction method with dSPE clean-up. The pesticides that were extracted were assessed qualitatively using the GC-MS method.

## 2. Methodology:

### 2.1.Study area:

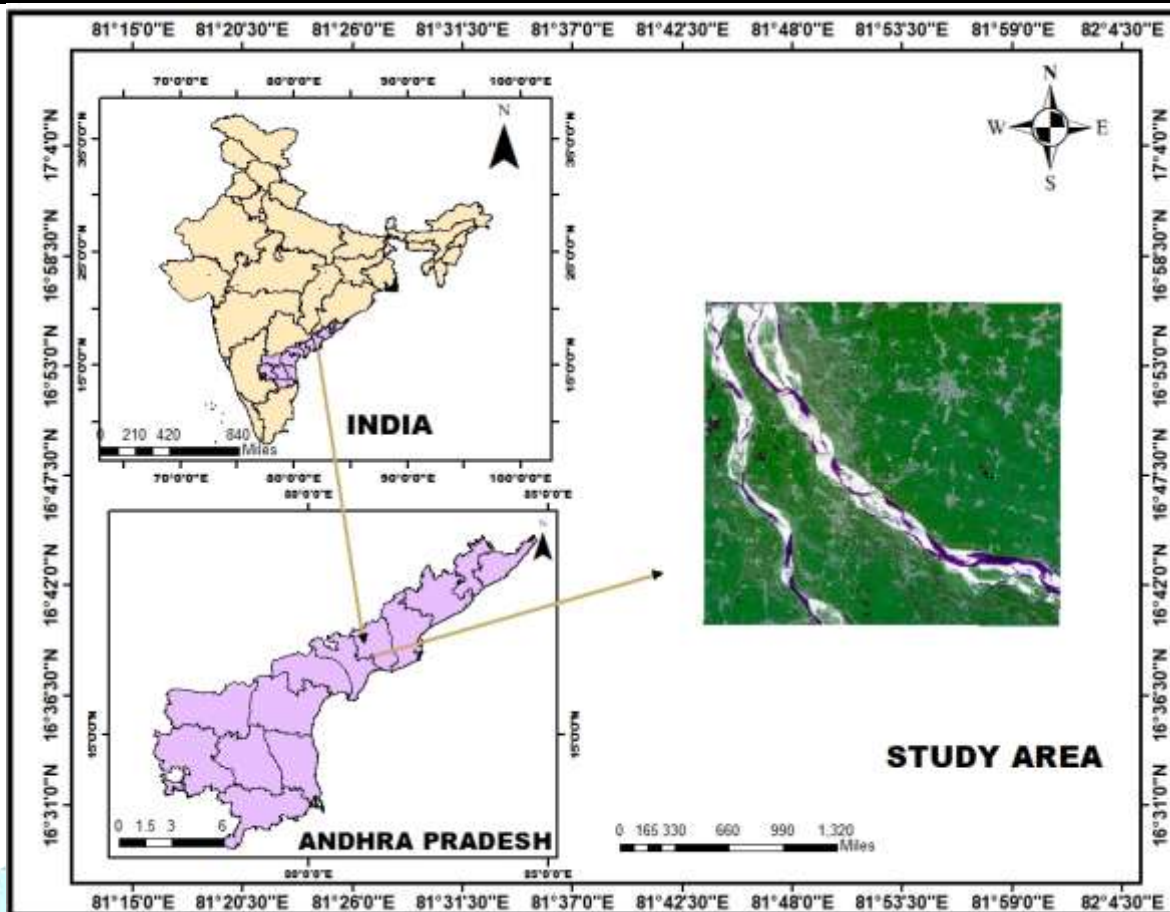
The soil samples were collected from 8 villages of near to Rajamahendravaram, East Godavari in Indian state of Andhra Pradesh. The study area is lush green fertile soil (Deltaic alluvium, Red clayey soil and Deltaic alluvial soil) with grey brown to black in colour, moderate to poorly permeable and fine to medium in texture. The study area is in the prevalent canal irrigated areas. The site codes and coordinates of 8 sampling villages represented in table 1 and Figure 1.

The major crops cultivated in this study area are Banana, coconut, paddy and vegetables.

**Table 1: Sampling sites along with their coordinates**

S.No	Name of the sampling site	Site code	Longitude	Latitude
i.	Kadiyapulanka	KDPL	81.8131 °E	16.8925 °N
ii.	Pottilanka	PTL	81.8082 °E	16.9021 °N
iii.	Choppella	CPL	81.8483 °E	16.7383 °N
iv.	Jonnada	JND	81.8627 °E	16.6969 °N
v.	Aalamuru	ALM	81.8996 °E	16.7793 °N
vi.	Kapileswarapuram	KPLP	81.8641 °E	16.3232 °N
vii.	Korumilli	KRML	81.9108 °E	16.7541 °N
viii.	Kulla	KL	81.0068 °E	16.7541 °N





**Figure 1: Study Area**

## **2.2.Sample collection:**

The soil samples were collected from vegetable crops during harvesting season in the month of June 2022. Approximately 10 to 15 soil samples from each sampling site were collected at the depth of 15cm from surface soil and pooled together in a sterile polythene bag. After collection, the samples were immediately transported to the laboratory and stored at 4°C until further analysis.

## **2.3.Physiochemical analysis of soil samples:**

The collected soil samples were subjected to following physiochemical parameters analysis: The chemical parameters include pH (Potentiometry), Electrical conductivity (EC-conductometry), Total organic carbon (TOC-Wet oxidation), Available nitrogen (Alkaline permanganate), Available Potassium (Flame photometry) and Available Phosphorous (Spectrophotometry). The physical parameters include Bulk density, Particle Density, Porosity, Water holding capacity and Specific gravity [14,15].

