Journal of Entomology and Zoology Studies

Available online at www.entomoljournal.com

E-ISSN: 2320-7078
P-ISSN: 2349-6800
www.entomoljournal.com
JEZS 2020; 8(3): 1803-1811

Received: 25-03-2020
Accepted: 27-04-2020

Susheel Singh
Food Quality Testing Laboratory, NM College of Agriculture, Navsari Agricultural University, Navsari, Gujarat, India

Binduben V Bhuva
Food Quality Testing Laboratory, NM College of Agriculture, Navsari Agricultural University, Navsari, Gujarat, India

Vanrajsinh H Solanki
Food Quality Testing Laboratory, NM College of Agriculture, Navsari Agricultural University, Navsari, Gujarat, India

Keyur N Patel
Food Quality Testing Laboratory, NM College of Agriculture, Navsari Agricultural University, Navsari, Gujarat, India

KG Patel
Food Quality Testing Laboratory, NM College of Agriculture, Navsari Agricultural University, Navsari, Gujarat, India

Corresponding Author:
Susheel Singh
Food Quality Testing Laboratory, NM College of Agriculture, Navsari Agricultural University, Navsari, Gujarat, India

Persistence and downward movement of four termiticides in three representative soils of Gujarat under laboratory conditions

Susheel Singh, Binduben V Bhuva, Vanrajsinh H Solanki, Keyur N Patel and KG Patel

Abstract
Termiticides are generally applied to control the damage done by the devastating termites at pre-construction stage which are much higher than agricultural rate. Thus, such higher termiticidal application could pose a serious threat to water contamination with toxic residues. A study was performed to determine the persistency and downward movement of termiticides *viz.*,bifenthrin, chlorpyrifos, fipronil and imidacloprid in clay, sandy loam and sandy soils of Gujarat. The results of persistency study reveal that bifenthrin, chlorpyrifos, fipronil and imidacloprid were readily to fairly degradable and non-persistent to moderate persistent in soils (DT_{50} varied between 12.24-41 days) when applied at the rate of 2mg/kg (weight basis). Downward movement and depth wise distribution of these termiticides was determined by loading the pesticides at the rate of 2 mg/kg on 3 water saturated clay sandyloam and sandy soil columns. Bifenthrin residues confined to S-2 segments (6-12 cm) in all three soils while other termiticides moved from S-2 (6-12 cm) to S-5 (24-30 cm) in different soil columns. Maximum downward movement was recorded for imidacloprid in sandy soil column. The residues of above termiticides were BDL in leachates collected on any sampling day.

Keywords: Dissipation, DT_{50}, downward movement, persistence, termiticide

Introduction
Termites attack on annual and perennial crops, especially in the semi-arid and sub-humid tropics, cause significant yield losses. In India, termites are widely distributed in red, sandy loam, lateritic and red loam soils. They damage major field crops such as wheat, sugarcane, cotton, ground, pulses, forest plantation tress, perennial crops like tea *etc*. at all stages of growth cycle [1]. It is estimated that 20% of Australian [2] and up to 90% of Chinese homes are affected by termite damage [3, 4]. The economic losses associated with termite damage for Malaysia, India, Australia, China, Japan and United States are 10, 35, 100, 375, 800 and 1,000 million US dollars, respectively [5].
Pre-construction soil treatments with cyclodienes became the standard method of subterranean termite prevention. Cyclodien insecticides *viz*., aldrin, dieldrin, chlordane *etc*. were banned by several countries because of their higher persistence and toxicity to the non-target organisms. In recent years, insecticides such as chloronicotinyl (imidacloprid), neonicotinoid (thiamethoxam), phenyl pyrazole (fipronil) and pyrole (chlorfenapyr) have become popular alternatives of the toxic cyclodiene insecticides for the control of termites due to their non-repellent and long lasting nature. Generally, termiticides are applied onto soil or bedding materials before placement of the building foundation to create a continuous barrier around the building.It is important to know that when pesticides are applied to field, as the only small portion reaches to its target and remaining a large part is released into the environment. That may leads to some problems, such as toxicity to non-target organisms, leaching and accumulation.
Thus, to conciliate agricultural and environmental interests, present study was under taken to determine the persistence and downward movement of four termiticides *viz*., bifenthrin, chlorpyrifos, fipronil and imidacloprid in three representative soils of Gujarat (India) under laboratory conditions.

Materials and Methods

Soil: Soil samples (0–15 cm depth) were collected randomly from the research farms of Anand Agricultural University, Anand (N-S Latitude: 22°56 ′10.72 ″; E-W Longitude : 72°58′58.19″), Sardarkrushinagar Dantiwada Agricultural University, Dantiwada (N-S Latitude : 24°19 ′31.28 ″; E-W Longitude : 72°19′13.82″) and Navsari Agricultural University, Navsari(N-S Latitude : 20°56′3.91″; E-W Longitude : 72°53′33.22″), Gujarat, India which were not having history of soil application of bifenthrin, chlorpyrifos, fipronil and imidacloprid. The remains of vegetables, macro-fauna, stones *etc.*, were removed, followed by air drying at ambient room temperature. A careful homogenization was done for better reproducibility of the results while utmost care was taken maintain the original texture of the soils. Before using, soils were stored at ambient temperature and kept air dried. Thephysico-chemical properties of the soil are given below (Table 1).

