

Effect of Adsorption on Degradation of the Pesticide Aldicarb in the Soil

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Abstract – Chemical and microbial degradation of the pesticide aldicarb has been studied extensively in both laboratory and field. These studies exhibit that temperature and porosity are important factors affecting the degradation of aldicarb and its daughter product sulfoxide in the soil. Since microbial activity decreases with depth, chemical processes are important component of the degradation of the aldicarb. The rate of degradation is faster in the liquid state than the sorbed state. Sorption reduces the bioavailability of the chemical and is inversely related to porosity. Hence, rate of degradation of the aldicarb and the daughter product sulfoxide is inversely related to the porosity. **Copyright** © 2013 Praise Worthy Prize S.r.l. - All rights reserved.

Keywords: Aldicarb, Adsorption, Finite Element Method, Soil

I. Introduction

Sorption of pesticides in soil or other porous media is recognized to be an important process regulating pesticide transport and degradation in the environment [1], [2], [3]. The negative correlation between sorption and mobility has been well established [4], [5], [6], [7], [8]. However, the effect of sorption on degradation is much more complicated and depends on many factors related to microbial, soil, and environmental conditions and on the properties of the chemical of interest [9], [10], [11]. Completely opposite impacts have been observed for chemicals with different degradation routes and mechanisms.

Armstrong and Chesters [12] reported that degradation of atrazine was accelerated by adsorption to clay minerals, while Ogram et al. [13] found degradation of 2, 4-D was inhibited by adsorption.

In general, sorption is often considered a process that limits pesticide degradation [14], [15], [16], [17]. This can be understood on the basis of the reduced bioavailability of sorbed compounds to soil microorganisms. However, in the field, sorption might increase degradation as a whole by increasing the residence time of pesticides in the root zone where most microbial activity occurs [18].

The relationship between adsorption and degradation of chemicals obviously is a fundamental one underlying the environmental behavior of pesticides and other chemical contaminants.

Aldicarb is a commercial pesticide, used on a variety of crops, including cotton, fruits, potatoes, and beans.

This raises the possibility that general population may be exposed to aldicarb through the ingestion of contaminated water and foods.

This paper deals with the degradation kinetics of aldicarb and its toxic by-products, investigating both the degradation time-scale as well as the spatial concentration distribution of toxic components.

The effect of adsorption on degradation of the pesticide aldicarb has been quantitatively evaluated. In the study, the concentration of pesticide aldicarb was tracked with time over duration of 5 days. The concentration v/s time graphs have been reported for 3 different points in the soil sample which can be represented in 2D as shown in Fig. 1(a). The experiment was conducted for three soil samples having different porosity.

The water in the ring contained a chemical aldicarb, which migrates with the water into the soil at a constant concentration. Aldicarb, c_1 , transforms to a daughter product sulfone, c_2 , and sulfone transforms to sulfoxide, c_3 . In the soil, the chemicals degrade from microbial activity and also sorb onto soil particles. Aldicarb and sulfoxide volatilize to the atmosphere.

The sorption, biodegradation, and volatilization proceed in linear proportion to the aqueous concentrations c_1 , c_2 , and c_3 .

The soil was initially pristine with zero concentration of any chemicals. At the ground surface outside the ring, there is volatilization to the atmosphere for c_1 and c_3 .

TABLE I
POROSITY OF THE SOIL SAMPLES

SAMPLE NO.	SOIL LAYER	POROSITY
1.	UPPER LAYER	0.399
	LOWER LAYER	0.339
2.	UPPER LAYER	0.420
	LOWER LAYER	0.360
3.	UPPER LAYER	0.700
	LOWER LAYER	0.600

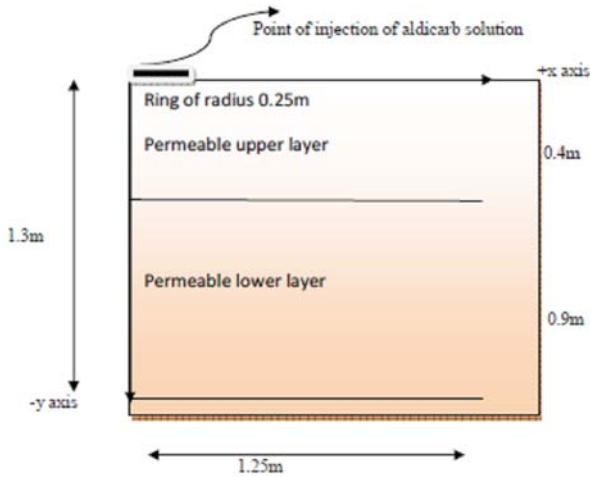


Fig. 1(a). Geometry of infiltration ring and the soil column

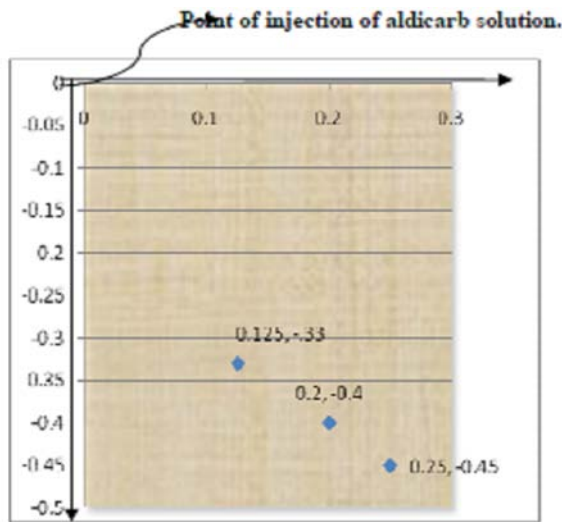


Fig. 1(b). The points under study shown: r co-ordinate along horizontal direction and z co-ordinate along vertical direction

The vertical axis is a line of symmetry. The other boundaries are posed such that the solutes can freely leave the soil column with the fluid flux.

The flow of the aldicarb solution from the ring into the soil sample and the subsequent degradation reaction chain was modeled using the software *Comsol Multiphysics* which works on the principle of Finite Element Method (FEM). The models were created using the input values of dispersivity, decay rate to daughters, biodegradation rate, tortuosity, hydraulic conductivity etc. The porosity of the soil samples was changed keeping all the other parameters listed in Table III constant and its effect on the rate of flow of chemicals and their degradation studied.

II. Aldicarb: Degradation Pathway

There are two degradation pathways for aldicarb. One degradation mechanism is oxidation; in which aldicarb is oxidized to aldicarb sulfoxide which in turn is oxidized to aldicarb sulfone. The other is hydrolysis, in which all the three carbamate compounds are concurrently

degraded to low toxicity (non-carbamate) compounds via the corresponding oximes and nitriles [19]. Although reduction of aldicarb sulfoxide (but not aldicarb sulfone to sulfoxide) back to aldicarb has been demonstrated under anaerobic laboratory conditions [20], [21], field data consistently show that neither sulfoxide nor sulfone is reduced back to its parent compound in the saturated or unsaturated zone. The degradation of aldicarb to sulfoxide and sulfone, primarily the result of microbial action, is relatively a fast process.

III. Reaction Chain Equations

The governing equation for solute transport in the chain reaction model describes advection and dispersion of a sorbing, volatilizing, and decaying solute in variably saturated soil [22]:

$$\frac{\partial}{\partial t}(\theta c) + \frac{\partial}{\partial t}(\rho_b c_p) + \frac{\partial}{\partial t}(a_v c_G) = \nabla \cdot [-\theta D_{LG} \nabla c + u c] = R_L + S_C \quad (1)$$

In this equation, θ is the liquid volume fraction ($\text{m}^3 \text{m}^{-3}$); c gives the dissolved concentration (kg/m^3); a_v equals the air volume fraction ($\text{m}^3 \text{m}^{-3}$); c_G is the solute concentration in air (kg/m^3); D_{LG} denotes the combination of hydrodynamic dispersion tensor for water and diffusion in air (m^2/d); u represents the Darcy velocity (m/d); R_L denotes reactions in water ($\text{kg} \text{m}^{-3} \text{d}^{-1}$); and S_C is the quantity of solute added per unit volume of porous medium per unit time ($\text{kg} \text{m}^{-3} \text{d}^{-1}$).

In this study, the gas-phase concentration, c_G , is a linear function of the liquid-phase concentration, c , related through an empirical constant k_G where $k_G = \partial c_G / \partial c$.

