Introduction:

Persistence of imidacloprid was studied under laboratory conditions in biotic and abiotic conditions on four types of soil, viz. sandy loam, clay, red and black soils, following treatment at 1.0, 2.0 and 4.0µg/g fortification levels. Imidacloprid degradation was more rapid in soil with cover crop than continual availability for uptake by roots (Mullins, et al. 1992b). Thus imidacloprid can persist in soil depending on soil type, *p*H, use of organic fertilizers and presence or absence of ground water. So a study planed to determination of the imidacloprid residue in soil in biotic and a biotic condition under the laboratory control conditions. The imidacloprid residue in the soil samples were measured by validated analytical method. The pesticides concentration and soil characteristics such as *p*H, temperature, moisture and cation exchange capacity are very important for degradation of imidacloprid in soil under laboratory condition. Hafez-HFH et al. 2003 reported that the persistence of diazinon and imidacloprid in soil under laboratory conditions. They also reported effect of soil microorganisms degradation of pesticides in silty loam soil. Pesticides degradation proceeded at a slower rate in sandy and sandy loam soil than that in silty loam soil. Soil microorganisms had a major role in the acceleration of pesticide degradation. At least two degradation products of diazinon and only one of imidacloprid were reported in non-sterilized soil. We studied and compared the degradation of imidacloprid in biotic and abiotic conditions under laboratory condition at 25 ± 2 °C.

MATERIALS AND METHOD

Soil Characterization

The soil characterization was performed to determine different physico-chemical properties viz., pH, organic carbon, water holding capacity (WHC) and clay content (particle size distribution) of soils collected from different parts of Gujarat India. The soil sampling was done following general sampling procedures and sampled soil was brought back to the laboratory in polyethylene bags. The soils were grounded in order to break the clods without any damage to the physical, chemical and biological characteristics. The soils were air dried and sieved through a 2 mm sieve. The detail of soil characterisation procedure is discussed in **chapter-2**

Soil Sterilisation

The collected soil sample was sterilized using autoclave at 121°C for 0.5 hour. The soil sample was removing from auto clave and dried in oven at 70 °C. This soil was used for persistence study of imidacloprid in abiotic condition.

Experimental setup for Biotic Degradation of Imidacloprid under Laboratory Condition

The experiments were carried out under laboratory conditions for residue and persistence study of imidacloprid in soil at 25 ± 2 °C. A quantity of 50g of each soil i.e. sandy loam, clay, red and black soil, was weighed and transferred into a beaker of 100 mL capacity and fortified at three levels, 1, 2 and 4 µg/g, with three replication by adding reference standard of imidacloprid, separately. During entire study period, the soil moisture was maintained at one third of water holding capacity by adding distilled water at regular intervals. The distilled water was added periodically and weight recorded to maintain the moisture for the soil at water holding capacity. The beaker was covered with polythene sheets with few holes and stored at 25 ± 2 °C. The periodic sample was drawn at intervals of 0, 1, 3, 15, 30, 45, 60, and 90 days after application. The samples were drawn for three replications of each treatment and along with control.

Experimental setup for Abiotic Degradation of Imidcloprid under Laboratory Conditions

The experiments were carried out under laboratory conditions for residue and persistence study of imidacloprid in soil at 25 ± 2 °C in abiotic conditions. The sterilised soils were used for abiotic studies. A quantity of 50g of each sterilised soil i.e. sandy loam, clay, red and black soil, was weighed and transferred into a beaker of 100 mL capacity and fortified at three levels 1, 2 and 4 µg/g with three replication by adding reference standard of imidacloprid, separately. During entire study period, the soil moisture was maintained at one third of water holding capacity by adding distilled water at regular intervals. The beaker was covered with polythene sheets with few holes and stored at 25 ± 2 °C in dark condition. The periodic samples were drawn at intervals of 0, 1, 3, 15, 30, 45, 60, and 90 days after application. The samples were drawn at

three replication of each treatment and along with control. The sample's extraction and cleanup procedure was same for biotic and abiotic condition samples analysis.

Extraction and Sample Clean-up

A quantity of 50g soil sample was weighed and transferred into 250 mL capacity of conical flask and 100 mL methanol was added into the same flask. The flask was placed onto orbital shaker for 30 minutes for 120 rpm. After shaking, the solution was filtered into round bottom flask of 500 mL capacity through Whatman filter paper No.1 containing a bed of anhydrous sodium sulphate. The residual cake was re-extracted twice with additional volume of 50 mL methanol. The methanol extracts were collected, pooled and concentrated to volume of 5 to 10 mL using vacuum evaporator at $\leq$ 40 °C. The concentrated extract was subjected to further clean up by column chromatography.

Clean-up by Column Chromatography

The chromatographic column [60 cm x 25 mm (OD]) was packed with 10g activated florisil with 2-3 cm layer of anhydrous sodium sulphate. The column was pre-conditioned with 25 mL of methanol and concentrated extract was loaded onto top of the column and eluted with 100 mL acetonitrile. Eluate was concentrated to dryness using rotary vacuum evaporator at $\leq$ 40 °C and residue re-dissolved in 5mL acetonitrile. The acetonitrile extract was transferred into volumetric flask 10 mL capacity through Whatman No. 1 filter paper and final volume was made upto the mark with acetonitrile. The quantitative determination of imidacloprid residue in soil was carried out using reversed phase HPLC method. The detailed instrument parameters and validation of imidacloprid in soil is described in **chapter-2**

Results and Discussion

Imidacloprid dissipation in biotic conditions in soil: The residue data of imidacloprid in four types of soil are depicted in **table 1a and 1b**. The residue data of imidacloprid in different soil is presented in figure **1 to 4**. The figure **1 to 4** shows that the residue concentration decreases with days after application. The initial deposits of imidacloprid varied from 0.81 – 0.87 µg g^{-1} in sandy loam soil, clay soil, black and red soil @ 1.0 µg g^{-1}. The initial deposits of imidacloprid varied from 1.69 – 1.74 µg g^{-1} and 3.39-3.45 µg g^{-1} in sandy loam soil, clay soil, black and red soil @ 2.0 and 4.0µg/g.