Table 1: Physico-chemical properties of experimental soils

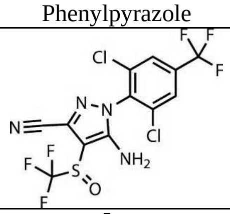
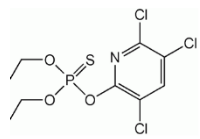
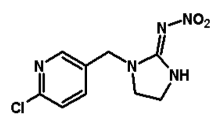
Sr. No.	Physico-chemical property	Soil Site		
		Navsari	Anand	Dantiwada
1.	Mechanical Analysis			
(i)	Coarse sand (%)	1.23	2.57	51.27
(ii)	Fine sand (%)	15.21	71.23	33.01
(iii)	Silt (%)	26.39	19.43	8.52
(iv)	Clay (%)	57.17	6.00	4.01
2.	Textural class	Clayey	Sandy loam	Sandy
3.	Chemical properties			
(i)	pH(1:2.5)	7.34	7.62	7.51
(ii)	EC at 25° C (dS/m)	0.38	0.32	0.47
(iii)	Organic C (%)	0.58	0.45	0.28
(vi)	Bulk density (g cc^{-1})	1.37	1.35	1.52
(vii)	WHC (%)	56.52	43.64	26.6

Chemicals and apparatus: LC-MS grade acetonitrile was purchased from J.T. Baker (NJ, USA). Acetone, *n*-hexane, anhydrous sodium sulfate (Na_2SO_4), analytical reagent (AR) grade sodium acetate, sodium chloride were obtained from Thermo Fisher India (ltd.) Mumbai, India. Primary secondary amine (PSA, 40 lm) was purchased from Agilent Technologies, Bangalore, India. Analytical weighing balance (Contech made; 320±0.001 g sensitivity), centrifuge (Eppendorf), ultrasonic bath (Oscar electronics, Mumbai, India) and low volume concentrator (TurboVap LV, Caliper made) were used in analysis.

Termiticides

The analytical reference substances of four termiticides *viz.* bifenthrin (purity, 98.8%) chlorpyrifos (purity, 99.7%), fipronil (purity, 97.5%) and imidacloprid (purity, 99.9%) was purchased from Sigma Aldrich Chemicals Pvt. ltd., (Bangalore, India). The physicochemical properties of above mentioned termiticides is given in Table 2.

Table 2: Physico-chemical properties of termiticides [6]

Particulars	Bifenthrin	Fipronil	Chlorpyrifos	Imidacloprid
Chemical name	2-Methyl-3-phenylphenyl) methyl (1*S*,3*S*)-3-[(*Z*)-2-chloro-3,3,3-trifluoro prop-1-enyl]-2,2-dimethyl cyclopropane-1-carboxylate	5-amino-1-[2,6-dichloro-4-trifluoro methyl)phenyl] -4-(trifluoromethyl) sulfinyl]-1*H*-pyrazole-3-carbonitrile)	O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate	1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylideneamine
Mol.wt(g/mol)	422.9	473.2	350.6	255.7
CAS No.	82657-04-3	120068-37-3	2921-88-2	138261-41-3
Group	Synthetic pyrethroid	Phenylpyrazole	Organophosphate	Neonicotinoid
Structural formula				
Vapour pressure	2.41 x 10^{-5} Pa at 25 °C	3.73 x 10^{-7} Pa at 25 °C	2.49 x 10^{-3} mmHg at 25 °C	3.99 x 10^{-10} mmHg at 20 °C
Water solubility (mg/l)	<0.001	1.9 (pH 5.0) at 20 °C 2.4 (pH 9.0) at 20 °C	1.4	610 (at 20 °C)
Octonal-water coeff.(K_{ow})	1.0x10^6	1.0x10^4	4.7	0.57 at 21 °C
Soil sorption coeff. (K_{oc})	1.31-3.02x10^5	825	360-31000	249-336

Dissipation and persistence of termiticides in soils: Approximately 1.0 kg air dried, disaggregated and sieved clayey, sandy loam and sandy soil was placed in glass container. The individual soil was fortified by uniform spraying of 100 ml acetone-hexane mixture containing 2.0 mg/kg pesticides mixture on soil weight basis. A representative (10 ±0.1) g sample was collected in duplicate along with untreated control sample of each soil type on 0 (2 hrs after application), 1, 5, 10, 20, 30 and 60 days after application and was analysed for termiticides residues. The dissipation kinetics of different termiticides was determined following first order degradations kinetics. Simultaneously, the dissipation half-life of these termiticides were also determined by using the following formula:

$$\text{Dissipation Half-life (days)} = \frac{\ln(2)}{k}$$

Where k is Dissipation rate

Downward movement and depth wise distribution of termiticides in soil column

For *insitu* downward movement study, a PVC column (36 cm long, 6 cm interior diameter) was taken and mark into five sections each of six centimetres. The bottom ring was filled with the layer of cotton and muslin cloth which was fixed with the help of thread on the outer side of column to collect clear leachates. The columns were hand packed with concerned soils upto 30 cm mark from the bottom ring. The upper 6 cm of PVC pipe was kept clear from the soil for proper moisture supplementation. For applying the pesticides, soil was wetted to their apparent water holding capacity by applying 0.01M $CaCl_2$ solution to the top of the column in 50 ml increments at an interval of 24 hours. After this initial equilibration, soil was fortified with pesticides @ 2mg/kg on soil basis on the top of the column. The total loading of different termiticides were 2112, 2368 and 2536 µg/g respectively for clay, sandy loam and sandy soil considering weight of each type of soil in columns. Top of the column was covered with aluminium foil to prevent volatilization losses. The entire experiment was conducted at room temperature. The totals of 12 columns were prepared (9 treatments + 3 controls). The bulk density of different soil columns was also determined considering its volume upto 30 cm height and weight of the soil filled. First irrigation was given after 24 hours of fortification followed by subsequent irrigations with aqueous solution of 100 ml $CaCl_2$ (0.01M) per day until the end of the experiment. The leachates were collected in a glass bottle and analysed on 5th, 10th, 15th 20th 25th and 30 days after loading of the termiticides. At the termination of experiment, the soil columns were cut into five, 6 cm segments i.e., S-1 (0-6 cm), S-2 (6-12cm), S-3 (12-18cm), S-4 (18-24 cm) and S-5 (24-30cm), the soil inside the column was dried under shade on aluminium foil separately. The weight of dried soil collected from each segments of the column was recorded. From the dried soil, 50g of soil was used for pesticide residue estimation in duplicate. Other relevant details of soil columns and weight of soil/segment is mentioned in Table 3.