The linear partition coefficient k_p (m^3/kg) gives the solid-phase concentration, c_p , by multiplication with the liquid-phase concentration, c , such that $k_p = \partial c_p / \partial c$. The air volume, a_v , varies with the liquid volume fraction as $a_v = \theta_s - \theta$.

Because $c_p = k_p c$ and $c_G = k_G c$, and the pore space θ_s and bulk density ρ_b do not change, the time derivatives in the solute-transport equation can be expanded to:

$$\frac{\partial}{\partial t}(\theta c) + \frac{\partial}{\partial t}(\rho_b k_p c) + \frac{\partial}{\partial t}(a_v k_G c) = \theta \frac{\partial c}{\partial t} + \rho_b k_p \frac{\partial c}{\partial t} + a_v k_G \frac{\partial c}{\partial t} + (1 - k_G) c \frac{\partial \theta}{\partial t} \quad (2)$$

Inserting this expansion in the solute-transport equation results in:

$$\left[\theta + \rho_b k_p + a_v k_G \right] \frac{\partial c}{\partial t} + \left[(1 - k_G) c \frac{\partial \theta}{\partial t} \right] + \nabla \cdot [-\theta D_{LG} \nabla c + u c] = R_L + R_p + S_C \quad (3)$$

In Eq. (3), the first bracketed term explains the change in solute mass per volume per time for the liquid-, solid-, and air-phase concentrations. The second term explains the changes in storage because the water content in the soil varies in time.

The third bracketed expression represents the overall solute flux due to liquid dispersion, diffusion (liquid and air), and advection with moving water. The right side explains reactions and generalized sources.

Solute spreading now includes mechanical dispersion in water plus molecular diffusion for water and air. These three processes appear in the liquid-gas dispersion tensor, whose entries are:

$$\left. \begin{aligned} \theta D_{LGii} &= \alpha_1 \frac{u_i^2}{|u|} + \alpha_2 \frac{u_j^2}{|u|} + \theta D_m \tau_L + \alpha v D_G k_G \tau_G \\ \theta D_{LGij} &= \theta D_{LGji} = (\alpha_1 - \alpha_2) \frac{u_i u_j}{|u|} \end{aligned} \right\} \quad (4)$$

In equation (4), D_{LGii} are the principal components of the liquid-gas dispersion tensor; D_{LGji} and D_{LGij} are the cross terms; α is the dispersivity (m) where the subscripts 1 and 2 denote longitudinal and transverse flow, respectively. D_m and D_G (m^2/d) are molecular diffusion, while τ_L and τ_G give the tortuosity factors for liquid (water) and gas (air), respectively.

The three solutes—aldicarb, c_1 (parent); sulfoxide, c_2 (tracked daughter of c_1); and sulfone, c_3 (tracked daughter of c_2)—have different decay terms, R_{Li} , partition coefficients, k_{pi} , and volatilization constants, k_{Gi} . All of the solutes attach to soil particles. Two of the solutes volatilize; sulfone does not. The decay chain for each solute is:

$$\left. \begin{aligned} \sum R_{L,1} &= -\theta c_1 (\phi_{L,1} + \phi'_{L,1 \rightarrow 2}) \\ \sum R_{L,2} &= \theta c_1 \phi'_{L,1 \rightarrow 2} - \theta c_2 (\phi_{L,2} + \phi'_{L,2 \rightarrow 3}) \\ \sum R_{L,3} &= \theta c_2 \phi'_{L,2 \rightarrow 3} - \theta c_3 (\phi_{L,3} + \phi'_{L,3 \rightarrow N}) \end{aligned} \right\} \quad (5)$$

where ϕ represents a decay or biodegradation rate (d^{-1}); ϕ' denotes decay to a tracked species (d^{-1}); and arrows indicate which species are involved in a tracked decay-production term. Production is positive; decay is negative. For example, c_1 biodegrades at a rate of $\phi_{L,1}$ and also produces c_2 at a rate of $\phi'_{L,1}$. Being multiplied by $-\theta c_1$ denotes that decay reduces concentrations. Given that the decay of c_1 produces c_2 , the term $\theta c_1 \phi'_{L,1 \rightarrow 2}$ appears as a source (positive) for c_2 .

Even with no fluid moving across the surface; outside the ring volatilization to the atmosphere reduces concentrations. This condition can be described as:

$$-n \cdot (-\theta D_{LG} \nabla c) = -\frac{D_{mG}}{d} k_G (c - c_{atm}) \partial \Omega \text{ Surface} \quad (6)$$

where d is the thickness of a stagnant boundary layer at the soil surface and c_{atm} is the concentration of the solute in the atmosphere.

The only contaminant source is the dissolved aldicarb in the ring. No fluid moves through the side walls or base. Chemical transport is symmetric about the line $r = 0$.

The boundaries are defined as:

$$\left. \begin{aligned} c &= c_1 & \partial \Omega \text{ Ring} \\ n \cdot [-\theta D_L \nabla c] &= 0 & \partial \Omega \text{ Surface} \\ n \cdot [-\theta D_L \nabla c u_c] &= 0 & \partial \Omega \text{ Axis symmetry} \\ n \cdot [-\theta D_L \nabla c] &= 0 & \partial \Omega \text{ Sides} \\ n \cdot [-\theta D_L \nabla c] &= 0 & \partial \Omega \text{ Base} \end{aligned} \right\} \quad (7)$$

(where n is the unit normal to the boundary. Initial concentrations are zero everywhere)

TABLE II
DATA FOR THE CHEMICALS ALDICARB AND THE DAUGHTER PRODUCTS OF ALDICARB DEGRADATION, NAMELY SULFOXIDE AND SULFONE

VARIABLE	UNIT	DESCRIPTION	ALDICARB	SULFONE	SULFOXIDE
ρ_b	kg/m ³	Bulk density	1300	1300	1300
D_m	m ² /d	Molecular diffusion (liquid)	0.00374	0.00374	0.00374
D_G	m ² /d	Molecular diffusion (gas)	0.432	0.432	0.432
α_l	m	Longitudinal dispersivity (liquid)	0.005	0.005	0.005
α_2	m	Transverse dispersivity (liquid)	0.0001	0.0001	0.0001
k_p	m ³ /kg	Partition coefficient (solid)	0.0001	0.00005	0.0002
τ_L	-	Tortuosity factor (liquid)	$\theta^{7/3} \theta_s^{-2}$		
τ_G	-	Tortuosity factor (gas)	$(1-\theta)^{7/3} \theta_s^{-2}$		
k_G	-	Volatilization coefficient (gas)	1.33×10^{-7}	0	0.00133
ϕ'_{Li}	d ⁻¹	Decay rate to daughters (liquid)	0.36	0.024	0.0024
ϕ_{Li}	d ⁻¹	Biodegradation rate (liquid)	.2	.01	.05
d	m	Boundary layer thickness (gas)	.005	.005	.005
c_{si}	kg/m ³	Concentration in ring	1.0	0	0
c_{oi}	kg/m ³	Initial concentration in soil	0	0	0

TABLE III
THE MATERIAL PROPERTIES USED FOR THE MODELING
OF THE FLUID FLOW

VARIABLE	UNITS	DESCRIPTION	UPPER LAYER	LOWER LAYER
K_s	m/d	Saturated hydraulic conductivity	0.298	0.454
θ_s	-	Porosity/void fraction	0.399/0.420	0.339/0.360
θ_r	-	Residual saturation	0.0001	0.0001
K_s	m/d	Saturated hydraulic conductivity	0.298	0.454
α	m^{-1}	alpha parameter	1.74	1.39
n	-	n parameter	1.38	1.60
m	-	m parameter	1-1/n	1-1/n
l	-	Pore connectivity parameter	0.5	0.5
m	-	m parameter	1-1/n	1-1/n
l	-	Pore connectivity parameter	0.5	0.5

IV. Result and Discussions

The points (in cylindrical co-ordinates with $r = 0$ at source point of aldicarb) in soil sample under study are Fig. 1(b).

TABLE IV
POINTS IN THE SOIL SAMPLE WHERE CONCENTRATION
HAS BEEN MEASURED

S.NO.	POINT (r, z)
1.	(0.125,-0.330)
2.	(0.200,-0.400)
3.	(0.250,-0.450)

The porosity of the soil is 0.399 for upper layer and 0.339 for lower layer of the sample. The models have been shown in Figs. 2(a)-(e). From Fig. 3, it can be observed that rate of aldicarb sorption in the soil sample is initially high up to 1 day and then it tends to decrease. Further there is no appreciable change in aldicarb concentration; it attains saturation concentration of $\sim 0.73 \text{ kg/m}^3$ in 48 hours. Also the concentration remains zero for approximately 12 hours after the start.

