

Research Article

Effect of repeated atrazine and pendimethalin application on their bound residues in long term fertilized soil of semi-arid tropic region in India

RagaPriya A

Department of Soil Science and Agricultural Chemistry, Tamil Nadu Agricultural University
Coimbatore - 641003 (Tamil Nadu), India

Janaki P*

Department of Soil Science and Agricultural Chemistry, Tamil Nadu Agricultural University
Coimbatore -641003 (Tamil Nadu), India

Arulmozhiselvan K

Department of Soil Science and Agricultural Chemistry, Tamil Nadu Agricultural University
Coimbatore - 641003 (Tamil Nadu), India

*Corresponding author. Email: janaki.p@tnau.ac.in

Article Info

[https://doi.org/10.31018/
jans.v12i4.2367](https://doi.org/10.31018/jans.v12i4.2367)

Received: September 3, 2020

Revised: October 19, 2020

Accepted: November 7, 2020

How to Cite

RagaPriya A et al. (2020). Effect of repeated atrazine and pendimethalin application on their bound residues in long term fertilized soil of semi-arid tropic region in India. *Journal of Applied and Natural Science*, 12(4): 471- 477. <https://doi.org/10.31018/jans.v12i4.2367>

Abstract

Repeated and long term application of same herbicides forms bound residues in soil and becomes point source of pollution over a period of time and harms the soil microorganisms. Among the different herbicides, the atrazine and pendimethalin is widely and repeatedly used molecule in maize and sunflower cultivation for weed control, respectively. Hence the present study was undertaken to investigate the bound residue of the applied herbicides in soil under long term fertilized condition with varied nutrient sources since 1909 in North-Western agro-climatic zone of Tamil Nadu under the semi-arid tropic region of India. Soil samples were collected at the time of maize and sunflower harvest and analysed for the bound fraction of atrazine and pendimethalin compounds respectively. The results showed that the repeated application of these herbicides at recommended dose formed a considerable amount of non-extractable bound residues in soil. While the bound fraction of parent atrazine was found below detectable limit, pendimethalin was at a quantifiable level in the soil irrespective of fertilization sources. However the bound form of atrazine metabolites, namely Des ethyl Deisopropyl atrazine (DEDIA) and Hydroxy atrazine (HA) was extracted from the maize cultivated soil. Bound forms of HA (4.34%) and DEDIA (3.43%) and pendimethalin (3.14%) to the applied quantity were witnessed at a higher amount in control plot than the fertilized plots. The omission of any one major nutrient recorded elevated DEDIA bound form than the HA fraction. The non-extractable bound residues of both the herbicides were detected at different proportions according to the herbicide nature, sources of fertilization and the crops cultivated in the soil. The fraction of bound form of atrazine metabolites was detected at higher level than the pendimethalin in soil. The present study revealed that the bound residues of atrazine, its metabolites and pendimethalin can be mineralized into the soil solution and bio-augmented over a period of time under the conditions of repeated application. Hence the remobilization of bound residues of these herbicides must be considered while gauging the environmental hazard and effect on non-target organisms.

Keywords: Atrazine metabolites, Bound residue, Fertilization, Maize, Pendimethalin, Sunflower

INTRODUCTION

In recent years, there has been a growing concern about the possible release of bound pesticide residues from the soil and its relevance with toxicological and/or ecological implications. It is thought that the activity of microorganisms is the primary factor responsible for the release of bound residues. However, in nature, bound residues can be released by physico-chemical mechanisms or through biochemical processes. Other factors are changes in agricultural practices and the introduction of certain chemicals that may change the

chemistry of the soil. The release of bound residues reintroduces the compounds into the soil solution, which may eventually lead to their uptake by plants. It is conceivable that soil-bound pesticide residues may enter into the aquatic environment, be released, and subsequently be accumulated in aquatic food chains (Navarro *et al.*, 2007; Schaffer *et al.*, 2018; Gabriel Perez-Lucas *et al.*, 2018). Viti *et al.* (2020) reported that the bound residues of metribuzin and its metabolites can become bio-available consequently mineralized or returned to the soil solution, which could have negative effects on subsequent crops or non-target

organisms.

The non-extractable residues (NER) present in the soil are chemical species (parent compound and metabolites, or fragments) originating from pesticides used according to good agricultural practice, that cannot be extracted by methods which do not significantly change the chemical nature of these residues (USEPA, 2014). Studies to determine remobilization and release of bound residues are normally carried out following exhaustive extraction of all free compounds (Nelson *et al.*, 1983; Hatzinger and Alexander, 1995; Alexander, 2000; Reid *et al.*, 2000).