The % dissipation of imidacloprid in/on soil treated @ 1 μg g^{-1} was 30.59, 39.29, 39.08 and 39.51% after 15 days of application in sandy loam, clay, black and red soil respectively and the corresponding value @ 2 and 4 μg g^{-1} was 26.4, 38.95, 33.91, 37.85, % and 25.66, 35.88, 32.75% and 35.10 respectively. The dissipation data is depicted **table 2a and 2b.** The dissipation data of imidacloprid in different soil is presented in figure **5 to 8**. The figures **5 to 9** show that the degradation of imidacloprid increases with date after application. After 90 days application maximum degradation of imidacloprid in black soil was observed to be 82.76% @ 1 μg g^{-1}. The half life of imidacloprid in different soils followed first order kinetics with half life value varying from 39.10 – 50.10 days (**table 3 and figure 9)**. Similar half life values have been reported earlier (Sarkar-MA *et. al*. 2001) for imidacloprid. They observed dissipation of imidacloprid in soil DT50 values ranging from 28.7 to 47.8 days. The shortest half-lives (28.7 and 35.8 days) were observed in the lateritic soil for both liquid and powder formulations. The residue data was subjected to first order kinetics Log Ct = Log Co −kt/2.303, where Ct is concentration after a lapse of time 't', Co is apparent initial concentration and 'K' is the dissipation constant.

For our study, the half life calculation data is presented in table **5a to 5k.** The data i.e. log residue and time was subjected to simple linear regression analysis (Y = a − bx) and the value of K was calculated by the formula: k = b × 2.303. The value of half life was calculated from the value of k by the formula: $t_{1/2}$= 0.693/k. The dissipation of imidacloprid was found to be faster in black soil followed by sandy loam, clay and red soil with half life value of 50.10, 42.74 and 45.69, respectively. The half life value was found to depend on concentration of imidacloprid in soil (**figure 10)**. The faster dissipation in black soil could be attributed to higher *p*H (7.47) and high organic matter (0.86%) as compared to other soils, which might have induced greater microbial activity. Similar results have also been reported by Supernal Pal et. al (2006). They reported faster dissipation of pyrazosulfuron-ethyl under alkaline conditions followed by acidic and neutral. The bio efficacy of pyrazosulfuron-ethyl may be affected as it suffers faster degradation in alkaline soil. We also found that black soil has higher *p*H than other soils under study. The degradation of imidacloprid in black soil was found to be faster than in other soils.

Imidacloprid dissipation in abiotic conditions in soil: The half life of imidacloprid in different soils followed first order kinetics with half life values varying from 44.47 –

53.2 3@ 1.0 0μg g^{-1} in sandy loam soil. The higher half life was observed in sandy loam soil 71.89 days. The half life of imidacloprid was also dependent on the concentration. The caparison of half life of imidacloprid is depicted in table 4. The shortest half-lives, 48.65, 51.23 and 56.82 days, were observed in the black soil. The half life value was found to depend on concentration of imidacloprid in soil in abiotic conditions (**figure 11)**. We also found that black soil has higher *p*H than other soils. The degradation of imidacloprid in black soil is therefore faster than in other soils in abiotic conditions.

CONCLUSION

The effect of soil characteristics and dose on the dissipation of imidacloprid from different type of soil has been studied. The degradation of imidacloprid in soil depends upon organic carbon content, moisture and soil *p*H. The degradation of imidacloprid was found to be faster in black soil followed by sandy loam, clay and red soil, with half life values of 50.10, 42.74 and 45.69, respectively. Persistence was dependent on the concentration of imidacloprid. The degradation of imidacloprid in soil depends upon organic carbon content, moisture and soil *p*H. In general, the imidacloprid was found safe from environmental contamination point of view as their half-life value were less than 50 days in all other soils.

In abiotic conditions half life of imidacloprid was higher as compared to the biotic condition. Half life depends on concentration of dose level of imidacloprid. We found that higher value of half life in sandy loam soil in abiotic condition was due to sandy loam soil having more sand so moisture is not retained for longer time restricting microbial growth.

Table 1a Imidacloprid Residue in Soil at Different Days of Application in Soil

DAT	Imidacloprid Residue in Soil at Different Days of Application					
	Sandy loam soil			Clay soil		
	1.0µg g^{-1}	2.0µg g^{-1}	4.0µgg^{-1}	1.0µgg^{-1}	2.0µg g^{-1}	4.0µg g^{-1}
0	0.87	1.7	3.39	0.84	1.72	3.4
1	0.81	1.64	3.29	0.77	1.6	3.2
3	0.75	1.53	3.1	0.64	1.35	2.68
7	0.68	1.4	2.82	0.59	1.21	2.45
15	0.59	1.25	2.52	0.51	1.05	2.18
30	0.52	1.15	2.31	0.45	0.95	1.89
45	0.48	0.98	2.06	0.33	0.68	1.35
60	0.32	0.65	1.35	0.25	0.52	1.16
90	0.19	0.51	1.05	0.15	0.35	0.72

Table 1b Imidacloprid Residue in Soil at Different Days of Application in Soil

DAT	Imidacloprid Residue in Soil at Different Days of Application					
	Sandy loam soil			Clay soil		
	1.0µg g^{-1}	2.0µg g^{-1}	4.0µgg^{-1}	1.0µgg^{-1}	2.0µg g^{-1}	4.0µg g^{-1}
0	0.81	1.69	3.39	0.87	1.74	3.45
1	0.78	1.63	3.27	0.82	1.65	3.28
3	0.65	1.4	2.88	0.74	1.51	3.02
7	0.58	1.27	2.65	0.65	1.32	2.72
15	0.49	1.05	2.2	0.53	1.15	2.32
30	0.39	0.84	1.7	0.41	0.85	1.81
45	0.32	0.67	1.35	0.31	0.68	1.35
60	0.22	0.5	1.14	0.25	0.51	1.15
90	0.19	0.42	0.86	0.15	0.32	0.82