## **2.4.QuEchERs extraction and dSPE cleaning:**

The freeze-dried soil samples were homogenized and sieve through the 2mm mesh. 5 grams ( $5.0 \pm 0.2$ g) of each soil sample hydrated in 10mL distilled water in a falcon conical tube for 30 minutes. To this 10mL of MeCN with 1% acetic acid was added and samples were homogenized for 15 minutes followed by incubated on mechanical shaker for 10 minutes. After incubation QuEchERs extraction salts (1g NaCl, 0.5g sodium citrate, 0.5g disodium citrate and 4g anhydrous  $\text{MgSO}_4$ ) were added to the all the samples, shaken thoroughly for 1 minute and centrifuged at 4000 rpm for 10 minutes at 4°C. The pellet was discarded and 900mg of  $\text{MgSO}_4$ , 150mg of PSA and 150mg of  $\text{C}^{18}$  were added to the supernatant and reaction mixtures were vortexed

for 10 minutes. The solutions were centrifuged at 4000rpm for 5 minutes at 4°C and the supernatant was concentrated to dryness under steam of nitrogen gas in a water bath at 40°C. The obtained residue was redissolved in ethyl acetate (1g mL<sup>-1</sup>) and filtered through PTFE membrane syringe filters (0.22µm). The samples were stored at 4°C until further use.

### 2.5. Qualitative analysis of multiresidue pesticides using GC-MS:

Aliquots of the standard and samples were injected onto the GC-EI-MS and the indoxacarb separated and detected by using gas chromatography (GC 2010, Shimadzu, Japan) and confirmed on mass spectrometry (GC-MS QP 2010 plus, Shimadzu, Japan) with a DB-1MS fused-silica capillary column (30 m x 0.25 mm x 0.25 µm). An injection volume of 1 µL was made with the injector at 280 °C in split less mode with a 74.2 Kpa pressure. The flow of carrier gas (He) through a GC column was set at 1.06 mL/min with a linear velocity of 38.1 cm/sec. The initial oven program was 90 °C for 1.0 min and then increased at 25 °C/min until 280 °C and hold for 10.4 minutes. The MS interface and ion source temperature was set at 280 and 230 °C, respectively. The MS was operated in electron-ionization (EI) mode. Data acquisition was made in the full-scan mode or total ion chromatogram, mass spectra in the range 60-600 m/z was recorded at 70 eV. The ions of indoxacarb pesticide were selected from the full-scan or total ion chromatogram using the NIST library. To enhance the sensitivity of the target insecticide, selective ions were used in the selected ion monitoring (SIM) mode and the dwell time of each ion was set at 30 ms. Data recording and instrument control were performed by the GC-MS solution 2.5 software[1,6].

## 3. Result and Discussion:

### 3.1. Physicochemical properties of soil:

Soil serves as a vital reservoir for water and plays a crucial role in regulating nutrient cycling. The interplay between the water phase and soil components, such as aluminium, silica, and calcium, significantly influences soil chemistry. Changes in soil chemistry, in turn, directly impact the physical conditions of the soil. The dynamics of soil are contingent upon the interactions between physical and chemical properties. These properties, acting as determining factors, ultimately shape the overall development and productivity of crops. The intricate relationships among soil components, along with the presence of a diverse range of fauna and microbiota, collectively influence agricultural production[16,17]. In the present study, the physiochemical parameters of various soil samples were analysed using standard assays and represented in table 2 & 3. There is no observed large-scale variation among all physiochemical parameters across the various study sites. As represented in table 2 & figure 2, the bulk density varied from 1.27 Mg m<sup>-3</sup> in CPL to 1.47 Mg m<sup>-3</sup> in KRML, while the particle density ranged from 2.4 Mg m<sup>-3</sup> in KRML to 2.67 Mg m<sup>-3</sup> in KL. Porosity percentages were found to be between 42.87% in KPLP and 49.11% in CPL. The water holding capacity of the samples ranged from 41.82% in JND to 43.87% in KRML. Specific gravity values varied from 2.26 in KDPL to 2.66 in KL. Bulk density is a variable characteristic of soil that is influenced by factors such as variations in rainfall, root growth, and not an inherent attribute of soil. Bulk density serves as a primary indication for evaluating soil quality and is commonly used in different predictive models for assessing soil quality. It also serves as an

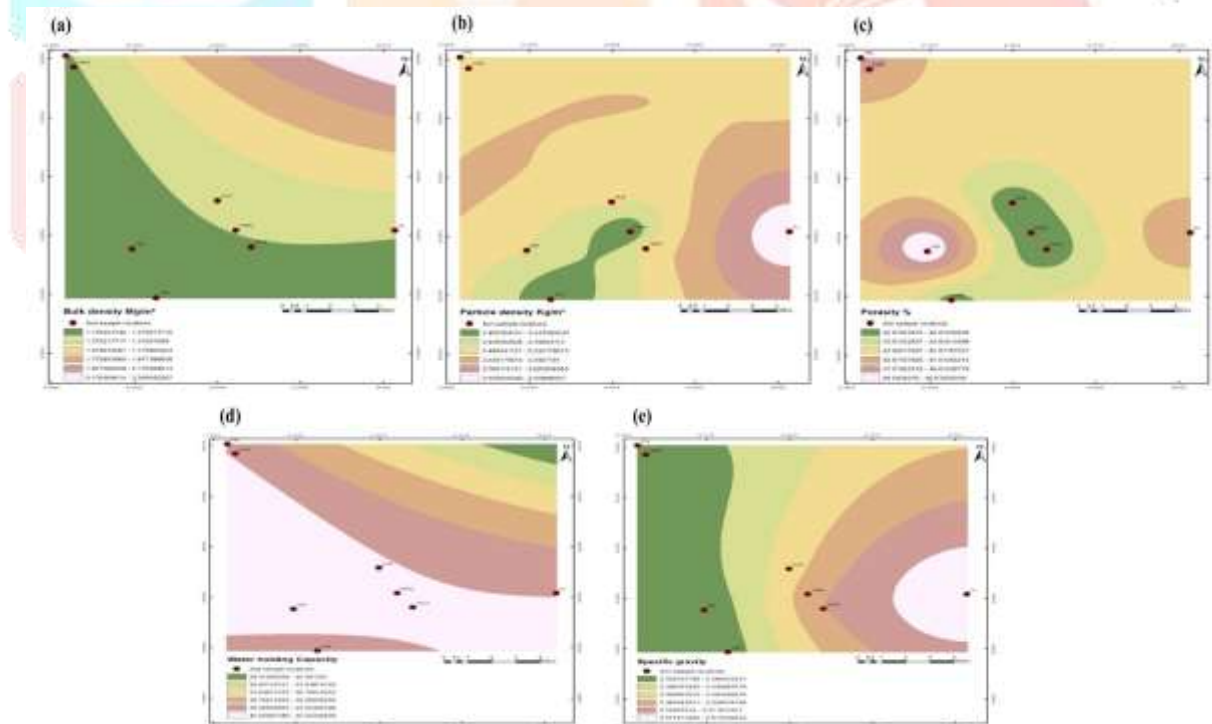
indicator of both soil compaction and soil porosity[18,19].The microbial diversity is significantly influenced by the water holding capacity of soil. Water acts as both a vital transport medium for substrates and a critical factor in hydrolysis activities. Excessive water hampers the rate at which oxygen spreads in water, leading to a decrease in the functioning of aerobic soil microorganisms. However, it may enhance the activity of anaerobic soil microbes [20,21]. The particle density of an aggregate is defined as the quotient of the mass of a certain amount of the aggregate and the total volume of all individual particles in that amount. This volume encompasses the empty spaces inside the particles, but it does not account for the gaps between the particles. The particle density is determined by the specific density of the material and the void content of the particles[22].