The pesticides or their degradation products, when exposed to the soil environment continuously for a long time, can form bound fractions (non-extractable residues) with the organic matter or clay minerals (Kearney, 1982). Its formation is mediated by the activities of soil microorganisms, chemical concentration (Kaufman and Blake, 1973; Lichtenstein *et al.*, 1977), soil organic matter and clay content (Smith and Phillips, 1975) and organic sources added to the soil (Pateiro-Moure *et al.*, 2013; Rasul *et al.*, 2008; Viti *et al.*, 2020).

The formation of soil-bound residues is a detoxication process catalyzed by soil microorganisms. Mainly the microbial lactase and peroxidase enzymes act in coupling and polymerization reactions to bind pesticides metabolites to soil organic matter (Bollag and Loll, 1983). Chemical reactions also are important in the formation of bound residues. The s-triazine residue is primarily chemical, and microorganisms act only in the production of various metabolites (Bollag and Loll, 1983). Bound residues may also be formed through the uptake of herbicide or metabolites and the subsequent release of these materials through decomposition of the crop residues in the soil. Loiseau and Barriuso (2002) reported atrazine bound residues, in the range of 10–40% of the applied atrazine, were obtained by laboratory incubation (56 d) of four soils and had different capacities to degrade atrazine in relation to the presence or absence of a microflora that is capable to mineralize the triazine ring. Viti *et al.* (2020) reported higher mineralization of herbicides in sandy loam soil where filter cake was added, and the maximum mineralized diuron, hexazinone, and metribuzin bound residues, observed was 7.7, 46.7, and 8.1% respectively.

Despite the introduction of numerous novel herbicides and new technology such as herbicide-tolerant crops, atrazine and pendimethalin respectively belonging to triazine and dinitroaniline groups are used widely and continuously in India as well as globally for the control of complex weed flora in different crops like maize, sugarcane, sunflower, cotton etc (Janaki *et al.*, 2012a, 2012b, 2015 and 2019; Janaki and Murali Arthanari, 2020). Most of the studies on these herbicides were undertaken to show their dynamic persistence, sorption and leaching behavior only limited work has been

reported on their bound residues in soil due to repeated application (Janaki *et al.* 2012b, 2019 and Janaki and Murali Arthanari, 2020). Thus, the present study was formulated to find out the non-extractable fraction of herbicides in soil under long-term fertilization through different organic and inorganic sources of nutrients in North Western agro-climatic zone of Tamil Nadu under semi-arid tropic region of India.

MATERIALS AND METHODS

Experiment site characters: The Permanent Manure Experiment of Tamil Nadu Agricultural University, Coimbatore initiated in 1909 was used to carry out the present investigation. The experimental site is geographically located in North Western agro-climatic zone of Tamil Nadu and is delineated under semi-arid tropics of India. It lies between 11° 01' N to 11° 01' N latitude and 76° 93'E to 76° 93' E longitudes with an altitude of 426.7 m above the mean sea level. The mean annual rainfall of Coimbatore was 674.2 mm, and the mean maximum and minimum temperatures were 31.5°C and 21.3°C, respectively.

The pre-sowing soil samples collected from each treatment plots of the experimental field in three replicates were analyzed for the initial physico-chemical and biological properties. The soil of the experimental field was sandy clay loam in texture belonging to Palathurai series, classified taxonomically as *Typic Haplustalf*. Regularly the maize and sunflower crops were cultivated during *Kharif* and *Rabi* seasons with test varieties of CO(HM)6 and CO2, respectively.

Field experiment details: The field experiment was laid out in randomized block design, and sampling was done in three replicates from the non-replicated larger plots size (100 m²) by temporarily marking replications. Every year the experiment was conducted during 2015-16 with two crops viz., sunflower and maize during *Rabi* (February-May) and *Kharif* (July-October) seasons respectively with eighteen treatments. For the present study the soil samples were collected from sixteen treatments viz., T₁-control (No manure/fertilizer), T₂-100% N alone, T₃-100% NK, T₄-100% NP, T₅-100% NPK (old dose), T₆-100% PK, T₇-100% K alone, T₈-100% P alone, T₉-100% NPK (new dose), T₁₀-100% NPK + Farmyard manure (FYM) @ 12.5 t/ha, T₁₁-Farmers practice, T₁₂-no manure no crop, T₁₃-STCR-IPNS, T₁₄-FYM on Nitrogen equivalent basis (NEB), T₁₅-Poultry manure (PM) on NEB and T₁₆- residue mulch (RM). Each plot in the experimental field was ploughed with animal drawn plough, and the land was prepared to fine tilth without disturbing the layout every season. After ploughing, the bunds and irrigation channels of each plot were rectified. All the cultural practices and plant protection measures for maize and sunflower were followed as per the recommendations of the crop production guide of Agricultural crops in Tamil Nadu.

Herbicides application: Atrazine 50% wettable powder (WP) @ 0.5 kg ai ha⁻¹ and pendimethalin as 30% emulsion concentrate (EC) @ 1.0 kg ai ha⁻¹ was applied to the maize and sunflower field respectively as pre-emergence on 3rd day after sowing to all the treatments uniformly. These two herbicides have been applied regularly for the respective crops since 2009.