As the second point (0.200,-0.400) lies further away from the source of aldicarb, it is seen that aldicarb concentration is zero up to approximately 18 hours (Fig. 4). The sorption of aldicarb is high due to low porosity of the soil and as such the aldicarb solution doesn't reach the point even up to 18 hours. Also, the rate of increase of aldicarb concentration decreases very sharply after 2 days, and the concentration assumes a constant value of $\sim 0.62 \text{ kg/m}^3$ after 72 hours. The third point (0.250,-0.450) lies further away from the source of aldicarb and it is observed that aldicarb concentration is zero up to approximately 24 hours (Fig. 5).

Also, the rate of increase of aldicarb concentration decreases after 48 hours, and assumes a constant value of $\sim 0.54 \text{ kg/m}^3$ after 96 hours. As the flow of the aldicarb solution takes place from the ring into the soil, the processes of adsorption, absorption and advection occur

simultaneously. These processes, especially adsorption, are responsible for gradual decrease in the aldicarb concentration as we move down the soil sample. The process of sorption reduces the aldicarb concentration in solution which moves down the soil sample through pores [18].

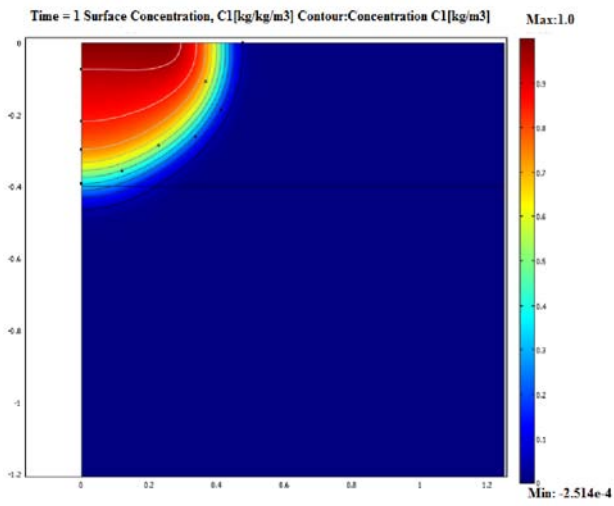
The porosity of the soil is 0.420 for upper layer and 0.360 for lower layer of the sample for the following figures showing variation of aldicarb concentration (kg/m^3) with time (day). The points of the sample under study are same as before. The nature of the graph remains the same, the only difference being in the saturation value attained in all the three cases (Figs. 6, 7 and 8). For the first point (0.125,-0.330) the saturation concentration is $\sim 0.72 \text{ kg/m}^3$ which is same as before indicating that porosity does not affect much the flow of aldicarb solution from the ring up to small depth in the soil sample.

For the points (0.200,-0.400) and (0.250,-0.450) the saturation concentration was found to be $\sim 0.57 \text{ kg/m}^3$ and $\sim 0.49 \text{ kg/m}^3$ respectively. The increased porosity helps flow of the aldicarb solution through the soil sample and thereby decreasing the time available for sorption of the chemical on the soil particles. As such lower saturation concentration is observed at the two points.

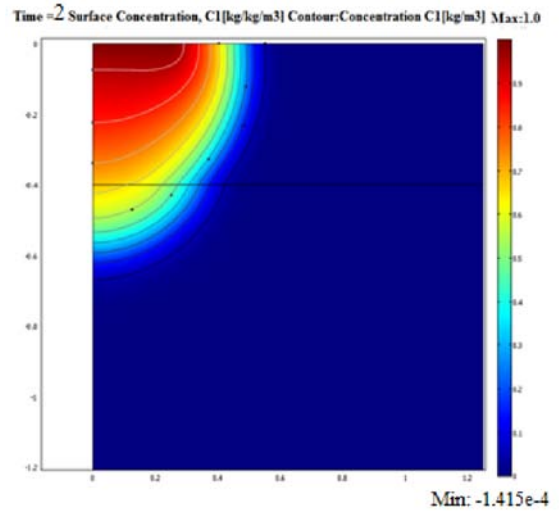
Similar trend was found for the clayey soil sample with porosity 0.700 for the upper layer and 0.600 for the lower layer for the first two points (0.125,-0.330) and (0.200,-0.400) under study while for the third point (0.250,-0.450) anomalous behavior was observed (Figs. 9, 10, 11). The saturation concentration of aldicarb for point (0.125,-0.330) was 0.58 kg/m^3 . For the other two points, the graph line shows continuous increase even at the end of 5 days. Also, for point (0.250,-0.450) the rate of increase of aldicarb concentration is initially low and picks up day 1 onwards only. The concentration remains zero for appreciable time (18 hours as compared to 12 hours for the first two samples) even in case of the point closest to the source.

The high porosity of clayey soil which is approximately twice of that of the first soil sample provides easy passage to the aldicarb solution and as such the retention of aldicarb due to adsorption or absorption doesn't occur initially. As we see in the Figs. 3-11, with increase in the porosity of the two layers of the soil sample the saturation concentration of aldicarb decreases. This can be explained by the fact that increased porosity of the soil permits more amount of aldicarb solution to pass through and also at a greater pace. As such the sorption of aldicarb on soil particles and hence the saturation concentration decreases [18].

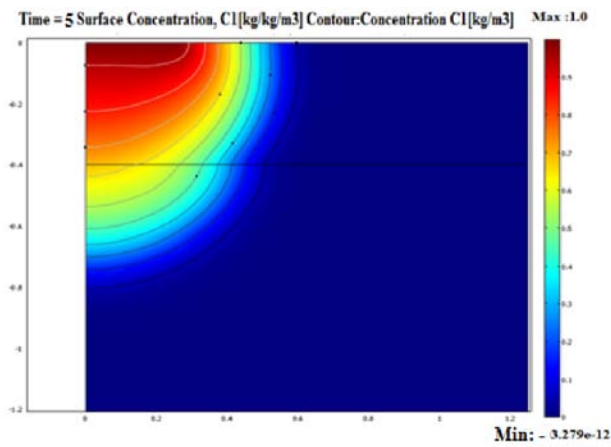
The rate of increase of aldicarb concentration tends to decrease with time. This can be attributed to decrease in number of free sites for adsorption to occur. As the process of sorption proceeds (adsorption is the main contributor in overall sorption) the adsorbing sites on the soil continue being occupied with the chemical until a saturation limit for soil sample is reached when all the adsorbing sites are occupied.



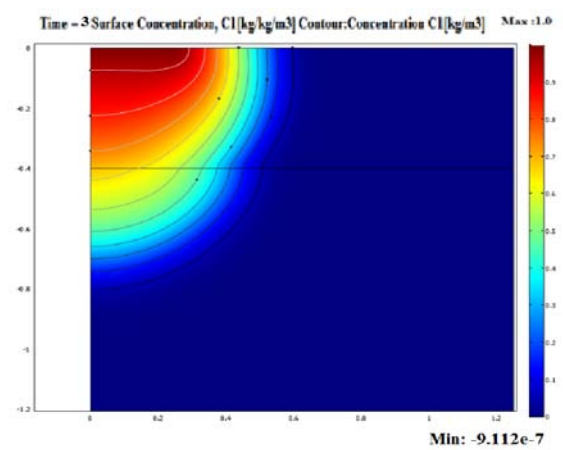
(a) Day



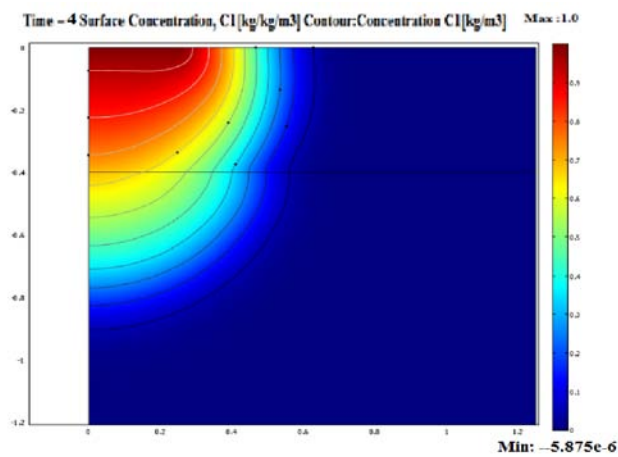
(b) Day 2



(c) Day 3



(d) Day 4



(e) Day 5

Figs. 2. Models showing flow of aldicarb in the soil sample with different porosity