Table 3: Details of soil columns and weight of dried soil recovered from different segments soil column

Column details	Wt. of soil filled@ (g)	Weight of the dried soil/segment of column++					
		S-1 (0-6 cm)	S-2 (6-12 cm)	S-3 (12-18 cm)	S-4 (18-24 cm)	S-5 (24-30cm)	Wt. soil recovered (g)
Clay	1056	185.7	215.3	235.2	202.1	197.6	1035.8
SL	1184	216.2	225.8	245.0	256.3	215.7	1159.0
Sandy	1268	214.4	236.3	254.7	290.5	233.9	1229.9
@ Mean weight of three columns, ++ Mean weight of three segments, SL- Sandy loam							

Termiticide extraction and cleanup

Soil: A representative air dried soil sample (10 ±0.1 g) was accurately weighed in a 50 ml capacity polypropylene centrifuge tube. To the sample, 20 ml LC-MS grade acetonitrile was added and mixed thoroughly. Samples were kept in deep freezer for 20 minutes followed by addition of $MgSO_4$ (4 g) and anhydrous NaCl (1 g). The soil sample was then vortexed for 1.0 min. The sample was subjected to centrifugation at 3500 rpm for 3 min. The supernatant (10.0 mL) was carefully transferred to a 15 ml capacity polypropylene centrifuge tubes containing $MgSO_4$ (1.5 g) and PSA (0.25 g). Centrifuge tubes were then shaken vigorously. Samples were then subjected to centrifugation at 2500 rpm for 2.0 min. The supernatant (4.0 ml) was transferred to 15 ml capacity test tube. Samples were evaporated to dryness with N_2 concentrator (TurboVap) at 45 °C and final volume was made up to 1.0 ml with *n*-hexane:acetone (3:1) for bifenthrin, chlorpyrifos and fipronil. However, for imidacloprid, the supernatant (0.5 mL) was transferred to a 15 mL capacity test tube and final volume was made upto 2 mL with LC-MS grade acetonitrile. These samples were then subjected to chromatographic analysis for the quantification of termiticides residues.

Water/Leachate: The water/leachates sample (250 mL) transferred into 1000 mL capacity separatory funnel and NaCl (40 g) was added until dissolved. The residue was extracted twice with methylene chloride 50 mL and shaken vigorously. The lower organic phase was collected followed by passing through the anhydrous Na_2SO_4 bed. The combined DCM phase was subject to complete evaporation using rotary vacuum evaporator at 45° C. The concentration step was repeated thrice in the presence of n-hexane to remove the traces of methylene chloride. Final volume was made up to 2.0 mL with *n*-hexane:acetone (1:1, v/v). Out of 2.0 mL final volume, 1.0 mL was used to determine the GC-ECD amenable termiticides. However, remaining 1.0 mL was evaporated to dryness on TurboVap and reconstituted to 1.0 mL with LC-MS grade acetonitrile to quantify the imidacloprid residues on HPLC.

Instruments: Thermo made Gas Chromatograph equipped with Electron Captured Detector (TRACE GC ULTRA) and High Performance Liquid Chromatograph equipped with UV-VIS detector (Thermo-made; Finnigan Surveyor Plus) with autosamplers were used for the quantification of the residues of above termiticides.

Instrumental parameters

A) Bifenthrin, Fipronil, Chlorpyrifos: The gas chromatographic separation was performed on capillary column (AB-5, 30 m x 0.25 mm i.d., 0.25 µm FT). The 1.0µL sample was injected under splitless mode into GC. Ultra-pure helium (99.999%) gas was used as carrier gas at a flow rate of 1.0 mL/min. The oven temperature was initially maintained at 150 ºC for 1 minute and programmed with the ramp of 10 ºC/min to attain the final temperature of 290 ºC which was maintained for 4.0 minutes. Injector and detector temperatures were maintained at 230 and 300 ºC, respectively. The reference current of ECD was 1.0 nA. The makeup gas of ECD were nitrogen and its flow was 40 mL/min. The retention time for fipronil, chlorpyrifos and bifenthrin were 7.85, 10.16 and 14.40 min, respectively. The total run time needed to separate these termiticides on GC-ECD was 19.0 minutes.

Imidacloprid: Analysis of imidacloprid was performed at 270 nm wavelength. The solvent compositions were acetonitrile and water as 60:40 (v/v) using reverse phase Hypersil Gold C18 (Particle Size: 5µm; 250 mm x 4.0 mm I.D) column with flow rate of 1 mL/min under isocratic flow mode. The injection volume was 20 µL. The imidacloprid was eluted at 5.22 min while the total run time was 9.0 minutes.

Results and Discussion

Primary gas chromatographic analysis reveals that there was no interfering peaks were observed at the retention time of bifenthrin, chlorpyrifos, fipronil and imidacloprid on HPLC. This allows for clear identification and quantification of all analytes. The results obtained in the linearity study reveals that response of different insecticides *viz*., bifenthrin, chlorpyrifos, fipronil were linear in the range 0.05 to 1.0 mg/kg while that for imidacloprid was 0.05 to 2.0 mg/kg on their respective instruments. The coefficient of determination (R^2) recorded for all the insecticides were 0.99.