Fertilizer application: The first crop of maize was fertilized with recommended dose of 250: 75: 75 kg N, P₂O₅, K₂O ha⁻¹ and followed by the second crop of sunflower with the recommended dose of 60: 90: 60 kg N, P₂O₅, K₂O ha⁻¹. The 25 per cent of N, 100 per cent of P₂O₅ and K₂O of the recommended fertilizer were applied as basal; remaining 50 and 25 per cent of N as urea was top-dressed at 25 and 45 days after sowing (DAS), respectively for both the crops.

For maize crop, the INM treatment, namely FYM @ 12.5 t ha⁻¹ was imposed 20 days before sowing of the crop. Based on the N content in FYM (0.56 %) and poultry manure (2.18 %), organic manures were applied at 100% N equivalent basis on 20 days before sowing. For farmers practice, 125 kg diammonium phosphate (DAP) ha⁻¹ was applied basally, and then 125 kg urea ha⁻¹ and 125 kg MOP ha⁻¹ were applied at 25 DAS, and 125 kg urea ha⁻¹ was applied at 45 DAS. In the STCR-IPNS treatment, the soil test based fertilizer requirements were calculated for targeted yield of 9 t ha⁻¹ and then imposed. For the sunflower crop also, above treatments were followed in the same way except for farmers practice in which only 125 kg DAP ha⁻¹ was applied.

Soil and plant samples collection: The soil samples from the plots treated with atrazine 50% WP at 0.5 kg ai ha⁻¹ as pre-emergence and pendimethalin as 30% emulsifiable concentrate (EC) were collected to determine the degradation and persistence of atrazine and pendimethalin. Soil samples at five randomly selected places were collected at 0 (2 hr), 3, 7, 15, 30, 45, 60 and 90 DAHA and at harvest. About 500 g of soil samples collected from the plots were stored in the deep freezer at -4°C until analysis for residues and biological properties. The initial and post-harvest soil samples were shade dried, powdered and sieved through a 2 mm mesh sieve before the analysis of physico-chemical properties. The results were expressed on dry weight basis.

Non-extractable bound residues extraction: The non-extractable bound residues of atrazine metabolites and pendimethalin were extracted from the representative soil samples from the respective field using methanol: water (70:30 v/v) and acidified methanol: water: HCl (75:24:1 v/v) respectively as extractant. For extraction, the soil : solvent mixture was shaken vigorously for 24 hrs and ultrasonicated at 60°C for 5 hrs with the constant frequency of 50 Hz pulses operating at 20 Hz pulses at a sweep bandwidth of 45 KHz and 170 W. Then the soil suspension was centrifuged at 5000 rpm for 10 minutes. The suspension was decant-

ed after centrifugation, filtered and concentrated to dryness and re-dissolved in HPLC acetonitrile for bound residues quantification.

RESULTS AND DISCUSSION

The study revealed the non-extractable bound residues of atrazine and pendimethalin and its metabolites in the soil as influenced by their repeated application for the past seven years and also on the different sources of fertilizer nutrients under maize-sunflower cropping system.

Atrazine bound residues: The non-extractable bound residues of atrazine in the soil samples collected at the time of maize harvest were extracted by the combination of vigorous shaking extraction (SE) and ultra-sonic extraction (UE). Though this fraction is usually measured or detected by isotopic techniques, the present study was tried to evaluate the conventional methods for extracting the non-extractable bound residues of atrazine and detection using HPLC. The shaking extraction for 24 hrs followed by 5 hrs of ultra-sonication with the specified conditions extracted detectable quantities of HA and DEDIA in the soil collected during maize harvest (Table 1) but not the parent atrazine compound. Similar results were also reported by Capriel and Haisch (1984). Viti *et al.* (2020) performed three extractions using methanol and chloroform with 30 minutes shaking at 300 rpm followed by centrifugation at 3000 rpm each time for extracting the triazine herbicide metribuzin and its metabolite from sandy loam soil. This showed that the harsh extraction is essential to extract the non-extractable residues from the soil that received atrazine repeatedly for a long time (Hatzinger and Alexander, 1995; Noordkamp *et al.*, 1997; Alexander, 2000; Reid *et al.*, 2000; Schaffer *et al.*, 2018). Irrespective of treatments, the HA and DEDIA concentrations ranged from 0.0035 to 0.0217 and 0.0032 to 0.0171 mg kg⁻¹ and the higher concentration of both the compounds were recorded under control treatment. Though, the DEDIA was detected almost in all the treatments, the HA was present in quantifiable limit (LOQ=0.003 mg kg⁻¹ by the method for both the compound) only in control, N alone, no manure, no crop residue and residue mulching treatments. This showed that the imposed treatments had a significant influence on the formation of non-extractable bound residues of atrazine or its degradation products in soil. Khan, (1982) and Dec and Bollag (1988) reported that depending on the nature of the binding, immobilized compounds may be released back to the soil solution or mineralized as a result of changing environmental conditions in the soil beside influenced by the herbicide nature (Guimaraes *et al.*, 2018; Viti *et al.*, 2020). Since the atrazine is easily hydrolyzed by the removal of chlorine group (Janaki *et al.*, 2012b), its metabolites were detected as bound residues in the present study when compared to parent atrazine.