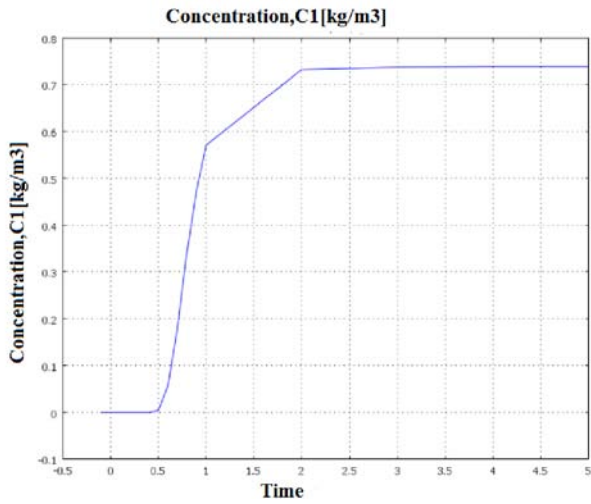


Fig. 3. Aldicarb concentration v/s time graph at point (0.125,-0.330)

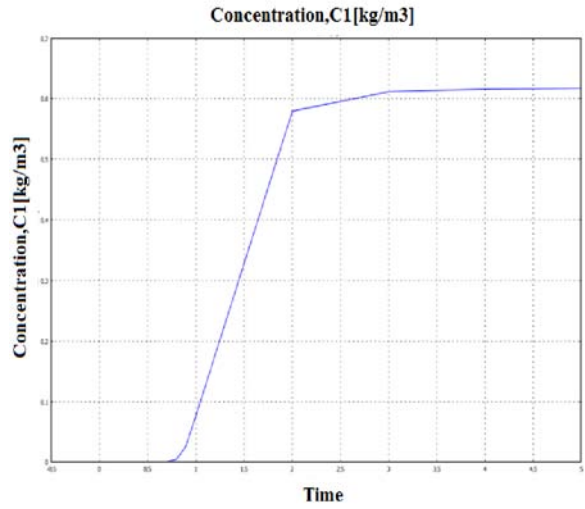


Fig. 4. Aldicarb concentration v/s time graph at point (0.200,-0.400)

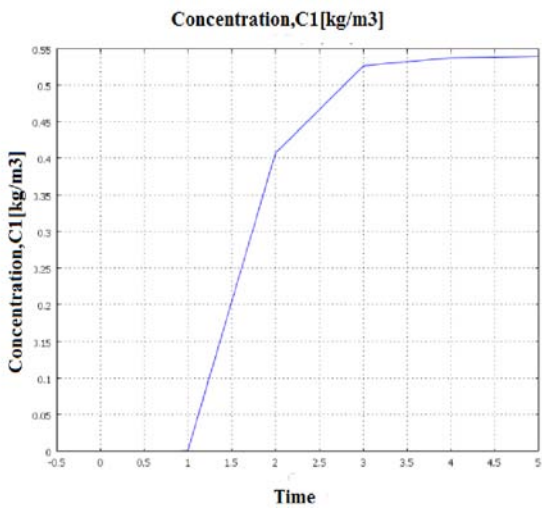


Fig. 5. Aldicarb concentration v/s time graph at point (0.250,-0.450)

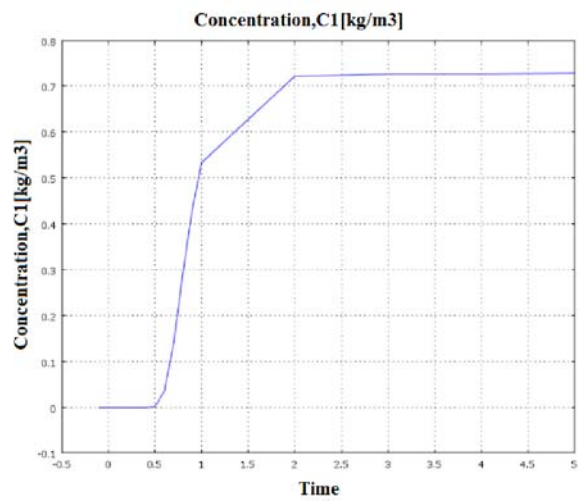


Fig. 6. Aldicarb concentration v/s time graph at point (0.125,-0.330)

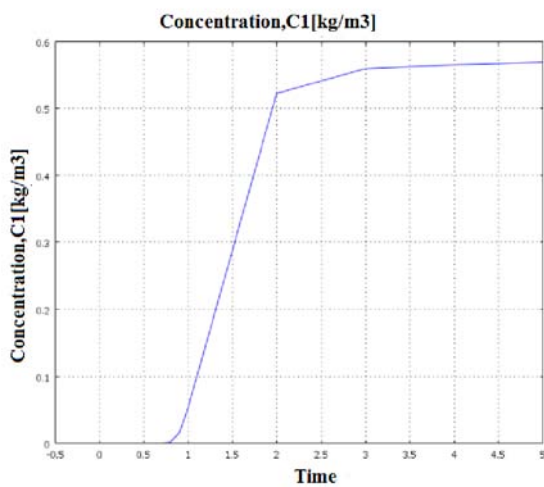


Fig. 7. Aldicarb concentration v/s time graph at point (0.200,-0.400)

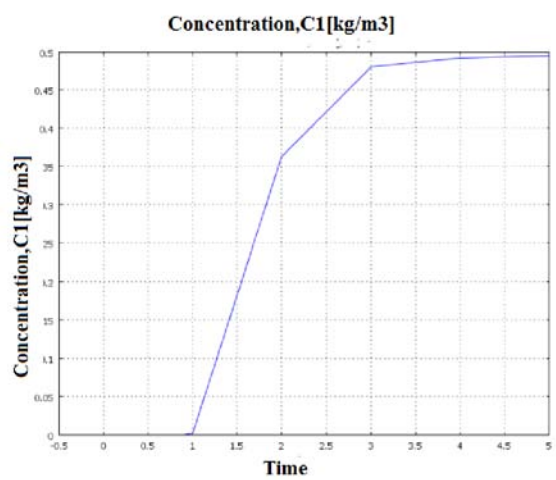


Fig. 8. Aldicarb concentration v/s time graph at point (0.250,-0.450)

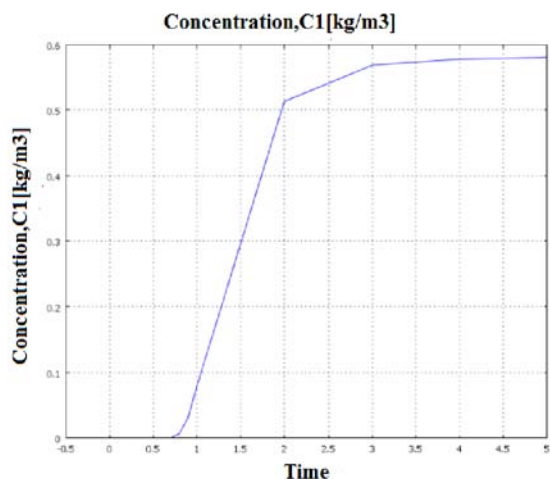


Fig. 9. Aldicarb concentration v/s time graph at point (0.125,-0.33)

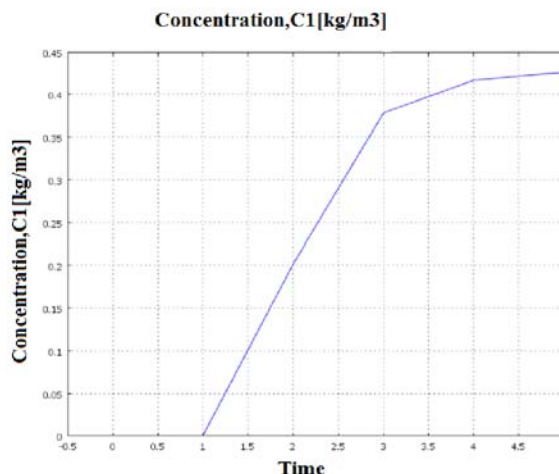


Fig. 10. Aldicarb concentration v/s time graph at point (0.200,-0.400)

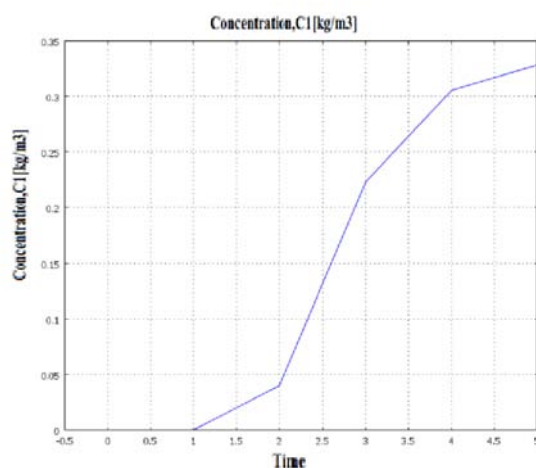


Fig. 11. Aldicarb concentration v/s time graph at point (0.250,-0.450)

Further, sorption occurs through absorption which is not a significant contributor.