The results obtained in the accuracy (% Recovery) and precision (% RSD) study revealed that the mean% recovery of bifenthrin, chlorpyrifos, fipronil and imidacloprid over three spiking levels were in the range of 89.79 to 112.61% from clay, sandy loam and sandy soils with% RSD varied in the range of 5.20 to 7.89%. However, % recovery and% RSD obtained for different termiticides from water/leachate were varied in the range of 97.40 to 105.47% and 4.98 to 9.28%, respectively (Table 4). The LOD and LOQ of different termiticides worked out for bifenthrin, chlorpyrifos, fipronil and imidacloprid in soils were in the range of 0.02 to 0.07 µg/g. However, the LOD and LOQ obtained in water/leachate analysis were in the range of 0.02 to 0.09 µg/L. The results obtained in the study reflects that the analytical procedure applied for residue analysis of 4 termiticides from soils (clayey, sandy loam, sandy) and water/leachate were accurate, precise and sensitive enough as recovery% RSD and LOQ were well within the acceptable [7, 8].

Persistence and dissipation pattern of termiticides in different soils: The results obtained in the study reveals that the residues of most of the termiticides were observed up to 60 days. However, the residue of chlorpyrifos in clayey soils and imidacloprid in clay and sandy loam soil were below detection limit on 60th day. All the termiticides followed first order degradation kinetics. The mathematical model is given below:

Ct=C0e-kt

Where, Ct = Concentration of the pesticide residue at time t

C0 = Initial concentration

k = Dissipation rate

The persistence of an insecticide is generally expressed in terms of half-life or DT_{50} of each termiticides in respective soil were worked out and the data obtained in the study is mentioned in Table-5.

Clayey Soil: The initial deposits of bifenthrin, chlorpyrifos, fipronil and imidacloprid were 1.72, 1.78, 1.66 and 2.04 mg/kg, respectively and were dissipated gradually with the time. More than half of the residues of termiticides (53.01 to 85.36%) were lost upto 30 days. The residues of imidacloprid and chlorpyrifos were below detection level on 60th day. The DT_{50} worked out for bifenthrin, chlorpyrifos, fipronil and imidacloprid were 19.68, 13.56, 18.03 and 18.24 days, respectively

Sandy loam Soil: The initial deposits of bifenthrin, chlorpyrifos, fipronil and imidacloprid were in the range of 1.74 to 1.99 mg/kg and were dissipated gradually with the time and detectable upto 60 days except imidacloprid. More or less approximately, 2/3rd portion of initial concentration of termiticides were lost upto 60 days. The residues of fipronil dissipated with slow pace among other termiticides upto 30 days as only 38.29% over its initial deposits were lost. The DT_{50} worked out for bifenthrin, chlorpyrifos, fipronil and imidacloprid were 25.09, 12.24, 23.16 and 12.65 days, respectively.

Sandy Soil: Dissipation trend observed for different termiticides in sandy soil was quite similar to that of sandy loam soil. But these termiticides were more persistent in sandy soil as DT_{50} was in the range of 14.54 to 41.81 days.

The DT50 of bifenthrin, chlorpyrifos, fipronil and imidaclopridrecorded in clay sandy loam and sandy soil were in the range of 19.68-32.37, 12.24-14.54, 18.03-41.81and 12.65-18.24 days, respectively. This classification signifies that persistence of different termiticides in clay, sandy loam and sandy soils is not alarming and posing no threat to soil or ground water contamination. On the basis of their degradability in soil, bifenthrin, chlorpyrifos, fipronil and imidacloprid can be either categorized under "Readily degradable" or "Fairly degradable" class because their dissipation half-lives were below 60 days as suggested by FAO [9] (Fig. 2).