Table 1. Non extractable bound residues (mg/kg) of atrazine and pendimethalin in soil at post harvest stage as influenced by the sources of fertilization.

Treatments	Atrazine metabolites*		Pendimethalin**
	HA	DEDIA	
T ₁ - Control	0.0217	0.0171	0.0157
T ₂ -N alone	0.0040	0.0036	0.0110
T ₃ -NK	<LOQ	0.0057	0.0020
T ₄ -NP	<LOQ	0.0033	0.0018
T ₅ -NPK-Old dose	0.0035	0.0038	0.0103
T ₆ -PK	<LOQ	0.0053	<LOQ
T ₇ -K alone	<LOQ	0.0146	<LOQ
T ₈ -P alone	<LOQ	0.0047	<LOQ
T ₉ -NPK-Revised dose	<LOQ	0.0050	0.0068
T ₁₀ -100% NPK+FYM	<LOQ	0.0166	0.0079
T ₁₁ -Farmers Practice	<LOQ	0.0092	0.0020
T ₁₂ -No Manure No Crop	0.0035	0.0050	0.010
T ₁₃ -STCR-IPNS	<LOQ	0.0155	LOQ
T ₁₄ -FYM-NEB	<LOQ	0.0105	0.0065
T ₁₅ -Poultry Manure-NEB	<LOQ	0.0032	0.0013
T ₁₆ -Residue Mulching	0.0056	<LOQ	0.0091

LOQ- Limit of Quantification (*0.003 and ** 0.001 mg kg⁻¹); HA-Hydroxy atrazine; DEDIA- Des ethyl Deisopropyl atrazine

The results showed that a significant amount of HA and DEDIA residues can persist in soil under field conditions when atrazine is repeatedly applied to the soil. The effect of different long term fertilization sources on bound residues of atrazine metabolites is presented in Fig 1. The bound HA and DEDIA, the main metabolites in the soil extract represent the 2.20 and 1.84 per cent of the applied atrazine to the maize field irrespective of fertilization sources. Donati and Funari (1993) and Khan and Ivarson (1981) found similar results for triazines and their degradation products. They identified de-isopropyl prometryn (54%) and hydroxyl propazine (8%), a degradation product of prometryn in un-extracted bound residues associated with the fulvic acid extraction by following one year of soil incubation after prometryn treatment. USEPA (2014) reported that the nature of the un-extracted residues is difficult to ascertain, in part, because the extraction procedures might have altered the extracted compounds.

Among the different treatments, the highest concentration of HA (4.34%) and DEDIA (3.43%) bound residues to the total applied atrazine was recorded in control (Fig 1). This could be ascribed to the poor crop root activity which is normally accountable for atrazine uptake by maize plant and its subsequent metabolization into nontoxic products. This was followed by N alone and NPK treatments for both the metabolites. These results could be credited to the lower OC status and type of OC fractions when compared to balanced fertilization, and organic sources applied treatments (Fig. 1). A similar result of OC influence on hexazinone dissipation was reported by Lalah *et al.* (2009) in the tropical clay and loam soils grown with sugarcane crop and Wang *et al.* (2012) in forest soils amended with

sewage sludge. Viti *et al.* (2020) found that the addition of vinasse has presented a greater percentage of re-extractable hexazinone and metribuzin residues than the filter cake in sandy loam soils cultivated with sugarcane. Xie *et al.* (1997), reported that the, most irreversibly sorbed atrazine was found in the bound-humic acid and mineral fractions of the soil. The s-triazine residue is primarily degraded chemically and microorganisms act only in the production of various metabolites (Bollag and Loll, 1983). Bound residues may also be formed through the temporary immobilization of herbicide or metabolites by the flora and fauna and subsequent release of these materials through decomposition of the crop residues in the soil. Abdelhafid *et al.* (2000) hypothesized that the increase in non-extractable residues was linked to the atrazine incorporation in the growing microbial biomass and shown that glucose addition did not modify atrazine mineralization, but increased the formation of bound fraction.