Table 2a Dissipation of Imidacloprid in Different Soils

DAT	Dissipation of Imidacloprid in Different Soils					
	Sandy loam soil			Clay soil		
	1.0µg g^{-1}	2.0µg g^{-1}	4.0µgg^{-1}	1.0µgg^{-1}	2.0µg g^{-1}	4.0µg g^{-1}
1	4.71	3.53	2..95	8.33	6.98	5.88
3	11.76	10	8.55	23.8	21.51	21.18
7	20	17.65	16.81	29.76	29.65	27.94
15	30.59	26.47	25.66	39.29	38.95	35.88
30	38.82	32.35	31.86	46.43	44.77	44.41
45	43.53	42.35	39.23	60.71	60.47	60.29
60	62.35	61.76	60.18	70.24	69.77	65.88
90	77.65	70	69.03	82.14	79.65	78.82

Table 2b Dissipation of Imidacloprid in Different Soils

DAT	Dissipation of Imidacloprid in Different Soils					
	Red soil			Black oil		
	1.0µg g^{-1}	2.0µg g^{-1}	4.0µg g^{-1}	1.0µg g^{-1}	2.0µg g^{-1}	4.0µg g^{-1}
1	3.7	3.55	3.54	5.75	5.17	4.93
3	19.75	17.16	15.04	14.94	13.22	12.46
7	28.4	24.85	21.83	25.29	24.14	28.16
15	39.51	37.85	35.1	39.08	33.91	32.75
30	51.85	50.3	49.85	52.87	51.15	47.54
45	60.49	60.36	60.18	64.37	60.92	60.87
60	72.84	70.41	66.3	71.26	70.69	66.67
90	76.54	75.15	74.63	82.76	81.71	79.13

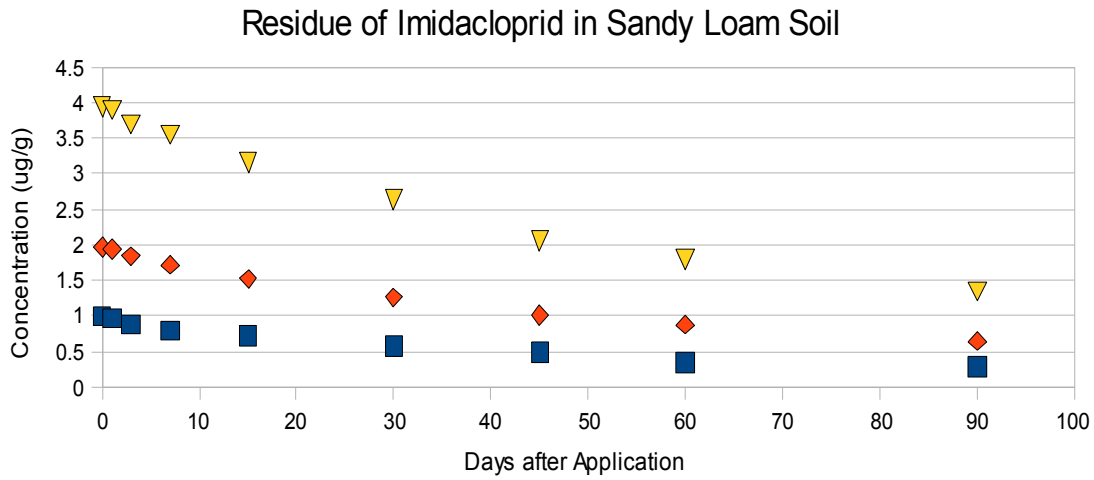
Table 3 Effect of Soil Characteristics and Dose on the Dissipation of Imidacloprid in Soil in Biotic conditions

Soil types	Half life –Value			Mean
	1.0µg g^{-1}	2.0µg g^{-1}	4.0µg g^{-1}	
Sandy loam soil	44.47	53.45	55.07	50.10
Clay soil	40.89	42.89	44.44	42.74
Red soil	44.77	45.60	46.70	45.69
Black oil	37.46	38.37	41.46	39.10
Mean	41.90	45.08	46.92	44.63

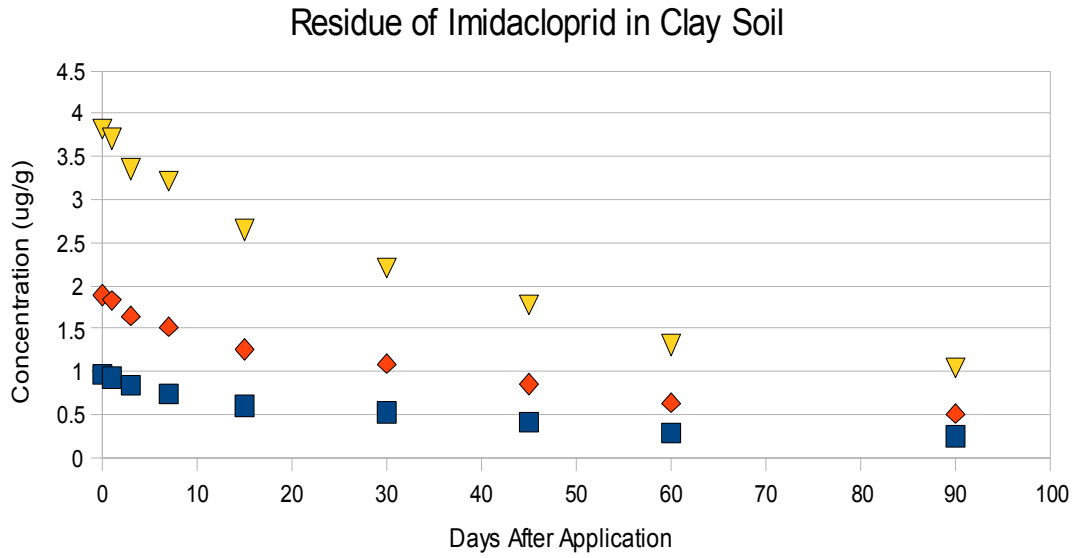
Table 4 Half Life Comparison of Imidacloprid in Soil in Biotic and abiotic Conditions