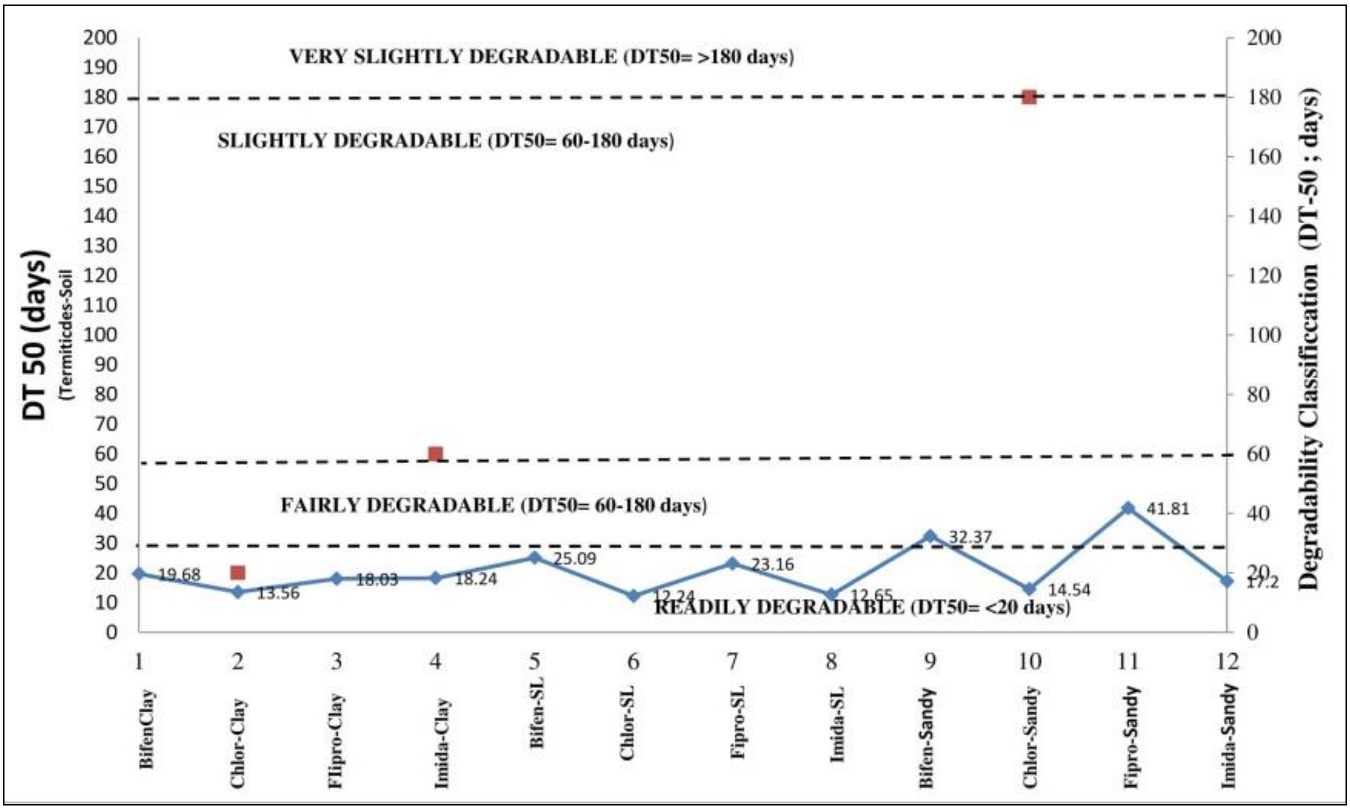


Fig 1: Degradability classification of termiticides in sandy sandy loam and clay soil

The insecticides, bifenthrin and imidacloprid were most stable and chlorpyrifos the least in all three mediums *viz*., one soil and two bedding materials (sand-dolomite and quarry sand) when applied at termiticidal application rates under standard laboratory conditions and the rate of degradation of bifenthrin and imidacloprid insecticides was adequately described by a first order kinetic model but chlorpyrifos degradation was biphasic, showing an initial faster degradation followed by a slower rate [10]. The degradation behaviour of bifenthrin, fipronil and imidacloprid in different soils also followed the first order degradation kinetics in present investigation as values of R^2 approaching to 1.0 which indicates that data is better fitted to the regression model. However, slight variation in R^2 was observed for fipronil, chlorpyrifos in sandy loam and bifenthrin in sandy soil where it was less than 0.9. However, it is believed that R^2 must equal the percentage of the response variable variation that is explained by a linear model, no more and no less. Therefore, smaller values of R^2 may be “good” for hard to predict Y variables [11]. This variation might be due variation in chemical structure, nature of pesticides, their interaction with soil and other matrices. There is no clear relationship between the chemical properties of pesticides and their rates of degradation can be established because several phenomena are simultaneously involved in the degradation of pesticides [12] as halogens, chlorine in particular, present in the moiety of pesticides can be toxic to microorganisms, which in turn could reduce the biodegradation of pesticides in soil but it is not always observed under field condition [13]. This statement is in agreement with present investigation as all termiticides are having halogen atoms in their moiety but their degradation behaviour in different soils is different.

Further, all four termiticides degraded fast in clay and sandy loam soil with respect to sandy soil in present investigation. The probable reason might be variable organic C content and clay content. In present investigation clay soil has more organic carbon (0.58%) with respect to sandy loam (0.45%) and sandy soil (0.28%). The organic matter particularly the soil organic C is the major sorbent of pesticides in soil due to its high chemical reactivity towards mineral surfaces and allowing various types of interaction with pesticides. Persistence of thiram recorded in black clayey soils having higher OC have the lowest the half-life [14] *vice-versa* situation (half-life of 1.0−2.6 years) was observed for imidacloprid in sandy soils of Florida US containing >90% sand [15] with a which signifies that persistent of imidacloprid is more in sandy textured soil. Further, there is a wide range of half-lives of chlorpyrifos reported in the literature for soil persistence, ranging from a few days to 4 years, depending on application rate, ecosystem type, and various environmental factors. The dissipative half-life is significantly longer in organic soil than mineral soil [16] which is contradictory to our finding where half-life of chlorpyrifos ranged between 12.24-14.54 days in clay, sandy loam and sandy soil. Bifenthrin and fipronil shows more or less same persistency in different soils with DT_{50} ranged between 19.68-32.37 and 18.03-41.81 days, respectively which differs from other studies [17]

Kinetic studies revealed that dissipation of fipronil followed first order with half-life of 23.35 days [18], biphasic first order with $t_{1/2}$ (10.81 days) [19] in light textured soil which is contrary to our study. In present study, the DT_{50} of fipronil was higher (41.81, 2316 days; sandy and sandy loam) then heavy textured clay soil (18.03 days). Persistence of fipronil was found to be more in clay loam soil than sandy loam soil and their half-life values were in the range of 33.34 to 37.63 days, respectively [20] which are slight differ from our investigation results. The probable explanation might be only parent compound *i.e.* fipronil was consider for residue analysis in present investigation but parent compound along with their metabolites were also considered for residue estimation above mentioned study.

Depthwise distribution of termiticides in different soil columns

The results obtained in the study reveals that maximum concentration of the residues of these compounds remain confined on the top section of the column (S-1) *i.e.* 0-6 cm. After termination of the experiment 58.21 to 97.85% residues of different termiticides were lost with respect to their initial loading concentration. The tabular representation of the depth wise distribution of the different termiticides in respective soil column is mentioned in Table 6. All termiticides moved upto S-2 to S-3 section in all soil columns. However, imidacloprid recorded the maximum movement *i.e.* upto S-5 section (24-30 cm) in sandy soil.

The residues of bifenthrin restricted to S-2 segment (6-12 cm) in all three soil columns. Total residues of bifenthrin detected in S-1 segment were 285.90, 272.45 and 212.29 µg/g in clay, sandy loam and sandy soil, respectively after termination of the experiment. These residues were 13.53, 11.50 and 8.37% of total loading of bifenthrin in clay, sandy loam and sandy soil. However, 79.14 to 85.55% of bifenthrin residues were lost or degraded in all three soil columns. Bifenthrin was strongly adsorbed to all the soil due to its high soil sorption coefficient (1.31-3.02 x10^5) while its low water solubility (<0.001mg/L) also ceased its movement in soil column. Therefore, its residues could not move beyond S-2 (6-12 cm) in any soil column. This phenomenon was also reported in other similar studies [21, 22].