Omitting any one major nutrient for longer time registered elevated DEDIA bound form than the HA fraction. However, HA bound fraction was below the detection limit in the plots where N fertilization is skipped continuously for both the crops. This showed the influence of nitrogen and balanced fertilization on the dissipation of atrazine and its bound residue formation in soil. Effect of N fertilization on herbicides dissipation upon continuous and repeated application was also reported by Chinnusamy *et al.* (2012) and Janaki *et al.* (2010, 2012a and 2012b) in rice, maize, sunflower etc. Comparison of different organic fertilization plots showed that the bound HA fraction was in the order of RM-NEB>PM-NEB>FYM-NEB and *vice versa* for DEDIA fraction. This illustrates that the application of

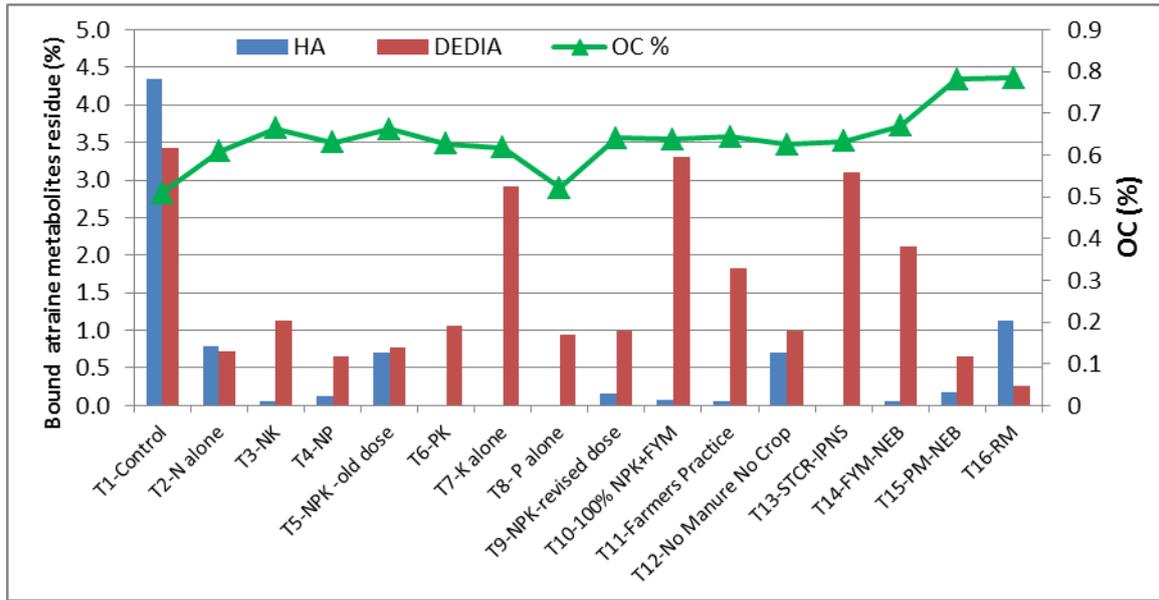


Fig. 1. Effect of long term fertilization through various sources on the bound residue of HA and DEDIA fractions after maize harvest and initial organic carbon (OC) status in soil.

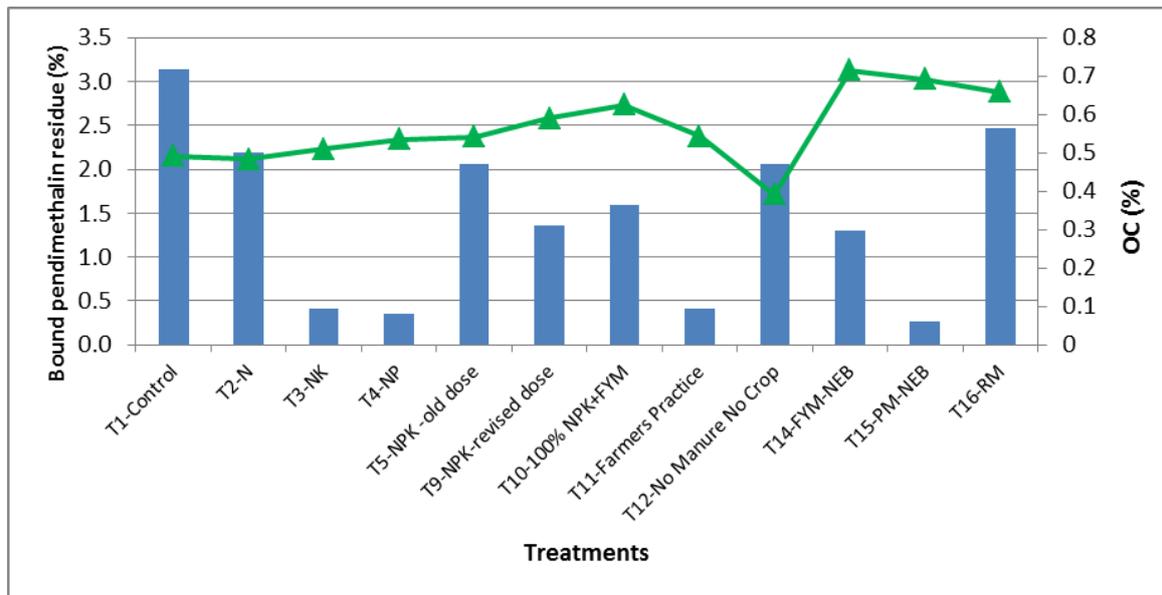


Fig. 2. Effect of long term fertilization through various sources on the bound residue of pendimethalin after sunflower harvest and initial organic carbon (OC) status in soil.