Soil Type	Biotic	Abiotic	Biotic	Abiotic	Biotic	Abiotic
	1.0 µg/g	**1.0 µg/g**	**2.0 µg/g**	**2.0 µg/g**	**4.0 µg/g**	**4.0 µg/g**
Sandy loam soil	44.47	55.23	53.45	65.12	55.07	71.89
Clay soil	40.89	52.16	42.89	54.75	44.44	68.35
Red soil	44.77	54.82	45.6	56.13	46.7	69.23
Black oil	37.46	48.65	38.37	51.23	41.46	56.82

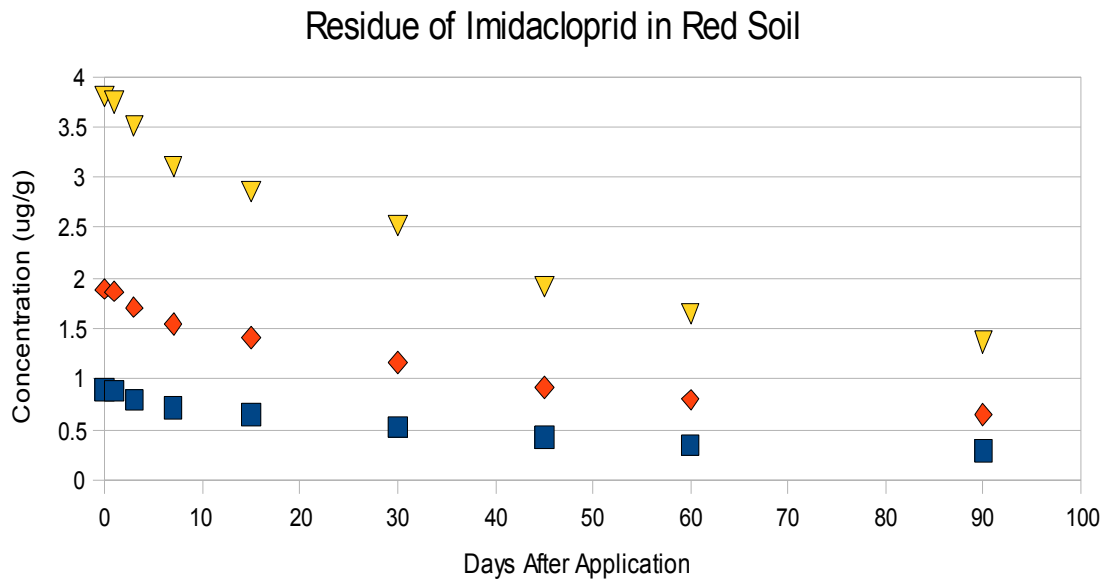
Figure 1 Residue of Imidacloprid on Sandy loam Soil