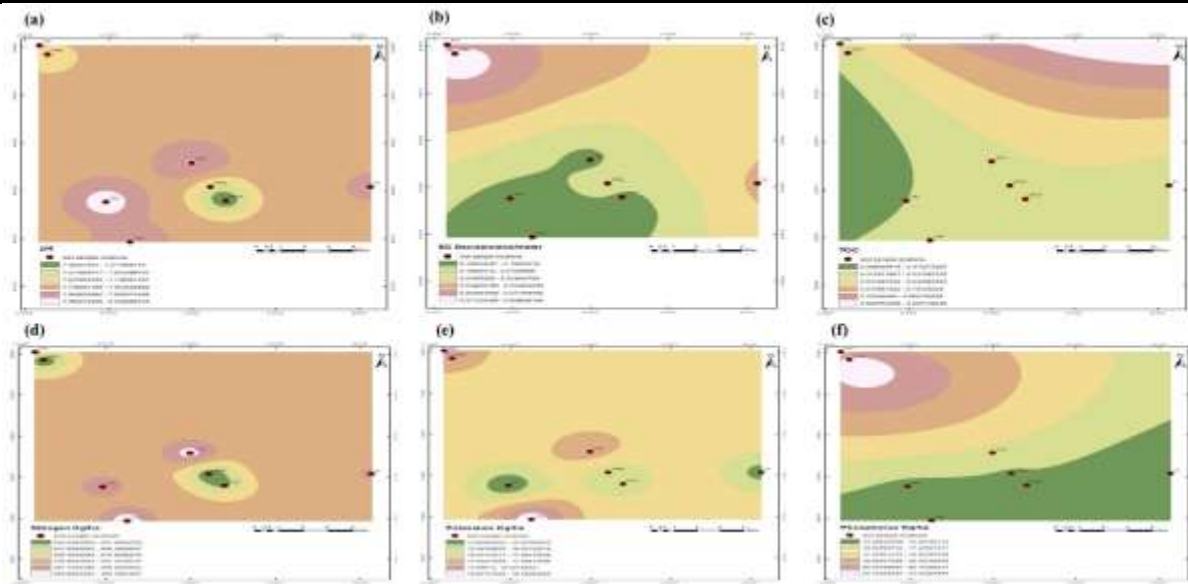
As depicted in Figure 3 & table 3, the soil samples exhibited a pH range from 7.4 in KPLP to 8.1 in CPL, while the electrical conductivity (EC) varied from 1.8 dS m<sup>-1</sup> in JND to 2.9 dS m<sup>-1</sup> in KDPL. The total organic carbon (TOC) content ranged from 0.41% in CPL to 0.53% in KDPL. Additionally, the available nitrogen content ranged from 233 kg ha<sup>-1</sup> in KRML to 321 kg ha<sup>-1</sup> in JND. The available potassium content varied from 14.78 kg ha<sup>-1</sup> in CPL to 19.41 kg ha<sup>-1</sup> in JND, and the available phosphorus content ranged from 14.41 kg ha<sup>-1</sup> in JND to 23.69 kg ha<sup>-1</sup> in KDPL. pH is a crucial soil characteristic that influences the availability of nutrients and the physical state of the soil, which in turn regulates the variety of microorganisms present in the soil. The pH level has a significant impact on the buffering capacity and overall quality of organic compounds present in soil. There is ample evidence that a decrease in soil pH leads to a reduction in living organisms' growth and activity[19]. Soil organic matter (SOM) is a combination of both decomposed and undecomposed microbes and plant waste. Soil organic matter (SOM) is a crucial indicator for monitoring soil degradation and erosion since it influences the soil's aggregation and stability. According to reports, SOM functions as a buffering agent that restricts abrupt chemical and temperature fluctuations in the soil[23]. Nitrogen is regarded as a crucial soil nutrient because it restricts soil productivity by influencing soil characteristics, plant growth, and microbial activity. Nitrogen is abundant in the atmosphere, but plants are incapable of using atmospheric nitrogen[24]. Potassium is the third most important necessary macronutrient for plant productivity, following nitrogen and phosphorus. It is plentifully present within the Earth's crust. Potassium is essential for promoting the growth of plant roots, enhancing crop yield, increasing plants' ability to withstand different types of stressors, and activating enzymes involved in metabolic activities in plants[25]. Phosphorus is crucial in the process of converting carbon biomass into soil organic matter. Soil phosphorus serves as an indicator of soil fertility, along with nitrogen, as it influences soil characteristics, plant development, and microbial activity and community structure. Phosphorus exists in various forms in the soil, but the most accessible form is when it is bound with organic matter. However, plants are unable to uptake this organic form of phosphorus[26][24].