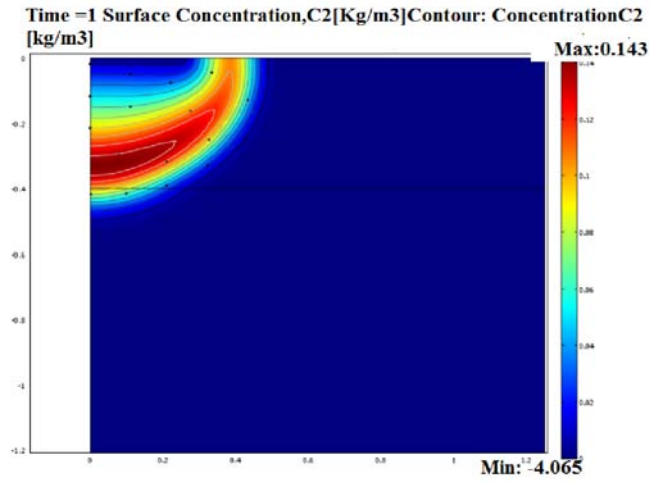
The concentration of the sulfoxide, the product of aldicarb degradation, was traced with time for the soil sample with porosity 0.399 for the upper layer and 0.339 for the lower layer (Figs. 12(a)-(e)). As the concentration of aldicarb decreased for points further away from the source point, the final concentration of sulfoxide at end of 120 hours was found to be maximum for the point farthest from the source point.

This illustrates the inverse relation between the degradation of aldicarb and its adsorption in the soil media. The degradation of aldicarb is faster in the liquid medium than in the sorbed state. The figure for sulfoxide concentration v/s time at the three points under study have been shown below (Figs. 13, 14, and 15). The saturation concentration of sulfoxide at points (0.125,-0.330), (0.200,-0.400) and (0.250,-0.450) was found to be 0.17kg/m^3 , 0.24kg/m^3 and 0.28kg/m^3 respectively. Also, the time lapse for in the increase of the concentration in all the three cases corresponds to the

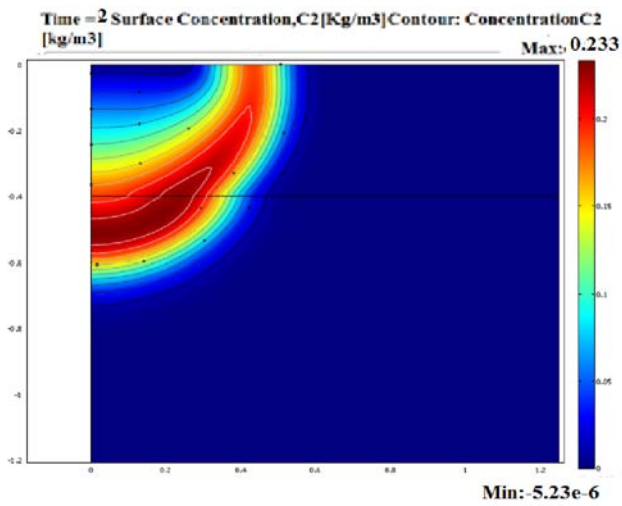
time lapse in case of aldicarb. This infers that the degradation reaction starts immediately. The saturation limit is also reached at same time, thereby it can be concluded that degradation and subsequent sorption of sulfoxide follow in close sequence.

The concentration of sulfone, the end product of the reaction chain, was also traced with time. The models have been shown in the Figs. 16(a)-(e).

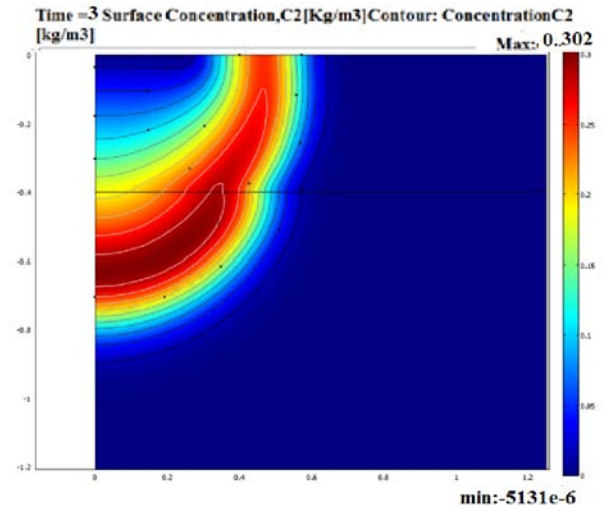
The concentration of sulfone was higher for points further away from the source at the end of 5 days (120 hours). This substantiates the fact that degradation of aldicarb and also further degradation of sulfoxide is faster in liquid medium than in the sorbed state (Figs. 17, 18 and 19). The saturation concentration of sulfone for the points (0.125,-0.330), (0.200,-0.400) and (0.250,-0.450) was found to be $\sim 1.2 \times 10^{-3}\text{ kg/m}^3$, $\sim 2.6 \times 10^{-3}\text{ kg/m}^3$ and $\sim 4.3 \times 10^{-3}\text{ kg/m}^3$ respectively. Anomalous behavior was found in case of sulfone concentration at point (0.125,-0.330) where the concentration decreases more prominently after 48 hours.



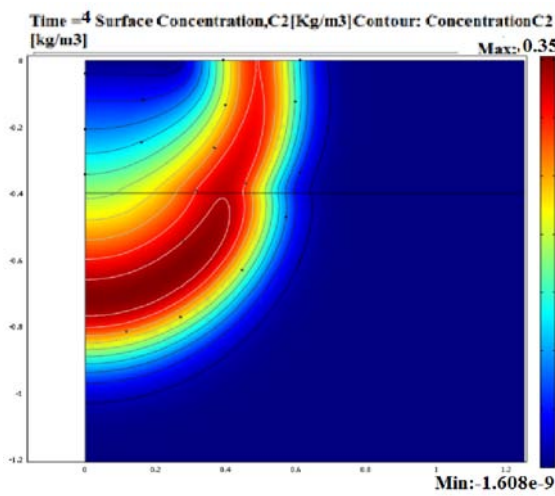
(a) Day 1



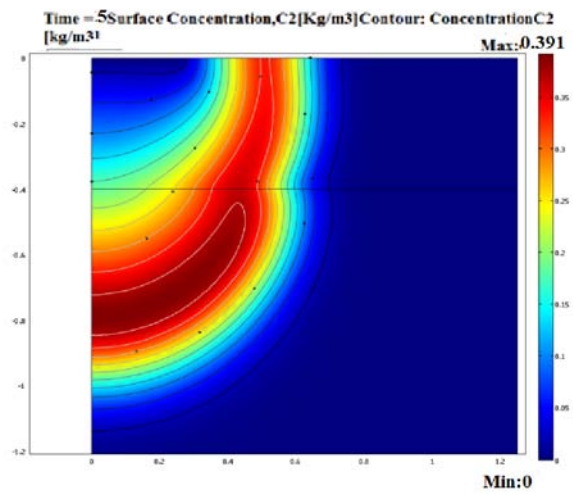
(b) Day 2



(c) Day 3



(d) Day 4



(e) Day 5

Figs. 12. Models showing flow of sulfoxide in the soil sample with different porosity