Figures 2 Residue of Imidacloprid on Clay Soil



Figures 3 Residue of Imidacloprid on Red soil



Figures 4 Residue of imidacloprid on Black soil

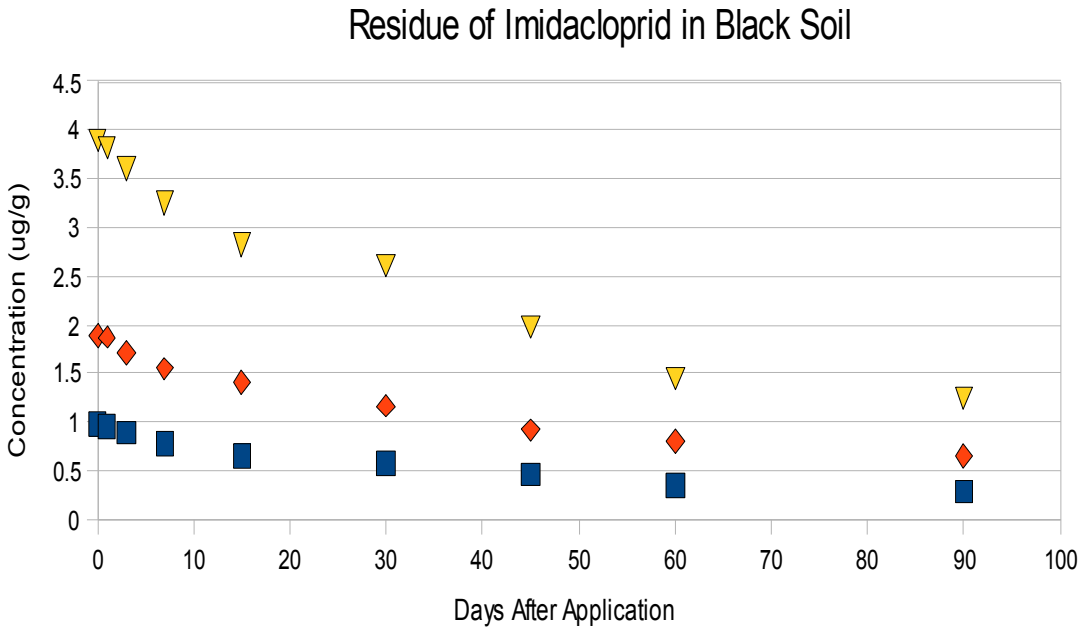


Figure 5 Residue of Imidacloprid on Sandy Loam Soil

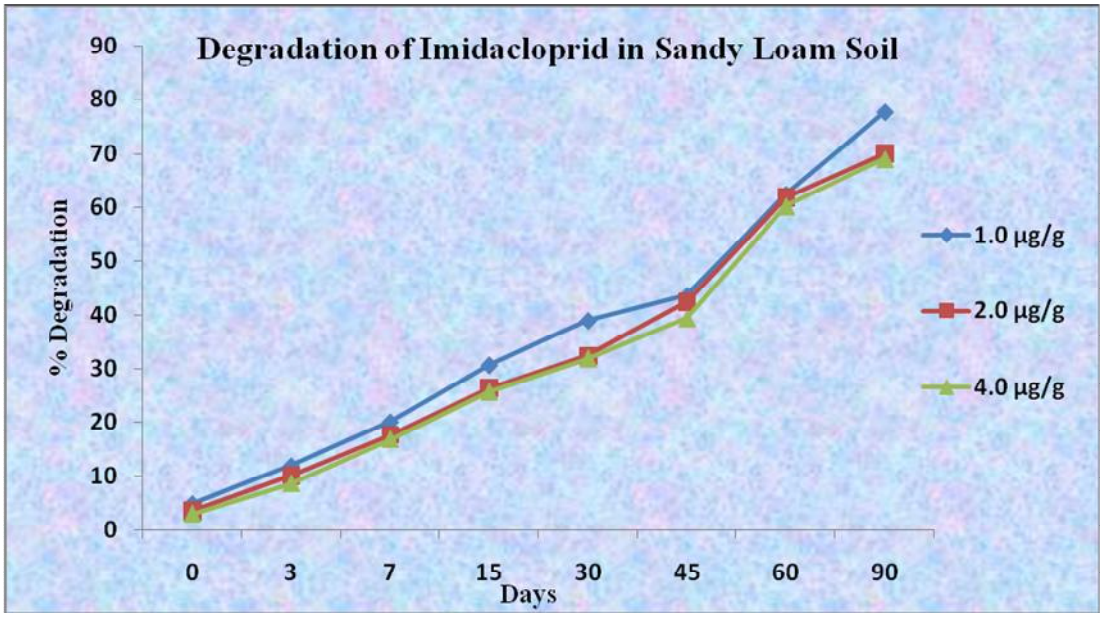


Figure 6 Residue of Imidacloprid on Black Soil Biotic Condition

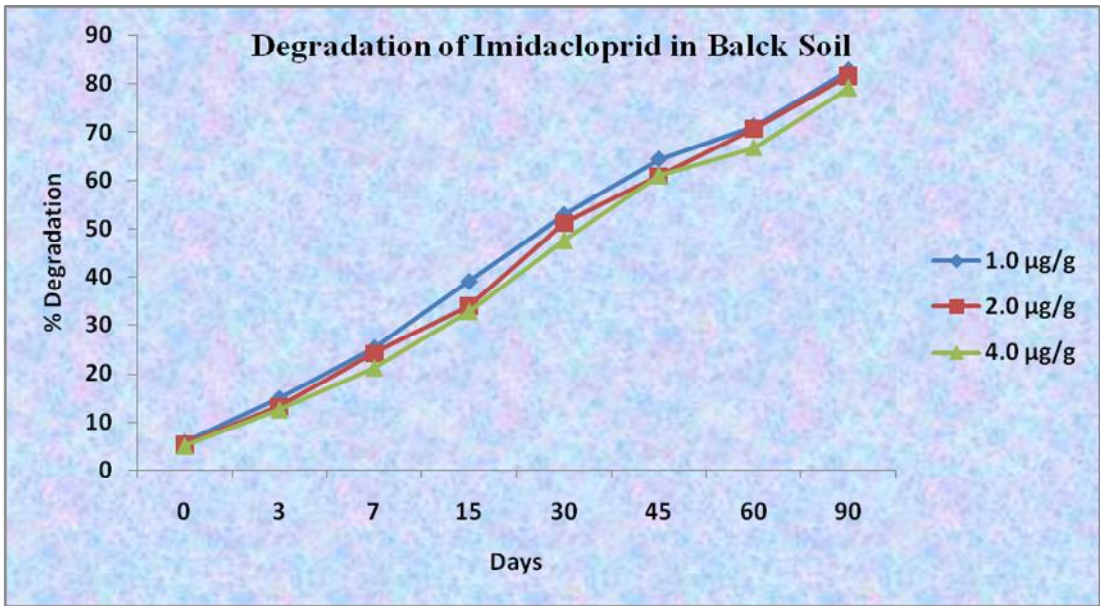


Figure 7 Residue of Imidacloprid on Red Soil Biotic Condition