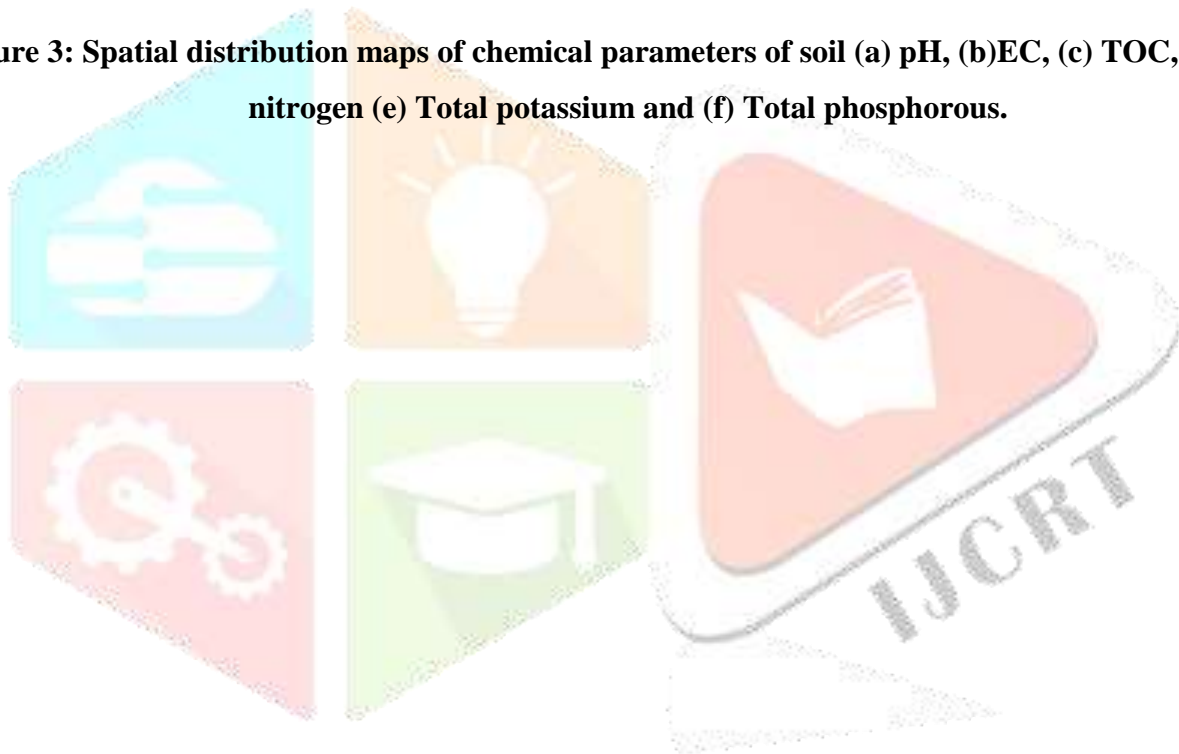
**Table 2: Physical parameters of soil**

S.No	Site Code	Bulk density (Mg m <sup>-3</sup> )	Particle density (Mg m <sup>-3</sup> )	Porosity (%)	Water holding capacity (%)	Specific gravity
1.	KDPL	1.4 ± 0	2.51 ± 0.03	47.14 ± 0.016	42.05 ± 0.041	2.26 ± 0
2.	PTL	1.31 ± 0.01	2.5 ± 0	48 ± 0.044	42.12 ± 0.016	2.46 ± 0.09
3.	CPL	1.27 ± 0.008	2.49 ± 0	49.11 ± 0.05	43.56 ± 0.219	2.33 ± 0.06
4.	JND	1.31 ± 0.02	2.41 ± 0.008	43.33 ± 0.004	41.82 ± 0.077	2.34 ± 0.004
5.	ALM	1.38 ± 0.004	2.5 ± 0.004	42.99 ± 0.01	42.67 ± 0.123	2.45 ± 0.036
6.	KPLP	1.31 ± 0.004	2.51 ± 0.01	42.87 ± 0	42.58 ± 0.042	2.56 ± 0
7.	KRML	1.47 ± 0.009	2.4 ± 0.02	43.44 ± 0.008	43.87 ± 0.120	2.53 ± 0.042
8.	KL	1.41 ± 0.035	2.67 ± 0	46.69 ± 0.02	42.44 ± 0.01	2.66 ± 0

**Figure 2: Spatial distribution maps of physical parameters of soil (a) Bulk density, (b) Particle density, (c) Porosity, (d) Water holding capacity and (e) Specific gravity**