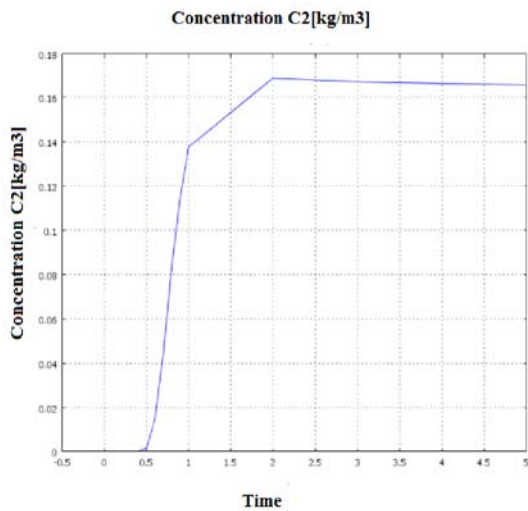


Fig. 13. Sulfoxide concentration v/s time graph at point (0.125,-0.33)

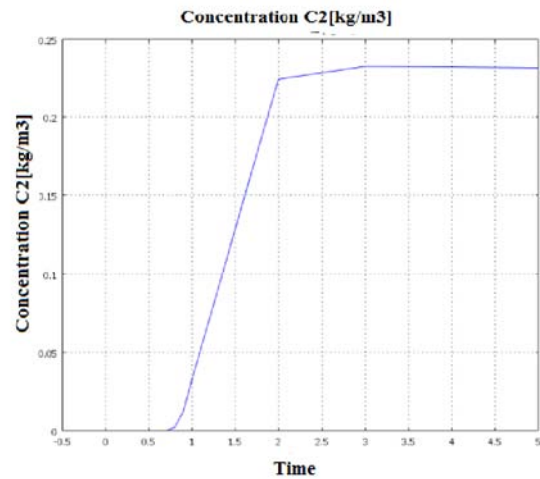


Fig. 14. Sulfoxide concentration v/s time graph at point (0.200,-0.400)

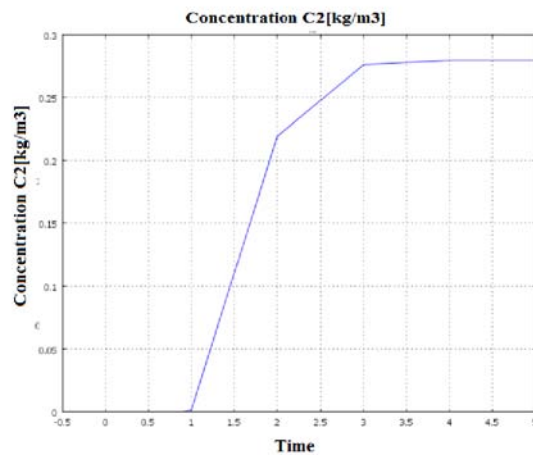


Fig. 15. Sulfoxide concentration v/s time graph at point (0.250,-0.450)

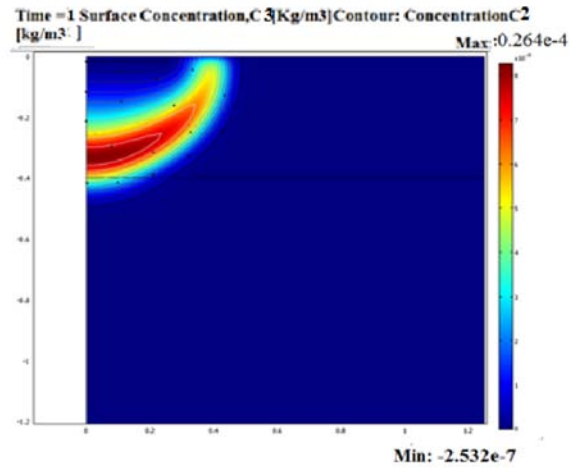
From day 1 to day 5, the aldicarb-to-sulfone ratio drops from about 5 to less than 2, and the aldicarb-to-sulfoxide ratio drops from more than 1000 to about 50.

For the soil sample with porosity 0.420 for the upper layer and 0.360 for the lower layer, similar graphs were plotted for both sulfone and sulfoxide and similar results were obtained. The saturation concentration of sulfoxide at points (0.125,-0.330), (0.200,-0.400) and (0.250,-0.450) was found to be 0.17kg/m^3 , 0.23kg/m^3 and 0.27kg/m^3 respectively (Figs. 20, 21 and 22), the difference being very minute compared to the concentrations in case of soil sample with porosity 0.339 for the upper layer and 0.399 for the lower layer. In case of sulfone, the saturation concentration for the points (0.125,-0.330), (0.200,-0.400) and (0.250,-0.450) was found to be $\sim 1.3 \times 10^{-3}\text{ kg/m}^3$, $\sim 2.6 \times 10^{-3}\text{ kg/m}^3$ and $\sim 4.4 \times 10^{-3}\text{ kg/m}^3$ respectively (Figs. 23, 24, and 25).

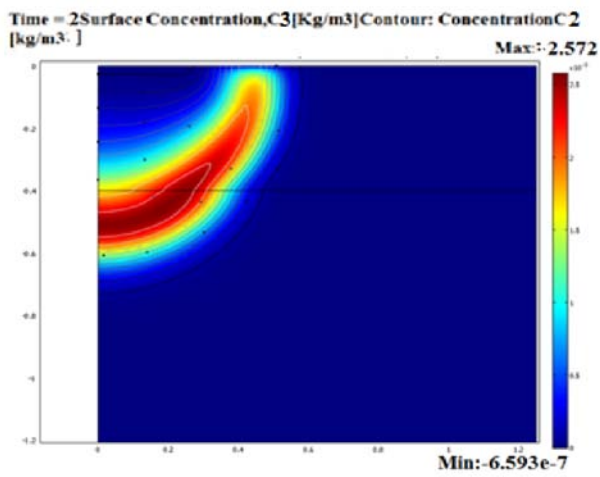
Similar plots for the clayey soil sample with defined porosity 0.700 for the upper layer and 0.600 for the lower layer were drawn. The concentration of sulfoxide v/s time graphs (Figs. 26, 27 and 28) and sulfone concentration v/s time graphs (Figs. 29, 30 and 31) have

been shown.

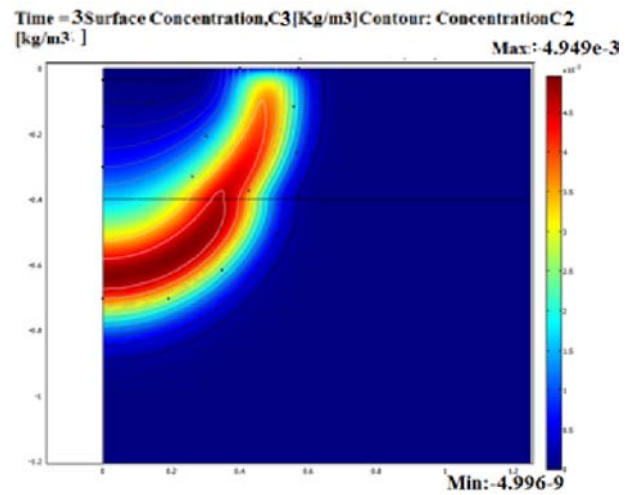
The saturation concentration attained for the first point (Fig. 22) is 0.26kg/m^3 . For the other two points saturation concentration is not achieved. However, the concentration at the end of 5th day is found to be 0.34 kg/m^3 (Fig. 23) and 0.38 kg/m^3 (Fig. 24). This further validates the fact that degradation of Aldicarb occurs at greater rate in the solution state. High porosity inhibits sorption. The concentration of sulfoxide at the end of 5th day is found to be greater than that in case of soil sample with lower porosity. The saturation concentration of sulfone is found to be $\sim 3.7 \times 10^{-3}\text{kg/m}^3$ (Fig. 25) for the first point (0.125,-0.330) which is almost thrice (2.84 times) the saturation value for soil sample with porosity 0.420 for upper layer and 0.360 for lower layer. For the other two points under study, constant concentration is not attained similar to the case of aldicarb and sulfoxide. The concentration at end of the 5th day is found to be $\sim 7.5 \times 10^{-3}\text{kg/m}^3$ (Fig. 26) and $\sim 0.0105\text{kg/m}^3$ (Fig. 27). The degradation of sulfoxide to sulfone also occurs at greater rate as compared to previous cases. Sorption also inhibits sulfoxide degradation.