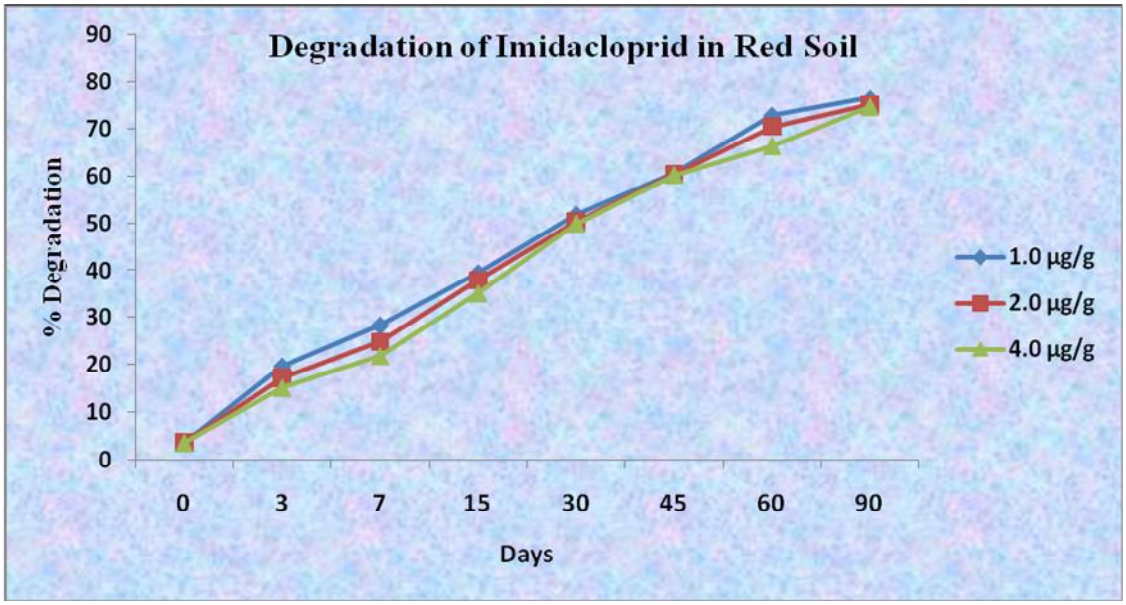


Figure 8 Residue of Imidacloprid on Clay Soil Biotic Condition

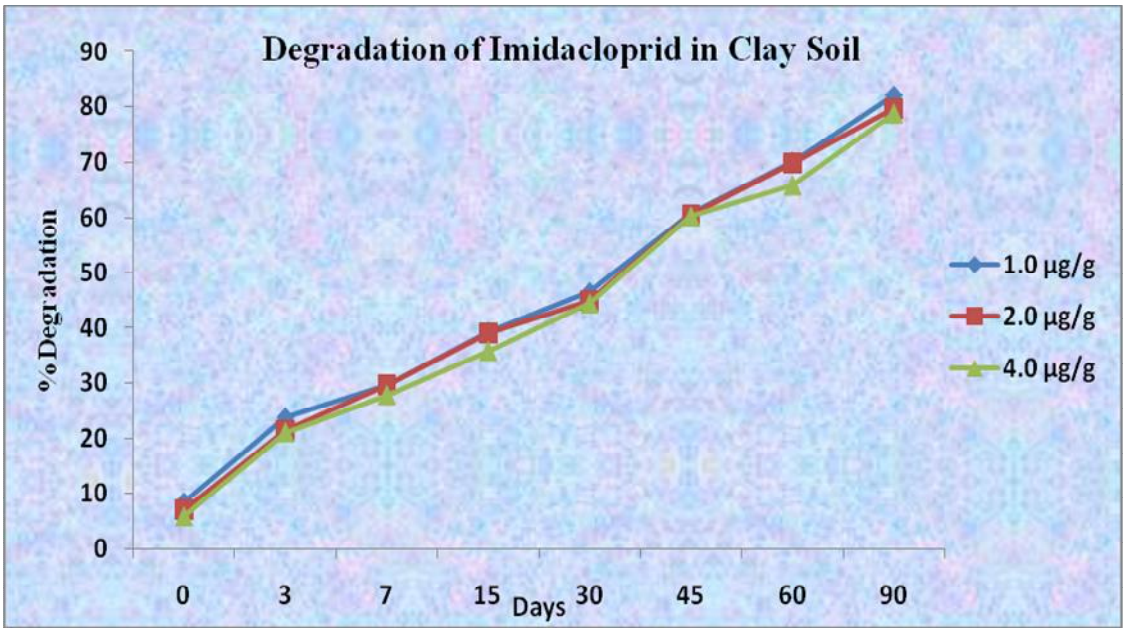


Figure 9 Half life of Imidacloprid on Soil in Biotic Condition

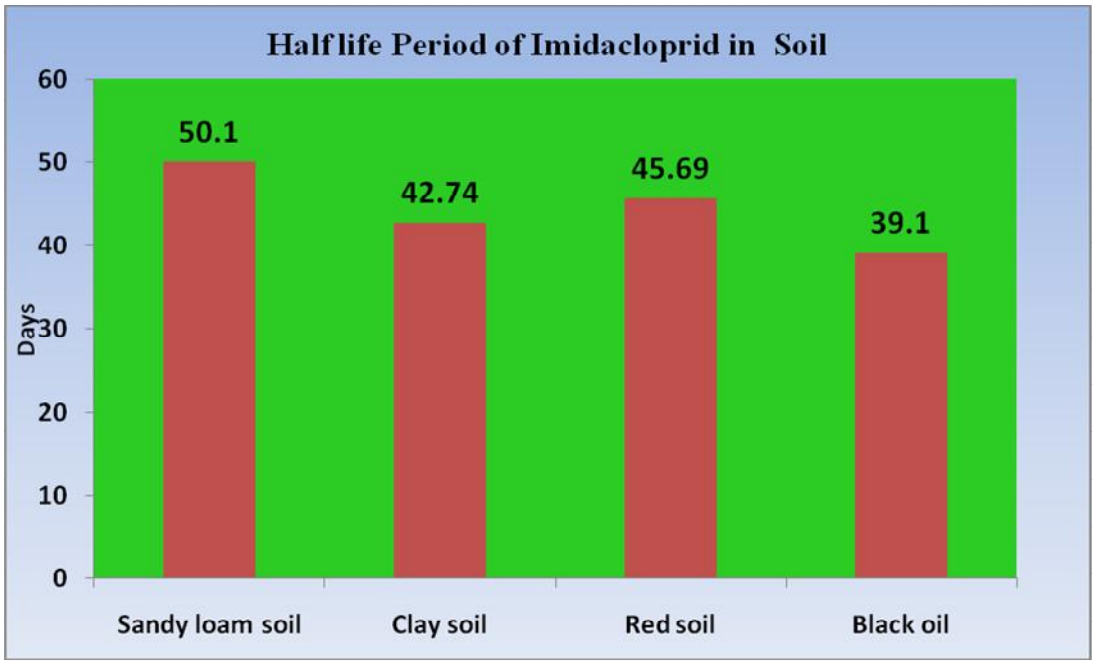


Figure 10 Half life of Imidacloprid in Soil at dose level in Biotic Condition

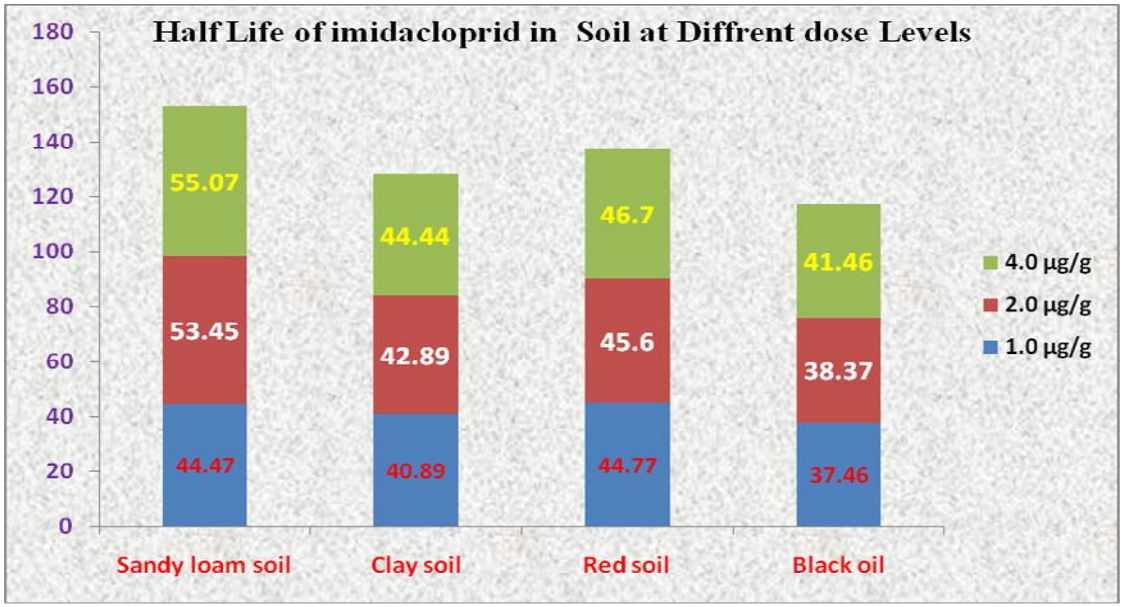


Figure 11 Half life of Comparison of imidacloprid in Biotic and Abiotic Condition in Soils