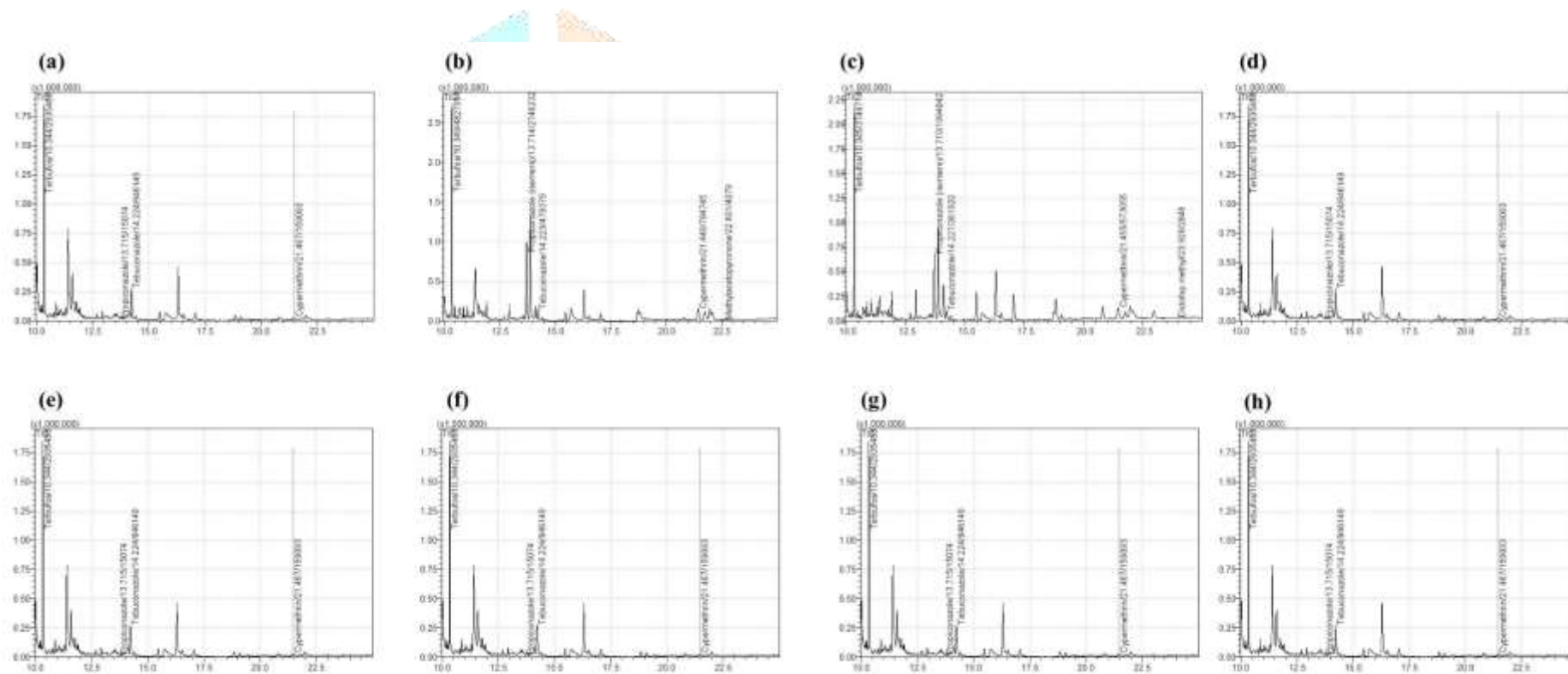
**Figure 3: Spatial distribution maps of chemical parameters of soil (a) pH, (b)EC, (c) TOC, (d) Total nitrogen (e) Total potassium and (f) Total phosphorous.**





**Table 3: Chemical parameters of soil**

S.No	Site Code	pH (Mean $\pm$ SD)	EC (dS m <sup>-1</sup> ) (Mean $\pm$ SD)	Total Organic Carbon (%) (Mean $\pm$ SD)	Available Nitrogen (Kg ha <sup>-1</sup> ) (Mean $\pm$ SD)	Available Potassium (Kg ha <sup>-1</sup> ) (Mean $\pm$ SD)	Available Phosphorus(Kg ha <sup>-1</sup> ) (Mean $\pm$ SD)
1.	KDPL	7.6 $\pm$ 0	0.29 $\pm$ 0.002	0.53 $\pm$ 0.002	233 $\pm$ 1.24	17.78 $\pm$ 0.10	23.69 $\pm$ 1.47
2.	PTL	7.8 $\pm$ 0.047	0.24 $\pm$ 0.002	0.47 $\pm$ 0.040	275 $\pm$ 0.004	18.47 $\pm$ 0.036	16.92 $\pm$ 0.54
3.	CPL	8.1 $\pm$ 0.040	0.19 $\pm$ 0	0.41 $\pm$ 0.042	303 $\pm$ 1.47	14.78 $\pm$ 0.040	15.42 $\pm$ 0.004
4.	JND	8 $\pm$ 0	0.18 $\pm$ 0	0.49 $\pm$ 0.140	321 $\pm$ 0.002	19.41 $\pm$ 0.024	14.41 $\pm$ 1.24
5.	ALM	8 $\pm$ 0.02	0.19 $\pm$ 0.001	0.49 $\pm$ 0.06	315 $\pm$ 1.24	17.61 $\pm$ 0.19	17.17 $\pm$ 0.02
6.	KPLP	7.4 $\pm$ 0.06	0.19 $\pm$ 0.004	0.49 $\pm$ 0.047	242 $\pm$ 0.54	15.71 $\pm$ 0.030	15.71 $\pm$ 1.47
7.	KRML	7.6 $\pm$ 0.04	0.22 $\pm$ 0.002	0.51 $\pm$ 0.002	233 $\pm$ 0.40	15.79 $\pm$ 0.008	15.68 $\pm$ 0.001
8.	KL	7.9 $\pm$ 0	0.24 $\pm$ 0.004	0.47 $\pm$ 0.047	296 $\pm$ 0.02	15.11 $\pm$ 0.030	14.42 $\pm$ 0



**Figure 4:** GC MS chromatogram of untargeted pesticides of agricultural soil samples from various sampling sites (a) KDPL (b) PTL (c) CPL (d) JND (e) ALM (f) KPLP (g) KRML and (h) KL.

### 3.2. Qualitative detection of pesticides using GC-MS analysis:

The soil samples of 8 sampling sites represented 4 common pesticide compounds namely Terbufos (Organophosphate insecticide), Propiconazole (Triazole fungicide), Tebuconazole (Triazole fungicide) Cypermethrin (Pyrethroid insecticide) and Diclofop-methyl (Herbicide) only detected in site CPL. The GC-MS chromatograms of Figure 4 and table 4 represents the found pesticide compounds in each sampling site. Terbufos, an organophosphate insecticide (*S-tert*-butylthiomethyl *O,O*-diethyl phosphorodithioate) used to prevent and control insects and nematodes on corn, sorghum, banana, sugar beet and vegetable crops [27,28]. Terbufos is metabolized and activated to its neurotoxic form via oxidative desulfuration. This active form of terbufos irreversibly inhibits acetylcholinesterase, leading to the accumulation of acetylcholine and the classic signs and symptoms associated with muscarinic and nicotinic receptor overstimulation [29]. Propiconazole is a pesticide that can be used for many purposes. The most likely ways that someone can be exposed to anything are by direct touch with the skin, breathing it in, or swallowing it. Within a 48-hour period, the human body absorbs 86% of a propiconazole dose and eliminates 95% of it through excretion. Propiconazole undergoes degradation, resulting in the formation of several triazole molecules. Propiconazole, when exposed to for a long period of time, leads to liver hypertrophy and tumours in mice, uterine lumen dilation in rats, developmental toxicity that indicates reduced pup weight at dosages that are toxic to the parents, and skeletal abnormalities in laboratory animals[30,31].