FYM of low C:N ratio favors degradation of atrazine to DEDIA than the high C:N ratio residue mulching. This could be ascribed to the sorption and immobilization of HA by the un-decomposed cellulolytic crop residues used as residue mulch. In general bound DEDIA residue was higher in all the fertilized treatments when compared HA bound fraction. Similar results were reported by the many researchers that the pesticide incubated on mulch or fresh organic matter resulted in a higher proportion of non-extractable residues than those incubated directly in soils (Barriuso *et al.*, 1991; Abdelhafid *et al.*, 2000; Rampoldi *et al.*, 2004). The environmental significance of a bound residue on its

bioavailability to plants and/or soil-inhabitation animals was reported by Calderbank (1989) and Viti *et al.* (2020).

Pendimethalin bound residue: The combination of shaking extraction for 12 hrs and then ultra-sonication for 5 hrs under the specified conditions using acidified methanol extracts detectable quantity of non-extractable pendimethalin bound residues from the soil (Table 1) collected at the time of sunflower harvest. Irrespective of treatments, the non-extractable pendimethalin fraction ranged from 0.0013 to 0.0157 mg kg⁻¹ and the higher concentration of compound was recorded under control treatment. Though, it was detect-

ed almost in all the treatments ((LOQ=0.001 mg kg⁻¹ by the method), 100% NPK supply through inorganic sources have higher bound pendimethalin fraction than the omission of any one or two major nutrients and also organic sources treatments. This showed that the imposed treatments have a significant influence on the formation of non-extractable bound residues of pendimethalin or its degradation products in soil.

The results showed that a significant amount of pendimethalin residues could persist in soil under field conditions when it was repeatedly applied for long term. The bound fraction represents only 1.70 per cent of the applied pendimethalin to the sunflower field (Fig 2). The present results are in line with Nelson *et al.* (1983) who found about 12 per cent of the applied pendimethalin fraction in bound fractions after 6 months period of incubation and Houot *et al.* (2000) who reported 4.7 % of the applied ¹⁴C activity in bound residues. The highest quantity of bound fraction to the total applied pendimethalin in a sunflower field (Fig. 2) was recorded in control (3.14%) and was followed by the residue mulching (2.46%), N alone (2.19%) and NPK-old dose (2.06%) treatments. The lower concentration of pendimethalin bound fraction in the organic sources except residue mulched treatments confirmed the enhanced microbial degradation of pendimethalin. Further, the nature of organic source influenced the quantity of bound residue of pendimethalin present in the soil. It was in the order of RM-NEB>FYM-NEB>PM-NEB among the organic source of fertilization. This could be attributed to an increase in sorption following the addition of exogenous organic matter and decreased mineralization as reported for dimefuron (Barriuso *et al.*, 1997) and metribuzin (Viti *et al.*, 2020).

Conclusion

The results of the present study showed that the herbicides viz., atrazine, its metabolites and pendimethalin form non-extractable bound residues in soil at different proportions according to the herbicide nature and sources of fertilization besides the crops cultivated in the soil of tropical region. The fraction of atrazine metabolite residues (0.0035 to 0.0217 mg/kg hydroxy atrazine and 0.0033 to 0.0171 mg/kg Des-ethyl Deisopropyl atrazine) in soil as bound form was higher than for the pendimethalin (0.002 to 0.0157 mg/kg). It was concluded that the repeated and long term application of the same herbicides formed bound residues in soil and over a period of time which may become point source of pollution and harms the soil microorganisms. Since the bound residues of atrazine and pendimethalin were altered by the sources of organic and inorganic fertilization, future research should focus on the influence of the type of organic manures, stages of decomposition of added crop residues, C:N ratio and pools of soil organic carbon

fractions.

ACKNOWLEDGEMENTS

The authors are thankful to the Directorate of Weed Research, Jabalpur and Department of Agronomy, Tamil Nadu Agricultural University, Coimbatore, for providing the necessary laboratory facilities to carry out the analytical work.

Conflict of interest

The authors declare that they have no conflict of interest.