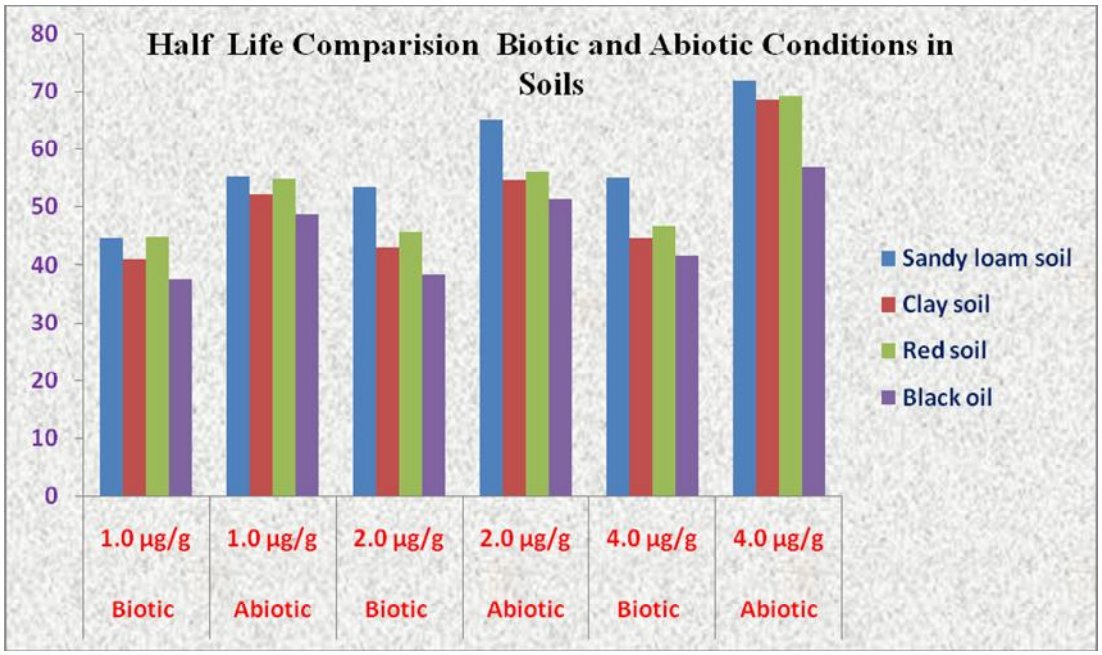


Table 5 a

Decay Time (Half Life and Waiting time Calculation

Test Substance – Imidacloprid Substrates – Sandy Loam Soil

Days (X)	Residues	Transformed RESIDUE (Y)
1	0.81	0.9085
3	0.75	0.8751
7	0.68	0.8325
15	0.59	0.7709
30	0.52	0.7160
45	0.48	0.6812
60	0.32	0.5051
90	0.18	0.2553

Mean of X (Days)	:	31.3750
Mean of Y (Transformed Residue)	:	0.6931
Correlation Coefficient (r)	:	-0.9844
Intercept (a)	:	0.9055
Slope (b)	:	-0.0068
DT 50 (Half Life)	:	44.4670 Days
Waiting Period	:	281.4690 Days

Table 5 b

Decay Time (Half Life and Waiting time Calculation

Test Substance – Imidacloprid Substrates –Sandy Loam Soil

Days (X)	Residues	Transformed Residues (Y)
1	1.64	1.2148
3	1.53	1.1847
7	1.40	1.1461
15	1.25	1.0969
30	1.15	1.0607
45	0.98	0.9912
60	0.65	0.8129
90	0.51	0.7076

Mean of X (Days)	:	31.3750
Mean of Y (Transformed Residue)	:	1.0269
Correlation Coefficient (r)	:	-0.9860
Intercept (a)	:	1.2036
Slope (b)	:	-0.0056
DT 50 (Half Life)	:	53.4465 Days
Waiting Period	:	391.2369 Days

Table 5 c

Decay Time (Half Life and Waiting time Calculation

Test Substance – Imidacloprid Substrates –Sandy Loam Soil

Days (X)	Residues	Transformed Residues (Y)
1	3.29	0.5172
3	3.10	0.4914
7	2.82	0.4502
15	2.52	0.4014
30	2.31	0.3636
45	2.06	0.3139
60	1.35	0.1303
90	1.05	0.0212

Mean of X (Days)	:	31.3750
Mean of Y (Transformed Residue)	:	1.3362
Correlation Coefficient (r)	:	-0.1599
Intercept (a)	:	1.5077
Slope (b)	:	-0.0055
DT 50 (Half Life)	:	55.0684 Days
Waiting Period	:	641.6685 Days

Table 5 d

Decay Time (Half Life) and Waiting time Calculation

Test Substance – Imidacloprid Substrates –Clay Soil

Days (X)	Residues	Transformed RESIDUE (Y)
1	0.77	0.8865
3	0.64	0.8062
7	0.59	0.7709
15	0.51	0.7076
30	0.45	0.6532
45	0.36	0.5563
60	0.25	0.3979

Mean of X (Days)	:	31.3750
Mean of Y (Transformed Residue)	:	0.6193
Correlation Coefficient (r)	:	-0.9917
intercept (a)	:	0.8503
Slope (b)	:	-0.0068
DT 50 (Half Life)	:	-0.0074
Waiting Period	:	251.3360 Days