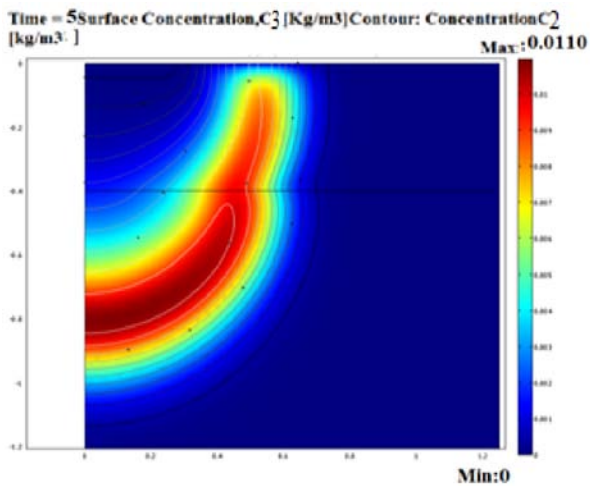
(a) Day 1



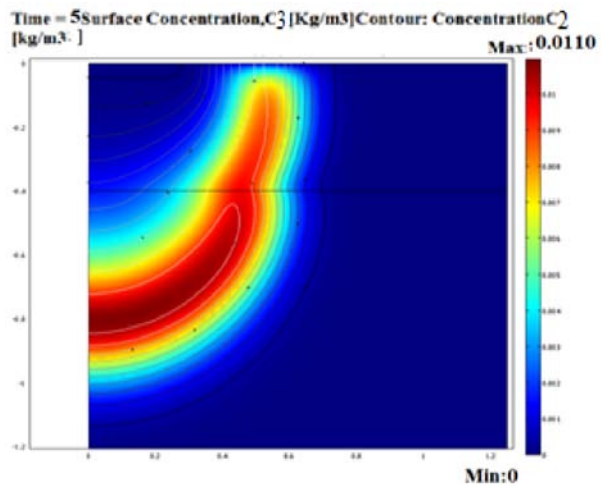
(b) Day 2



(c) Day



(d) Day 4



(e) Day 5

Figs. 16. Models showing flow of sulfone in the soil sample with different porosity

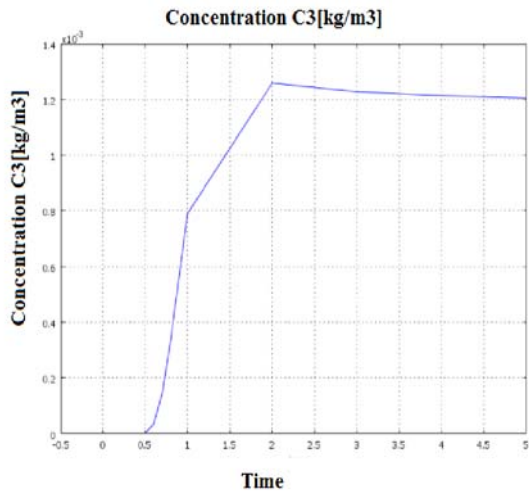


Fig. 17. Sulfone concentration v/s time graph at point (0.125,-0.330)

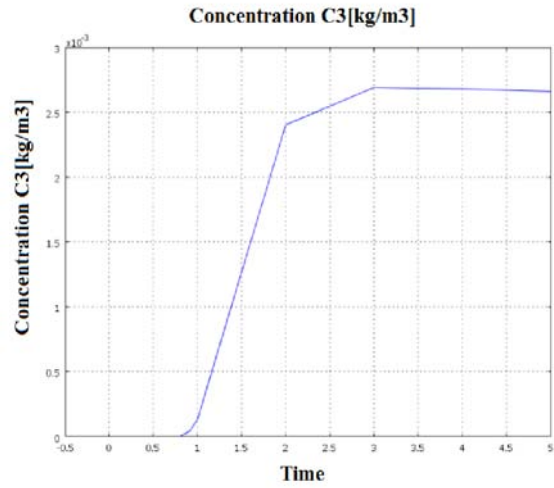


Fig. 18. Sulfone concentration v/s time graph at point (0.200,-0.400)

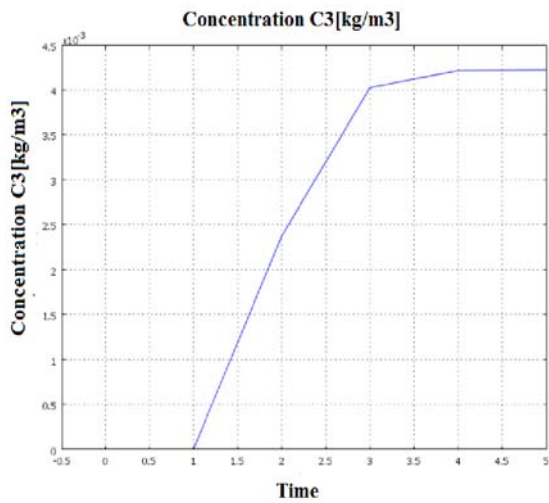


Fig. 19. Sulfone concentration v/s time graph at point (0.250,-0.450)

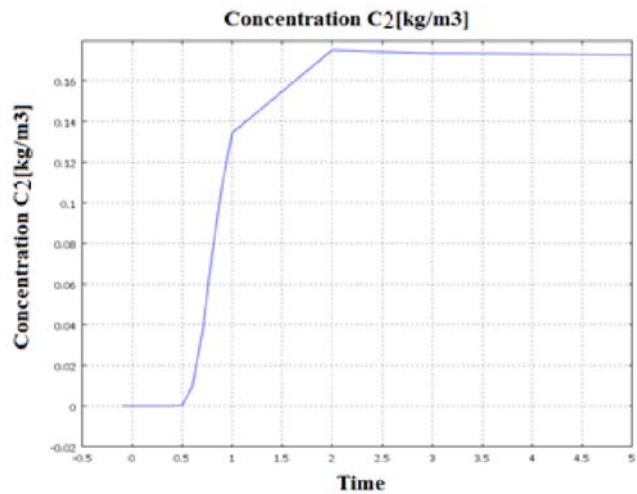


Fig. 20. Sulfoxide concentration v/s time graph at point (0.125,-0.33)

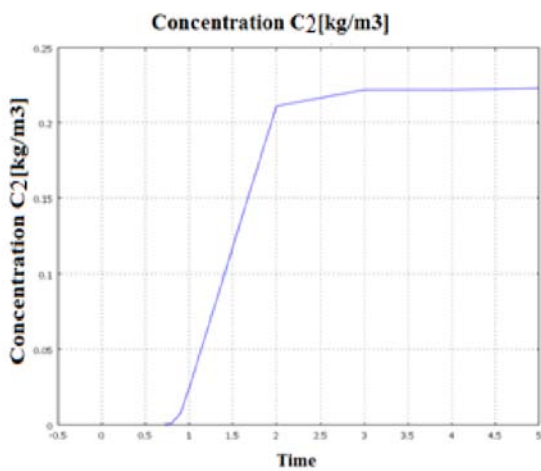


Fig. 21. Sulfoxide concentration v/s time graph at point (0.200,-0.400)

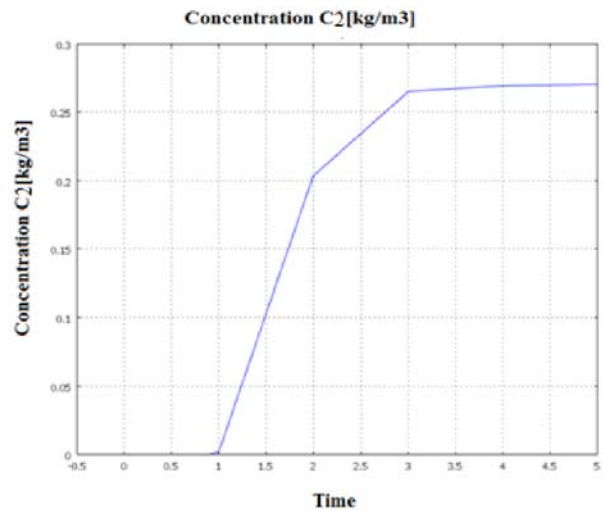


Fig. 22. Sulfoxide concentration v/s time graph at point (0.250,-0.450)

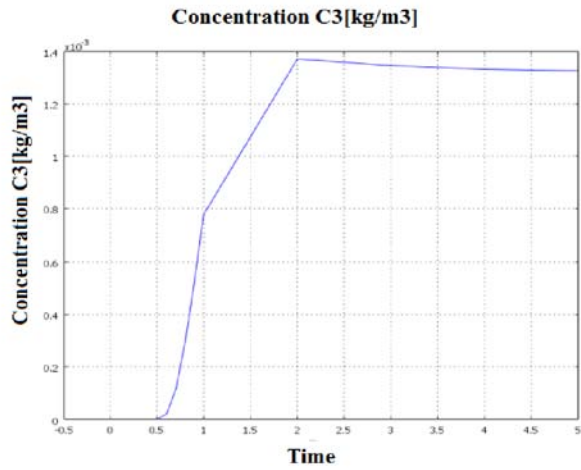


Fig. 23. Sulfone concentration v/s time graph at point (0.125,-0.33)