The residues of chlorpyrifos moved upto S-4 segment (18-24) in sandy loam and sandy soil while these were confine to S-3 segment in clay soil. The 0.79% residues of chlorpyrifos over total loading were detected in S-3 segment of clay while that for S-4 segments of sandy loam and sandy soil were and 1.62 and 1.26%, respectively. This reflects that 93.55, 86.97 and 82.26% of chlorpyrifos residues were lost in clay, sandy loam and sandy soil, respectively.

The movement of fipronil residues in clay, sandy loam and sandy soil were recorded upto S-2, S-3 and S-4 segments. The 0.91% residues of fipronil over total loading were detected in S-2 segment of clay while that for S-3 and S-4 segments of sandy loam and sandy soil were 1.36 and 0.80% respectively. The loss of fipronil residues in clay, sandy loam, sandy soil column were 97.85, 91.14 and 85.08%.

Maximum movement of residues in different soil column was observed in imidacloprid where these moved upto S-5 segment in clay soil. The% residues of imidacloprid recorded over its initial loading amount in S-4 segments of clayand sandy loam sandy soil columns were 2.39 and 0.97%, respectively while that for S-5 segment in sandy soil column was 1.48%. The loss of imidacloprid residues in clay, sandy loam, sandy soil columns was least with respect to other termiticides and was 58.21, 77.38 and 70.53% over initial loading amount of imidacloprid.

The movement of organic compounds depends upon sorption coefficient (K_{oc}). Pesticides with a small K_{oc} value are more likely to leach into groundwater than those with a large K_{oc} value. In present investigation, maximum downward movement was recorded in imidacloprid which has least K_{oc} value (249-336) with respect to other bifenthrin, fipronil and chlorpyrifos (Table-2). Simialrly, bifenthrin has highest K_{oc} (1x10^5) value whose impact on depthwise distribution of its residues is quite evident as its residues limited upto S-2 (6-12 cm) segment. Further, bifenthrin is a non-polar molecule that has a high octanol-water coefficient (K_{ow} = 1.0 x 10^6). Bifenthrin has a low water solubility and a correspondingly strong tendency to bind to soil might be a probable explanation of least downward movement of bifenthrin all three soil (clay, sandy loam and sandy) columns.

Chlorpyrifos and fipronilwas confined to S-2 and S-4 segments in different soil column. Chlorpyrifos is strongly associated with soil and sediment surfaces in aqueous systems. Therefore, soil column studies have universally concluded that chlorpyrifos is unable to leach significantly and exit the soil profile in leachate even under the most arduous conditions of simulated rainfall [16]. Similarly higher K_{ow} and lower K_{oc} of fipronilhavealso play a role in restricting the movement of fipronil in lower depth. Several Leaching studies confirm the restricted mobility of fipronil in soils since results showed fipronil moved upto 6-12cm [22] and 6-24 cm [23] which is in agreement with our finding.

A low K_{oc} value coupled with high water solubility facilitates imidacloprid to moved own in soil column which evident from the study where it moved in soil column beyond S-3 segments in all three soils. The water solubility and soil organic carbon-water partitioning coefficient values of imidacloprid affect longevity and movement of the chemical in soil. These factors might influence adsorption to soil and mobility of imidacloprid in the environment. A low K_{oc} value coupled with high water solubility suggests imidacloprid could leach down the soil column. However, imidacloprid leached below the citrus root zone (30-45 cm) after the soil-drench applications due to weak soil sorption co-efficient (K_{OC} = 163-230) [24].

Residues in leachates

Leachates collected from the different soils fortified with different pesticides were analyzed for pesticide residues on different time interval. The pesticide residues in all the leachates samples were below detection limit (Table 6).

Sandy soils are comparatively more permeable, well drained and are less water retentive in nature as compare to loamy and clayey soils which in turn are rich in clay, fine sand and silt particles. Sandy soil which was used in the experiment contains approximately 85% sand particles (Course sand +fine sand), low water holding capacity and organic carbon (Table 1). Soil organic matter acts as main sorbent in soil and attracting non-polar organic pesticide molecules [25]. Thus, termiticides used for loading in the leaching study were strongly adsorbed to different soil along with non-polar nature restricted the entry of termiticides residues in leachates. Although, clay soil have high water holding capacity but chances of hydrolytic degradation of these termiticides were also increases.

Conclusion

The findings of this study indicate that bifenthrin, chlorpyrifos, fipronil and imidacloprid were readily to fairly degradable and non-persistent to moderate persistent in soils (DT_{50} varied between 12.24-41 days) when applied at the rate of 2mg/kg (weight basis). The residues of bifenthrin confined to S-2 segments (6-12 cm) in all three soils while other termiticides moved from S-2 (6-12 cm) to S-5 (24-30 cm) in different soil columns when these pesticides were applied at the rate of 2 mg/kg on three water saturated clay sandy loam and sandy soil columns. Maximum downward movement was recorded for imidacloprid in sandy soil column. The residues of above termiticides were BDL in leachate collected from different soil columns on any sampling day.

Acknowledgement
The authors are thankful to all who in one way or another contributed in the completion of this research project particularly Director of research &Dean PG studies, Navsari Agricultural University, Navsari (Gujarat) for his encouragement and moral support to materialize this research project.