REFERENCES

1. Abdelhafid, R., Houot, S. and Barriuso, E. (2000). How increasing availabilities of carbon and nitrogen affect atrazine behaviour in soils. *Biol. Fertil. Soils*, 30: 333–340.
2. Alexander, M. (2000). Aging, bioavailability, and over estimation of risk from environmental pollutants. *Environ. Sci. Technol.*, 34: 4259–4265.
3. Barriuso, E., Schiavon, M., Andreux, F. and Portal, J.M. (1991). Localization of atrazine non-extractable (bound) residues in soil size fractions. *Chemosphere*, 22(12): 1131–1140.
4. Barriuso, E., Houot, S. and Serra-Wittling, C. (1997). Influence of compost addition to soil on the behaviour of herbicides. *Pesticide Science*, 49: 65–75.
5. Bollag, J.M. and Loll, M.J. (1983). Incorporation of xenobiotics into soil humus. *Experientia*, 39(11): 1221–1231.
6. Calderbank, A. (1989). The occurrence and significance of bound pesticide residues in soil. *Rev. Environ. Contam. Toxicol.*, 108: 71–103.
7. Capriel, P. and Haisch, A. (1984). Persistence of atrazine and its metabolites in soil eight years after a single herbicide application and their uptake by oat plants (No. *IAEA-TECDOC--306*). https://inis.iaea.org/search/search.aspx?orig_q=RN:16030537.
8. Chinnusamy, C., Janaki, P., Muthukrishnan, P. and S. Jeyaraman S. (2012). Long term herbicidal weed management integrated with nitrogen nutrient in transplanted rice-rice cropping system of Tamil Nadu, India. *Pak. J. Weed Sci. Res., Special Issue*. 18: 95-103.
9. Dec, J. and Bollag, J.M. (1988). Microbial release and degradation of catechol and chlorophenols bound to synthetic humic acid. *Soil Science Society of America Journal*, 52(5):1366-1371.
10. Donati, L. and Funari, E. (1993). Review of leaching characteristics of triazines and their degradation products. *Annali-Istituto Superiore Di Sanita*, 29: 225-225.
11. Gabriel Perez-Lucas, Nuria Vela, Abderrazak El Aatik and Simon Navarro (2018). Environmental risk of groundwater pollution by pesticide leaching through the soil profile, pesticides - use and misuse and their impact in the environment, Marcelo Larramendy and Sonia Soloneski, IntechOpen, DOI: 10.5772/intechopen.82418. Available from: <https://www.intechopen.com/books/pesticides-use-and-misuse-and-their-impact-in-the-environment/environmental-risk-of-groundwater-pollution-by-pesticide-leaching-through-the-soil-profile>.
12. Guimaraes, A.C.D., Mendes, K.F., Reis, F.C., Campion, T.F. Christoffoleti, P.J. and Tornisielo, V.L. (2018). Role of soil physicochemical properties in quantifying the fate of diuron, hexazinone, and metribuzin. *Environmental Sci-*