Tebuconazole was first released to the market in 1989 and primarily employed in the treatment of cereals. Currently, it is employed globally in many crops like peanuts, bananas, and soybeans as a foliar fungicide to manage a wide array of fungal diseases, as well as a seed treatment on barley. Tebuconazole is a fungicide with a wide range of effectiveness that falls under the triazole category. It also has the added benefit of regulating plant development. Nevertheless, excessive use of tebuconazole during leaf or seed treatment is expected to result in phytotoxicity and hinder plant growth[32,33]. Cypermethrin is a widely used synthetic pyrethroid pesticide. According to the National Pesticides Telecommunications Network, Cypermethrin exhibits severe toxicity towards fish, bees, and aquatic insects. The average residual level of any pesticide is mostly determined by the concentration of its active ingredient. A preharvest interval of 3 days may be appropriate for the dry season. However, during the early wet season when the crop canopy is smaller, there is a greater amount of cypermethrin residue deposited on the pods. In this instance, it is recommended to wait for a period of 10 days after spraying before safely using the crop. Juvenile animals exhibit heightened susceptibility to the acute toxicity of some pyrethroids, such as deltamethrin and cypermethrin, perhaps due to a reduced ability for metabolic detoxification[34,35]. The diclofop-methyl, which was first released in 1975 to the commercial market and its separated R stereoisomer diclofop-P-methyl, which was introduced in 2005. Diclofop-methyl (DM) is a herbicide belonging to the aryloxyphenoxy propionate class, which functions by inhibiting the activity of the enzyme acetyl-CoA carboxylase. Under specific climatic conditions, dimethyl (DM) undergoes hydrolysis to form its primary metabolite, diclofop (DC), which likewise has herbicidal properties. DM and DC are chiral compounds composed of enantiomers: R-DM and S-DM, and R-DC and S-DC, respectively. The herbicidal activity of R-DM and R-DC is greater than that of the equivalent S-enantiomers. On the other hand, S-DM and S-DC exhibit similar or higher toxicity to *Chlorella pyrenoidosa*,

*Chlorella Vulgaris*, and *Scenedesmus obliquus* freshwater algae compared to the respective R-enantiomers. In cabbage pickling, wine making, and soy sauce brewing operations, S-DM degrades more rapidly than R-DM. This specific breakdown of DM typically results in the enantioselective production of DC[36,37].

**Table 4: List of pesticides detected in each sampling site and their relative retention times and observed molecular weight ( $m/z$ ).**

S.No	Site code	Retention Time (Min)	Pesticide	Observed molecular weight ( $m/z$ )
1.	KDPL	10.34	Terbufos	288.40
		13.71	Propiconazole	342.22
		14.22	Tebuconazole	307.9
		21.45	Cypermethrin	416.3
2.	PTL	10.34	Terbufos	288.40
		13.71	Propiconazole	342.22
		14.22	Tebuconazole	307.9
		21.45	Cypermethrin	416.3
3.	CPL	10.34	Terbufos	288.40
		13.71	Propiconazole	342.22
		14.22	Tebuconazole	307.9
		21.45	Cypermethrin	416.3
		23.92	Diclofop methyl	341.20
4.	JND	10.34	Terbufos	288.40
		13.71	Propiconazole	342.22
		14.22	Tebuconazole	307.9
		21.45	Cypermethrin	416.3
5.	ALM	10.34	Terbufos	288.40
		13.71	Propiconazole	342.22
		14.22	Tebuconazole	307.9
		21.45	Cypermethrin	416.3
6.	KPLP	10.34	Terbufos	288.40
		13.71	Propiconazole	342.22
		14.22	Tebuconazole	307.9
		21.45	Cypermethrin	416.3



7.	KRML	10.34	Terbufos	288.40
		13.71	Propiconazole	342.22
		14.22	Tebuconazole	307.9
		21.45	Cypermethrin	416.3
8.	KL	10.34	Terbufos	288.40
		13.71	Propiconazole	342.22
		14.22	Tebuconazole	307.9
		21.45	Cypermethrin	416.3

### Conclusion:

This study emphasises the urgent problem of pesticide buildup in agricultural soils, specifically examining eight vegetable crop farms in East Godavari, Andhra Pradesh, India. By employing the QuEChERS-dSPE clean-up and GC-MS approach, our research identified the existence of five significant pesticide residues—Terbufos, Propiconazole, Tebuconazole, Cypermethrin, and Diclofop-methyl—suggesting a persistent dependence on these dangerous compounds despite their limited usage. These pesticides are recognised for their carcinogenic qualities as well as their ability to disrupt endocrine function, harm non-target creatures, and contribute to the emergence of pesticide-resistant pests. The consistency in physiochemical characteristics observed in all examined sites highlights the extensive distribution of this pollution. These findings emphasise the immediate requirement for strict regulatory measures and sustainable agricultural practices to reduce pesticide use. This will help protect the environment, prevent the accumulation of pesticides in organisms, prevent the loss of biodiversity, and reduce the severe health effects on humans and wildlife.

### Declaration:

The authors declare no competing interest

### Acknowledgment:

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### References:

- [1] M.J. Climent, M.J. Sánchez-Martín, M.S. Rodríguez-Cruz, P. Pedreros, R. Urrutia, E. Herrero-Hernández, Determination of pesticides in river surface waters of Central Chile using spe-GC-MS multi-residue method, J. Chil. Chem. Soc. 63 (2018) 4023–4031. <https://doi.org/10.4067/s0717-97072018000204023>.
- [2] M.Á. González-curbelo, D.A. Varela-martínez, D.A. Riaño-herrera, Pesticide-Residue Analysis in Soils by the QuEChERS Method: A Review, Molecules. 27 (2022) 1–23. <https://doi.org/10.3390/molecules27134323>.