Table 4: Method performance verification study in different soils and leachate for bifenthrin, chlorpyrifos, fipronil and imidacloprid

Sr. No	Pesticide	Matric/ type	% Mean recovery across the spiking levels	SD	% RSD	LOD*	LOQ**
1	Bifenthrin	Soil/Clay	100.94	5.16	5.20	0.02	0.05
		Soil/Sandy Loam	105.44	6.34	6.14	0.02	0.06
		Soil/Sandy	103.82	6.71	6.46	0.02	0.06
2	Chlorpyrifos	Soil/Clay	93.52	5.91	6.35	0.02	0.06
		Soil/Sandy Loam	105.60	5.68	5.39	0.02	0.05
		Soil/Sandy	104.58	5.94	5.70	0.02	0.06
3	Fipronil	Soil/Clay	89.79	5.56	6.19	0.02	0.05
		Soil/Sandy Loam	110.74	5.69	5.14	0.02	0.06
		Soil/Sandy	112.61	5.58	4.99	0.02	0.05
4	Imidacloprid	Soil/Clay	97.84	7.34	7.32	0.02	0.07
		Soil/Sandy Loam	96.86	7.75	7.89	0.02	0.07
		Soil/Sandy	93.36	6.04	6.46	0.02	0.07
5	Bifenthrin	Water/leachate	97.40	7.78	7.95	0.02	0.07
6	Chlorpyrifos	Water/leachate	105.47	9.72	9.28	0.03	0.09
7	Fipronil	Water/leachate	104.24	5.27	4.98	0.02	0.05
8	Imidacloprid	Water/leachate	98.56	8.80	9.03	0.03	0.09

(n=21) * LOQ (Soil-µg/g, **water/leachate- µg/L)

Table 5: Residues and dissipation of bifenthrin, chlorpyrifos, fipronil and imidacloprid in clay sandy loam and sandy soil

Soil Type	Pesticides	Residues (µg/g)* Days after application								Regression equation	(R^2)	DT_{50} (days)
		0	1	5	10	20	30	60	LOQ (µg/g)			
Clay	Bifenthrin	1.72 (-)	1.67 (2.91)#	1.55 (9.88)	1.29 (25.0)	1.16 (32.56)	0.59 (65.7)	0.21 (87.79)	0.05	y = -0.0153x + 2.2486	0.998	19.68
	Chlorpyrifos	1.78 (-)	1.62 (8.99)	1.33 (25.28)	0.94 (47.19)	0.47 (73.60)	0.26 (85.39)	BDL (-)	0.06	y = -0.0222x + 2.1988	0.976	13.56
	Fipronil	1.66 (-)	1.49 (10.24)	1.28 (22.89)	1.19 (28.31)	0.93 (43.98)	0.78 (53.01)	0.14 (91.57)	0.05	y = -0.0167x + 2.241	0.949	18.03
	Imidacloprid	2.04 (-)	1.86 (8.82)	1.65 (19.12)	1.48 (27.45)	1.10 (46.08)	0.59 (71.08)	BDL (-)	0.07	y = -0.0165x + 2.3111	0.964	18.24
Sandy Loam	Bifenthrin	1.99 (-)	1.61 (19.10)	1.25 (37.19)	1.17 (41.21)	0.75 (62.31)	0.69 (65.33)	0.33 (83.42)	0.06	y = -0.012x + 2.2019	0.951	25.09
	Chlorpyrifos	1.74 (-)	1.67 (4.02)	1.36 (21.84)	1.20 (31.03)	0.90 (48.28)	0.74 (57.47)	0.20 (88.51)	0.05	y = -0.0246x + 1.5591	0.930	12.24
	Fipronil	1.75 (-)	1.47 (16.00)	1.28 (26.86)	1.21 (30.86)	1.19 (32.00)	1.08 (38.29)	0.23 (86.86)	0.06	y = -0.013x + 2.2435	0.882	23.16
	Imidacloprid	1.87 (-)	1.84 (1.60)	1.64 (12.30)	1.07 (42.78)	0.59 (68.45)	0.40 (78.61)	BDL (-)	0.07	y = -0.0238x + 2.2872	0.987	12.65
Sandy	Bifenthrin	1.82 (-)	1.65 (9.34)	1.28 (29.67)	0.94 (48.35)	0.86 (52.75)	0.81 (55.49)	0.45 (75.27)	0.07	y = -0.0093x + 2.1742	0.900	32.37
	Chlorpyrifos	1.79 (-)	1.68 (6.15)	1.43 (20.11)	1.36 (24.02)	0.85 (52.51)	0.43 (75.98)	0.11 (93.85)	0.06	y = -0.0207x + 2.2805	0.991	14.54
	Fipronil	1.71 (-)	1.33 (22.22)	1.23 (28.07)	1.16 (32.16)	1.04 (39.18)	0.90 (47.37)	0.54 (68.42)	0.05	y = -0.0072x + 2.159	0.946	41.81
	Imidacloprid	2.29 (-)	1.84 (19.65)	1.62 (29.26)	1.20 (47.60)	0.95 (58.52)	0.73 (68.12)	0.17 (92.58)	0.07	y = -0.0175x + 2.314	0.984	17.20

* Mean of two replicates, #-figure in parenthesis is% dissipation over initial deposits)

Table 6: Depthwise distribution of bifenthrin, chlorpyrifos, fipronil and imidacloprid from sandy loam and clay soil

Pesticides	Soil type	Residues (µg/g)* recovered per segment (% Residues recovered over initial loading) Leaching depth (cm) S1 (0 to 6)	S2 (6 to 12)	S3 (12 to 18)	S4 (18 to 24)	S5 (24 to 30)	Residues retained over total loading	Residues in leachate (µg/L)	% Residues lost over total loading
Bifenthrin	Clay	285.90 (13.53)	19.37 (0.92)	BDL	BDL	BDL	305.27	BDL	85.55
	Sandy loam	272.45 (11.51)	101.6 (4.29)	BDL	BDL	BDL	374.06	BDL	84.20
	Sandy	212.29 (8.37)	316.67 (12.49)	BDL	BDL	BDL	528.96	BDL	79.14
Chlorpyrifos	Clay	72.40 (3.42)	47.36 (2.24)	16.46 (0.78)	BDL	BDL	136.22	BDL	93.55
	Sandy loam	118.93 (5.02)	94.83 (4.00)	56.34 (2.38)	38.45 (1.62)	BDL	308.55	BDL	86.97
	Sandy	218.72 (8.62)	122.89 (4.85)	(76.42) (3.01)	31.96 (1.26)	BDL	449.98	BDL	82.26
Fipronil	Clay	25.99 (1.23)	19.37 (0.92)	BDL	BDL	BDL	45.36	BDL	97.85
	Sandy loam	116.76 (4.93)	58.71 (2.48)	32.29 (1.36)	BDL	BDL	207.76	BDL	91.22
	Sandy	(253.03) (9.98)	(59.08) (2.33)	45.85 (1.81)	20.34 (0.80)	BDL	378.30	BDL	85.08
Imidacloprid	Clay	323.03 (15.29)	318.58 (15.08)	(190.50) (9.01)	(50.53) (2.39)	BDL	882.65	BDL	58.21
	Sandy loam	309.17 (13.06)	115.15 (4.86)	88.19 (3.72)	23.07 (0.97)	BDL	535.58	BDL	77.38
	Sandy	293.77 (11.58)	186.69 (7.36)	124.82 (4.92)	104.59 (4.12)	37.42 (1.48)	747.29	BDL	70.53