- ence and Pollution Research 25(13): 12419–12433.
13. Hatzinger, P.B. and Alexander, M. (1995). Effect of aging of chemicals in soil on their biodegradability and extractability. *Environmental science and technology*, 29(2): 537-545.
 14. Houot, S., Topp, E., Yassir, A. and Soulas, G. (2000). Dependence of accelerated degradation of atrazine on soil pH in French and Canadian soils. *Soil Biology and Biochemistry*, 32(5): 615-625.
 15. Janaki, P., Chinnusamy, C. Meena, S. and Shanmugasundaram, R. (2010). Persistence and degradation behaviour of butachlor and 2,4-d in rice soil under continuous and rotational use: effect of nitrogen sources and seasons” 3rd International Rice Research Conference on “Rice for Future Generations” held between 8th November and 12th November, 2010 at Hanoi, Vietnam.
 16. Janaki, P., Meena, S. and Chinnusamy, C. (2012a). Field dissipation of herbicides under different crops in Tamil Nadu. *Madras Agric J.* 99 (10-12): 794-798.
 17. Janaki, P., S Meena, S., and Chinnusamy, C., Murali Arthanari, P., and Nalini, K. (2012b). Field persistence of repeated use of atrazine in sandy clay loam soil under maize. *Madras Agric. J.*, 99 (7-9): 533-537.
 18. Janaki, P., Chinnusamy, C., Sakthivel, N., and Nithya, C. (2015). Field dissipation of pendimethalin and alachlor in sandy clay loam soil and its terminal residues in sunflower (*Helianthus annuus L.*). *Journal of Applied and Natural Science* 7 (2): 709-713. DOI: <https://doi.org/10.31018/jans.v7i2.670>
 19. Janaki, P., Meena, S., Shanmugasundaram, R., and Chinnusamy, C. (2019). Dissipation and impact of herbicides on soil properties in Tamil Nadu. In: Sondhia S., Choudhury P., Sharma A. (eds) *Herbicide Residue Research in India. Environmental Chemistry for a Sustainable World*, vol 12. Springer, Singapore. doi.org/10.1007/978-981-13-1038-6_5.
 20. Janaki, P. and Murali Arthanari, P. (2020). Effect of conservation agricultural practices on candidate herbicides persistence under maize-sunflower system in tropical Indian Conditions. *Int. J. Curr. Microbiol. App. Sci.*, 9(7): 1375-1388. DOI: <https://doi.org/10.20546/ijcmas.2020.907.159>.
 21. Kaufman, D.D. and Blake, J. (1973). Microbial degradation of several acetamide, acylanilide, carbamate, *toluidine and urea pesticides*. *Soil Biology and Biochemistry*, 5 (3): 297-308.
 22. Kearney, P. C. (1982). IUPAC pesticide commission report. *J. Assoc. off. Anal. Chem.*, 65: 1030–1032.
 23. Khan, S. U. (1982). Bound pesticide residues in soil and plants. *Residue Rev.*, 84: 1–25.
 24. Khan, S. U., and Ivarson, K. C. (1981). Microbiological release of un-extracted (bound) residues from an organic soil treated with prometryn. *Journal of Agricultural and Food Chemistry*, 29(6): 1301-1303.
 25. Lalah, J.O., Muendo, B.M. and Getenga, Z.M. (2009). The dissipation of hexazinone in tropical soils under semi-controlled field conditions in Kenya. *Journal of Environmental Science and Health Part B* 44(7): 690–696.
 26. Lichtenstein, E. P., Katan, J. and Anderegg, B. N. (1997). Binding of “persistent” and “non-persistent”¹⁴C-labeled insecticides in an agricultural soil. *J. Agric. Food Chem.*, 25: 43–47.
 27. Loiseau, L. and Barriuso, E. (2002). Characterization of the atrazine's bound (nonextractable) residues using fractionation techniques for soil organic matter. *Environmental science & technology*, 36(4): 683-689.
 28. Navarro, S., Vela, N. and Navarro, G. (2007). Review. An overview on the environmental behaviour of pesticide residues in soils. *Spanish Journal of Agricultural Research*. 5(3): 357-375.
 29. Nelson, J. E., Meggitt, W. F. and Penner, D. (1983). Fractionation of residues of pendimethalin, trifluralin, and oryzalin during degradation in soil. *Weed Science*, 31(1): 68-75.
 30. Noordkamp, E.R., Grotenhuis, J. T. C. and Rulken, W. H. (1997). Selection of an efficient extraction method for the determination of polycyclic aromatic hydrocarbons in contaminated soil and sediment. *Chemosphere*, 35(9): 1907-1917.
 31. Pateiro-Moure, M., Arias-Estevéz, M. and Simal-Gandara, J. (2013). Critical review on the environmental fate of quaternary ammonium herbicides in soils devoted to vineyards. *Environmental Science and Technology* 47(10): 4984–4998.
 32. Rampoldi, A., Hang, S. and Barriuso, E. (2004). Glyphosate mineralization: Effect of temperature and soybean and corn crop residues. *Chilean Journal of Agricultural Research* 68(1):13-20
 33. Rasul, G., K.S. Khan, T. Muller, and R.G. Joergensen. 2008. Soil microbial response to sugarcane filter cake and biogenic waste compost. *Journal of Plant Nutrition and Soil Science* 171(3):355–360.
 34. Reid, B. J., Jones, K. C. and Semple, K. T. (2000). Bioavailability of persistent organic pollutants in soils and sediments—a perspective on mechanisms, consequences and assessment. *Environmental Pollution*, 108(1): 103-112.
 35. Schaffer, A., Kastner, M. and Trapp, S. (2018). A unified approach for including non-extractable residues (NER) of chemicals and pesticides in the assessment of persistence. *Environmental Sciences Europe*. 30(1):51. DOI: 10.1186/s12302-018-0181-x.
 36. Smith, A.E. and Phillips, D.V. (1975). Degradation of alachlor by *Rhizoctonia solani*. *Agronomy Journal*, 67 (3): 347-34.
 37. USEPA, T. (2014). Guidance for addressing un-extracted pesticide residues in laboratory studies. By Donald J. Brady, <https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/guidance-addressing-unextracted-pesticide-residues>.
 38. Viti, M.L., Mendes, K.F., dos Reis, F.C., Guimaraes, A.C.D., Soria, M.T.M. and Tornisiolo, V.L. (2020). Characterization and metabolism of bound residues of three herbicides in soils amended with sugarcane waste. *Sugar Tech.* (2020). <https://doi.org/10.1007/s12355-020-00884-1>.
 39. Wang, X., Wang, H. and Tan, C. (2005). Degradation and metabolism of hexazinone by two isolated bacterial strains from soil. *Chemosphere* 61(10): 1468–1474.
 40. Xie, H., Guetzloff, T. F. and Rice, J. A. (1997). Fractionation of pesticide residues bound to humin. *Soil Sci.* 162:421–429.