- [3] K.- El Koura, Version of Record:  
<https://www.sciencedirect.com/science/article/pii/S0026265X18315923>, (2019).
- [4] H.W. Jo, M.G. Park, H.J. Jeon, J.K. Moon, S.E. Lee, Analysis of multiresidue pesticides in agricultural paddy soils near industrial areas in Korea by GC–MS/MS and LC–MS/MS using QuEChERS extraction with dSPE clean-up, *Appl. Sci.* 11 (2021). <https://doi.org/10.3390/app11188415>.
- [5] J. da Silva Sousa, H.O. do Nascimento, H. de Oliveira Gomes, R.F. do Nascimento, Pesticide residues in groundwater and surface water: recent advances in solid-phase extraction and solid-phase microextraction sample preparation methods for multiclass analysis by gas chromatography-mass spectrometry, *Microchem. J.* 168 (2021). <https://doi.org/10.1016/j.microc.2021.106359>.
- [6] N. Homazava, C. Gachet Aquillon, E. Vermeirssen, I. Werner, Simultaneous multi-residue pesticide analysis in soil samples with ultra-high-performance liquid chromatography–tandem mass spectrometry using QuEChERS and pressurised liquid extraction methods, *Int. J. Environ. Anal. Chem.* 94 (2014) 1085–1099. <https://doi.org/10.1080/03067319.2014.954558>.
- [7] A. Kouzayha, A. Rahman Rabaa, M. Al Iskandarani, D. Beh, H. Budzinski, F. Jaber, Multiresidue Method for Determination of 67 Pesticides in Water Samples Using Solid-Phase Extraction with Centrifugation and Gas Chromatography-Mass Spectrometry, *Am. J. Anal. Chem.* 03 (2012) 257–265. <https://doi.org/10.4236/ajac.2012.33034>.
- [8] K. Banerjee, S. Dasgupta, S.C. Utture, Chapter 9 - Application of GC–TOFMS for Pesticide Residue Analysis in Grapes, in: A.R. Fernandez-Alba (Ed.), *TOF-MS within Food Environ. Anal.*, Elsevier, 2012: pp. 367–413. <https://doi.org/10.1016/B978-0-444-53810-9.00005-5>.
- [9] S.E. Lewis, D.M. Silburn, R.S. Kookana, M. Shaw, Pesticide Behavior, Fate, and Effects in the Tropics: An Overview of the Current State of Knowledge, *J. Agric. Food Chem.* 64 (2016) 3917–3924. <https://doi.org/10.1021/acs.jafc.6b01320>.
- [10] G. Bhandari, K. Atreya, P.T.J. Scheepers, V. Geissen, Concentration and distribution of pesticide residues in soil: Non-dietary human health risk assessment, *Chemosphere.* 253 (2020) 126594. <https://doi.org/10.1016/j.chemosphere.2020.126594>.
- [11] J.-I. Hwang, S.-E. Lee, J.-E. Kim, Plant Uptake and Distribution of Endosulfan and Its Sulfate Metabolite Persisted in Soil., *PLoS One.* 10 (2015) e0141728. <https://doi.org/10.1371/journal.pone.0141728>.
- [12] M.C. Bruzzoniti, L. Checchini, R.M. De Carlo, S. Orlandini, L. Rivoira, M. Del Bubba, QuEChERS sample preparation for the determination of pesticides and other organic residues in environmental matrices: a critical review., *Anal. Bioanal. Chem.* 406 (2014) 4089–4116. <https://doi.org/10.1007/s00216-014-7798-4>.
- [13] M. Dušek, V. Jandovská, J. Olšovská, Analysis of multiresidue pesticides in dried hops by LC–MS/MS using QuEChERS extraction together with dSPE clean-up, *J. Inst. Brew.* 124 (2018) 222–229. <https://doi.org/10.1002/jib.490>.
- [14] S. Jehan, I. Ullah, S. Khan, S. Muhammad, S.A. Khattak, T. Khan, Evaluation of the Swat River, Northern Pakistan, water quality using multivariate statistical techniques and water quality index