Table 5 e

Decay Time (Half Life) and Waiting time Calculation

Test Substance – Imidacloprid Substrates –Clay Soil

Days (X)	Residues	Transformed RESIDUE (Y)
1	1.60	1.2041
3	1.35	1.1303
7	1.21	1.0828
15	1.05	1.0212
30	0.95	0.9777
45	0.68	0.8325
60	0.52	0.7160
90	0.35	0.5441

Mean of X (Days)	:	31.3750
Mean of Y (Transformed Residue)	:	0.9386
Correlation Coefficient (r)	:	−0.9910
Intercept (a)	:	1.1588
Slope (b)	:	−0.0070
DT 50 (Half Life)	:	**42.8859** Days
Waiting Period	:	307.5540 Days

Table 5 f

Decay Time (Half Life) and Waiting time Calculation

Test Substance – Imidacloprid Substrates –Clay Soil

Days (X)	Residues	Transformed RESIDUE (Y)
1	3.20	1.5051
3	2.68	1.4281
7	2.45	1.3892
15	2.18	1.3385
30	1.89	1.2765
45	1.35	1.1303
60	1.16	1.0645
90	0.72	0.8573

Mean of X (Days)	:	31.3750
Mean of Y (Transformed Residue)	:	1.2487
Correlation Coefficient (r)	:	-0.9924
Intercept (a)	:	1.4612
Slope (b)	:	-0.0068
DT 50 (Half Life)	:	**44.4427** Days
Waiting Period	:	363.3610 Days

Table 5 g

Decay Time (Half Life and Waiting time Calculation

Test Substance – Imidacloprid Substrates –red Soil

Days (X)	Residues	Transformed RESIDUE (Y)
1	0.78	0.8921
3	0.65	0.8129
7	0.55	0.7404
15	0.49	0.6902
30	0.39	0.5911
45	0.32	0.5051
60	0.22	0.3424

Mean of X (Days)	:	31.3750
Mean of Y (Transformed Residue)	:	0.6066
Correlation Coefficient (r)	:	-0.9718
Intercept (a)	:	0.8176
Slope (b)	:	-0.0067
DT 50 (Half Life)	:	**44.7670** Days
Waiting Period	:	270.3000 Days

Table 5 h

Decay Time (Half Life) and Waiting time Calculation

Test Substance – Imidacloprid Substrates – red Soil

Days (X)	Residues	Transformed Residues (Y)
1	1.63	1.2122
3	1.40	1.1461
7	1.27	1.1038
15	1.05	1.0212
30	0.84	0.9243
45	0.67	0.8261
60	0.50	0.6990
90	0.42	0.6232

Mean of X (Days) : 31.3750

Mean of Y (Transformed Residue) : 0.9445

Correlation Coefficient (r) : -0.9766

Intercept (a) : 1.1516

Slope (b) : -0.0066

DT 50 (Half Life) : **45.5961** Days

Waiting Period : 325.9000 Days

Table 5 i

Decay Time (Half Life) and Waiting time Calculation

Test Substance – Imidacloprid Substrates –red Soil

Days (X)	Residues	Transformed Residues (Y)
1	3.27	1.5145
3	2.88	1.4594
7	2.65	1.4232
15	2.20	1.3424
30	1.70	1.2304
45	1.35	1.1303
60	1.14	1.0569
90	0.86	0.9345

Mean of X (Days)	:	31.3750
Mean of Y (Transformed Residue)	:	1.2615
Correlation Coefficient (r)	:	-0.9824
Intercept (a)	:	1.4637
Slope (b)	:	-0.0064
DT 50 (Half Life)	:	**46.7000** Days
Waiting Period	:	382.2066 Days

Table 5 j

Decay Time (Half Life) and Waiting time Calculation

Test Substance – Imidacloprid Substrates –black soil

Days (X)	Residues	Transformed RESIDUE (Y)
1	0.82	0.9138
3	0.74	0.8692
7	0.65	0.8129
15	0.53	0.7243
30	0.41	0.6128
45	0.31	0.4914
60	0.25	0.3979
90	0.15	0.1761

Mean of X (Days)	:	31.3750
Mean of Y (Transformed Residue)	:	0.6248
Correlation Coefficient (r)	:	-0.9945
Intercept (a)	:	0.8770
Slope (b)	:	-0.0080
DT 50 (Half Life)	:	**37.4565** Days
Waiting Period	:	233.5457 Days

Table 5 k

Decay Time (Half Life) and Waiting time Calculation

Test Substance – Imidacloprid Substrates –black soil

Days (X)	Residues	Transformed Residues (Y)
1	1.65	1.2175
3	1.51	1.1790
7	1.32	1.1206
15	1.15	1.0607
30	085	0.9294
45	0.68	0.8325
60	0.51	0.7076

Mean of X (Days)	:	31.3750
Mean of Y (Transformed Residue)	:	0.9440
Correlation Coefficient (r)	:	-0.9966
Intercept (a)	:	1.1902
Slope (b)	:	-0.0078
DT 50 (Half Life)	:	**38.3700** Days
Waiting Period	:	279.1682 Days

References

Hafez-HFH,Thiemann-WHP, Capri-E Padovani-L and Trevisan-M., (2003), Persistence and biodegradation of diazinon and imidacloprid in soil.Chemistry,-Piacenza,-Italy, 35, (42); 26-30.

Sarkar-MA; Sankhajit-Roy; Kole-RK; Ashim-Chowdhury; Roy-S; Chowdhury-(2001), A Persistence and metabolism of imidacloprid in different soils of West Bengal. Pest-Management-Science., 57, (7) 598-602.

Suparna Pal, Surajit Dutta, Pramanik S K, Manojit Ghosh and Anjan Bhattacharyya, (2006), Effect of pH on dissipation of pyrazosulfuron-ethyl in water, Pesticide Research Journal. 18, (1), 98-100.

Mullion J.A.,R.F. Carsel, J.G. Scarbrugh and A.M. Ivery. (1993), A model for predicting fat in the crop root zone and unsaturated soil zone, user,s manual for release 2.0 EPA/600/R-046, USEPA Athens GA.