*n=2

References

1. Rajagopal D. Economically important termite species in India. Sociobiology. 2002; 40(1):33-46.
2. Scholz GH, Militz P, Gascon-Garrido MS, Ibiza-Palacios, Oliver-Villanueva JV. Improved termite resistance of wood by wax impregnation. Int. Biodeterior. Biodegradation. 2010; 64:688-693.
3. GEI. Demonstration project of alternatives to chlordane and mirex for termite control in China. Guangdong Entomological Institute. Bejing, China. From The World Bank. 2005, 6.
4. MRP. Maxwell Robinson Phelps Termite Report. Maxwell, Robinson and Phelps. 2010. http://www.pestcontrol-perth.com/wp content/uploads /2010/06/Maxwell-Robinson-Phelps-MRP-Termite-Report.pdf
5. Tsunoda K. Improved management of termites to protect Japanese homes. Proceedings of the 5th International Conference on Urban Pests, Perniagaan, Malaysia, 2005, 33-37.
6. NPIC 2014. http://npic.orst.edu
7. Chan CC, Lam H, Zhang X. Analytical method validation and instrument performance verification. Published by John Wiley & Sons, Inc., Hoboken, New Jersey, 2004.
8. SANCO. Guidance document on analytical quality control and validation procedures for pesticide residues analysis in food and feed. No. SANCO/12571/2013, 19 November 2013 rev, 2013.
9. FAO. Assessing soil contamination. A reference manual. Published by Food and Agriculture Organization of the United Nations, 2000, 79
10. Baskaran S, Kookana RS, Naidu R. Degradation of bifenthrin, chlopyrifos, and imidacloprid in soil and bedding materials at termiticidal application rates. Pesticide Science. 1999; 55:1222-1228.
11. Anonymous. Goodness of fit in linear regression. Retrieved from http://www.medicine.mcgill.ca/epidemiology/joseph/courses/EPIB-621/fit.pdf accessed on 15/07/2017.
12. Calvet R, Barriuso E, Bedos C, Benoit P, Charnay MP, Coquet Y. Les pesticides dans les sols. Consequences agronomiques et environnementales (Editions France Agricole), Dunod, ISBN 2-85557-119-7, Paris, 2005.
13. Naumann K. Influence of chlorine substituents on biological activity of chemicals: a review. Pest Management Science .2000; 56(1):3-21.
14. Srivastava RK, Singh BK, Mani D. Effect of organic matter on adsorption and persistence of thiram fungicide in different soils. Asian Journal of Chemistry. 2013; 25(1):292-296.
15. Leiva JA, Nkedi-Kizza P, Morgan KT, Qureshi JA. Imidacloprid sorption kinetics, equilibria, and degradation in Sandy Soils of Florida. Journal of Agricultural and Food Chemistry 2015; 63:4915-4921.
16. Gebremariam SY, Beutel MW, Yonge DR, Flury M, Harsh JB. Adsorption and desorption of chlorpyrifos to soils and sediments. Revolution Environmental Contamination Toxicology. 2012; 215:123-75.
17. Horwood M. Rapid degradation of termiticides under field conditions. Australian Journal of Entomology. 2007; 46:75-78.
18. Chopra I, Chauhan R, Kumari B, Dahiya K. Fate of fipronil in cotton and soil under tropical climatic conditions. Bulletin of Environmental Contamination and Toxicology 2011; 86:242-245.
19. Saini S, Rani M, Kumari B. Persistence of fipronil and its metabolites in soil under field conditions. Environmental Monitoring Assessment. 2014; 186(1):69-75.

20. Mandal K, Singh B. Persistence of fipronil and its metabolites in sandy loam and clay loam soils under laboratory conditions. Chemosphere. 2013; 91:1596-1603.
21. Singh S, Parmar KD, Joshi MN, Shah PG. Downward movement of five synthetic pyrethroids in three different soils of Gujarat. Pesticide Research Journal. 2012; 24(1):76-81.
22. Sreekumar L, Shah PG. Downward movement of agrochemicals in clayey, sandy and sandy loam soils. Pesticide Research Journal. 2014; 26(2):169-174.
23. Rhone-Poulenc Ag Company. Application for registration. Department of Pesticide Regulation, California Environmental Protection Agency, Sacramento, CA. 52062-071. 1998, (1).
24. Leiva JA, Nkedi-Kizza P, Morgan KT, Qureshi JA. Imidacloprid sorption kinetics, equilibria, and degradation in sandy soils of Florida. Journal of Agricultural and Food Chemistry. 2015; 63:4915-4921.
25. Rao PSC, Nkedi-kizza P, Davidson JM, Ou LT. Retention and transformations of pesticides in relation to non-point source pollution from croplands. In Agricultural management and water quality, IA. Schaller FW and Baily GW (eds), 1983, 126-140.