- (WQI) model, *Environ. Sci. Pollut. Res.* 27 (2020) 38545–38558. <https://doi.org/10.1007/s11356-020-09688-y>.
- [15] G.R. Reddy, T. Thomas, N. Swaroop, A.K. Singh, I.R. Naga, Assessment of Physico-Chemical Properties of Soil from Different Blocks of Adilabad District, Telangana, India, *Int. J. Plant Soil Sci.* 35 (2023) 121–130. <https://doi.org/10.9734/ijpss/2023/v35i153087>.
- [16] S. Maurya, J.S. Abraham, S. Somasundaram, R. Toteja, R. Gupta, S. Makhija, Indicators for assessment of soil quality: a mini-review, *Environ. Monit. Assess.* 192 (2020). <https://doi.org/10.1007/s10661-020-08556-z>.
- [17] N.A. Mofor, E.B.N. Tamungang, A.D. Mvondo-zé, G.K. Kome, K. Mbene, Assessment of Physico-Chemical and Heavy Metals Properties of some Agricultural Soils of Awing-North West Cameroon, *Arch. Agric. Environ. Sci.* 2 (2017) 277–286. <https://doi.org/10.26832/24566632.2017.020405>.
- [18] M. Casanova, E. Tapia, O. Seguel, O. Salazar, Direct measurement and prediction of bulk density on alluvial soils of central Chile, *Chil. J. Agric. Res.* 76 (2016) 105–113. <https://doi.org/10.4067/S0718-58392016000100015>.
- [19] J.S. Abraham, S. Sripoorna, J. Dagar, S. Jangra, A. Kumar, K. Yadav, S. Singh, A. Goyal, S. Maurya, G. Gambhir, R. Toteja, R. Gupta, D.K. Singh, H.A. El-Serehy, F.A. Al-Misned, S.A. Al-Farraj, K.A. Al-Rasheid, S.A. Maodaa, S. Makhija, Soil ciliates of the Indian Delhi Region: Their community characteristics with emphasis on their ecological implications as sensitive bio-indicators for soil quality, *Saudi J. Biol. Sci.* 26 (2019) 1305–1313. <https://doi.org/10.1016/j.sjbs.2019.04.013>.
- [20] G. Stefan, B. Cornelia, R. Jörg, B. Michael, Soil water availability strongly alters the community composition of soil protists, *Pedobiologia (Jena)*. 57 (2014) 205–213. <https://doi.org/10.1016/j.pedobi.2014.10.001>.
- [21] N. Yan, P. Marschner, W. Cao, C. Zuo, W. Qin, Influence of salinity and water content on soil microorganisms, *Int. Soil Water Conserv. Res.* 3 (2015) 316–323. <https://doi.org/10.1016/j.iswcr.2015.11.003>.
- [22] U.J. Alengaram, 2 - Valorization of industrial byproducts and wastes as sustainable construction materials, in: F. Colangelo, R. Cioffi, I. Farina (Eds.), *Handb. Sustain. Concr. Ind. Waste Manag.*, Woodhead Publishing, 2022: pp. 23–43. <https://doi.org/10.1016/B978-0-12-821730-6.00003-6>.
- [23] E.E. Oldfield, S.A. Wood, M.A. Bradford, Direct effects of soil organic matter on productivity mirror those observed with organic amendments, *Plant Soil.* 423 (2018) 363–373. <https://doi.org/10.1007/s11104-017-3513-5>.
- [24] D. Liu, K.M. Keiblinger, S. Leitner, U. Wegner, M. Zimmermann, S. Fuchs, C. Lassek, K. Riedel, S. Zechmeister-Boltenstern, Response of Microbial Communities and Their Metabolic Functions to Drying–Rewetting Stress in a Temperate Forest Soil., *Microorganisms.* 7 (2019). <https://doi.org/10.3390/microorganisms7050129>.
- [25] C.S. Rao, S. Karlapudi, Potassium Dynamics and Role of Non - exchangeable Potassium in Crop

- Nutrition, Indian J. Fertil. (2017) 80.
- [26] G.M. Filippelli, The global phosphorus cycle, *Phosphates Geochemical, Geobiol. Mater. Importance*. 48 (2019) 391–426. <https://doi.org/10.2138/rmg.2002.48.10>.
- [27] U.S. Epa, P. Programs, Interim Reregistration Eligibility Decision (IRED) for Terbufos, (2006).
- [28] P. Industry, 2000 and 2001 Market Estimates, (2001).
- [29] R.P. Pohanish, T, in: R.P. Pohanish (Ed.), *Sittig's Handb. Pestic. Agric. Chem.* (Second Ed., Second Edi, William Andrew Publishing, Oxford, 2015: pp. 769–838. <https://doi.org/https://doi.org/10.1016/B978-1-4557-3148-0.00020-0>.
- [30] P.K. Gupta, Chapter 37 - Herbicides and Fungicides, in: R.C. Gupta (Ed.), *Reprod. Dev. Toxicol.* (Second Ed., Second Edi, Academic Press, 2017: pp. 657–679. <https://doi.org/https://doi.org/10.1016/B978-0-12-804239-7.00037-8>.
- [31] S.C. Gad, T. Pham, Propiconazole, in: P. Wexler (Ed.), *Encycl. Toxicol.* (Third Ed., Third Edit, Academic Press, Oxford, 2014: pp. 1101–1104. <https://doi.org/https://doi.org/10.1016/B978-0-12-386454-3.01203-3>.
- [32] A.B. Tleuova, E. Wielogorska, V.S.S.L.P. Talluri, F. Štěpánek, C.T. Elliott, D.O. Grigoriev, Recent advances and remaining barriers to producing novel formulations of fungicides for safe and sustainable agriculture, *J. Control. Release*. 326 (2020) 468–481. <https://doi.org/https://doi.org/10.1016/j.jconrel.2020.07.035>.
- [33] E.F. McInnes, S. Papineni, M. Rinke, F. Schorsch, H.A. Marxfeld, Chapter 11 - Agrochemicals, in: W.M. Haschek, C.G. Rousseaux, M.A. Wallig, B. Bolon, K.M. Heinz-taheny, D.G. Rudmann, B.W. Mahler (Eds.), *Haschek Rousseaux's Handb. Toxicol. Pathol.* (Fourth Ed., Fourth Edi, Academic Press, 2023: pp. 727–763. <https://doi.org/https://doi.org/10.1016/B978-0-443-16153-7.00011-3>.
- [34] L.G. Costa, Chapter 9 - The neurotoxicity of organochlorine and pyrethroid pesticides, in: M. Lotti, M.L. Bleeker (Eds.), *Occup. Neurol.*, Elsevier, 2015: pp. 135–148. <https://doi.org/https://doi.org/10.1016/B978-0-444-62627-1.00009-3>.
- [35] C.S. Schasteen, Oilseeds, Legumes and Derived Products, in: G.W. Smithers (Ed.), *Encycl. Food Saf.* (Second Ed., Second Edi, Academic Press, Oxford, 2024: pp. 33–45. <https://doi.org/https://doi.org/10.1016/B978-0-12-822521-9.00159-3>.
- [36] N.C.P. de Albuquerque, D.B. Carrão, M.D. Habenschus, A.R.M. de Oliveira, Metabolism studies of chiral pesticides: A critical review, *J. Pharm. Biomed. Anal.* 147 (2018) 89–109. <https://doi.org/https://doi.org/10.1016/j.jpba.2017.08.011>.
- [37] A. Székács, 3 - Herbicide mode of action, in: R. Mesnage, J.G. Zaller (Eds.), *Herbicides*, Elsevier, 2021: pp. 41–86. <https://doi.org/https://doi.org/10.1016/B978-0-12-823674-1.00008-0>.