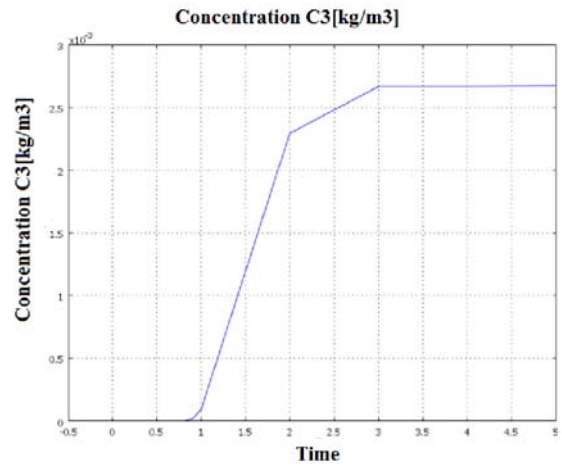


Fig. 24. Sulfone concentration v/s time graph at point (0.200,-0.400)

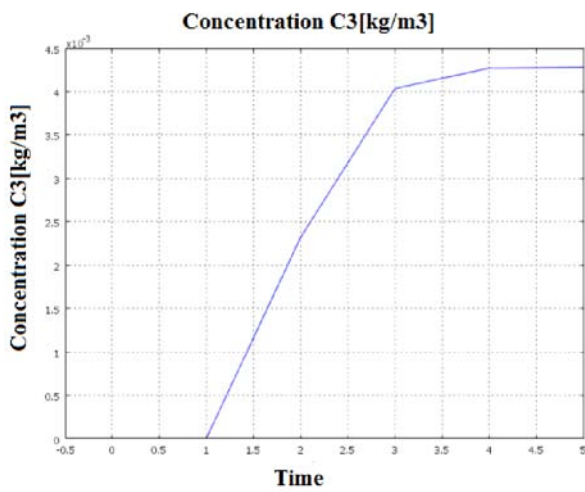


Fig. 25. Sulfone concentration v/s time graph at point (0.250,-0.450)

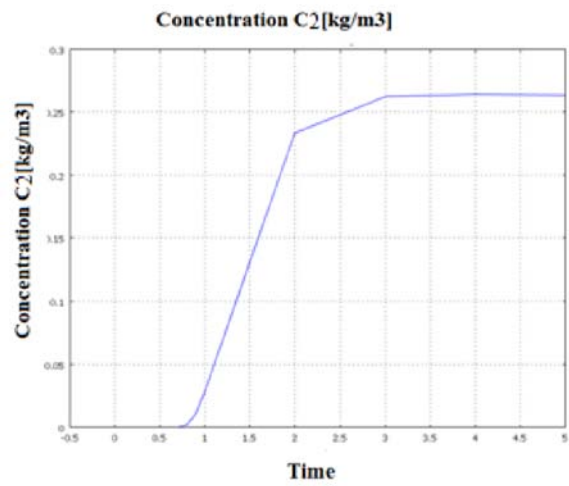


Fig. 26. Sulfoxide concentration v/s time graph at point (0.125,-0.33)

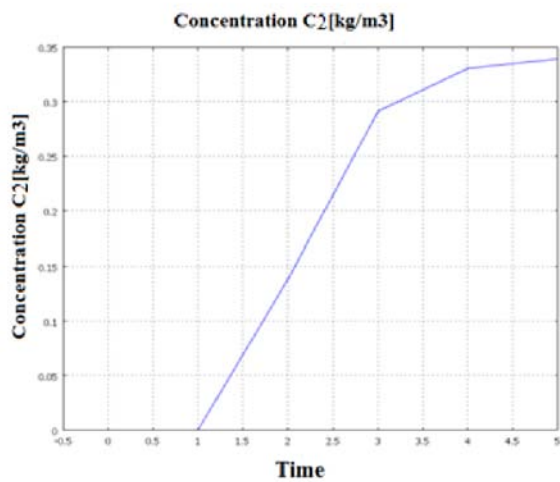


Fig. 27. Sulfoxide concentration v/s time graph at point (0.200,-0.400)

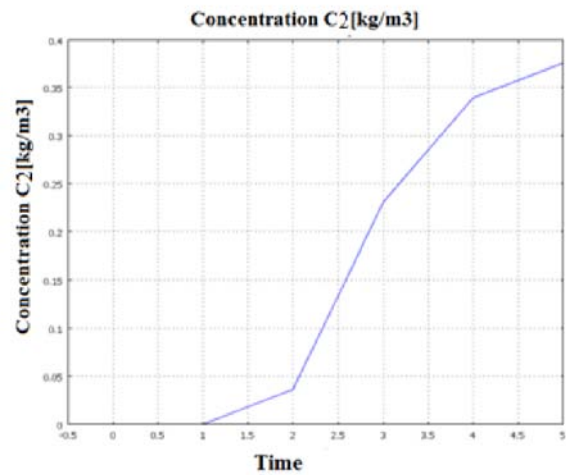


Fig. 28. Sulfoxide concentration v/s time graph at point (0.250,-0.450)

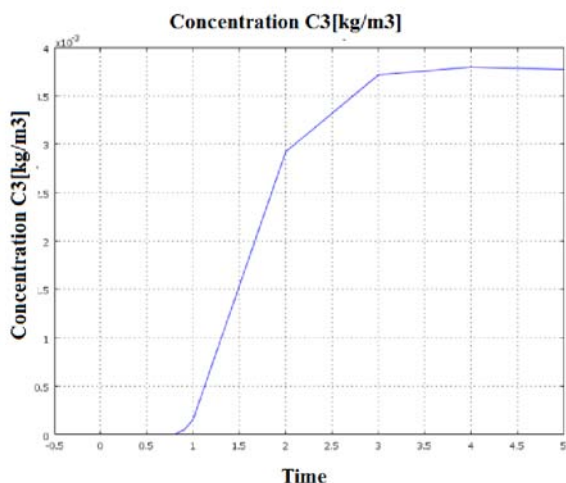


Fig. 29. Sulfone concentration v/s time graph at point (0.125,-0.33)

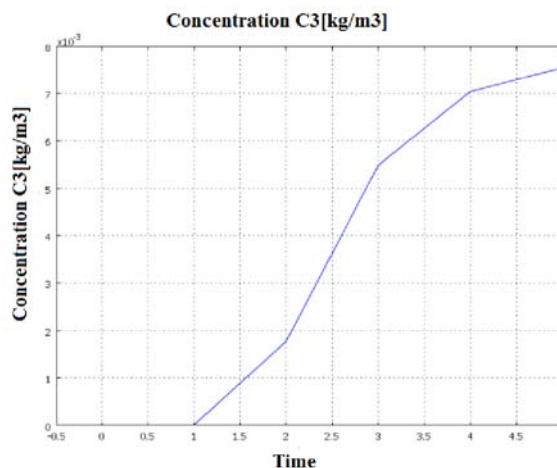


Fig. 30. Sulfone concentration v/s time graph at point (0.200,-0.400)

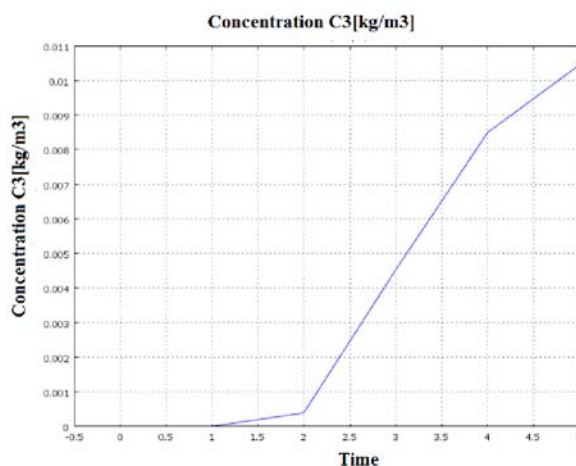


Fig. 31. Sulfone concentration v/s time graph at point (0.250,-0.450)

V. Conclusion

The porosity of the soil affects the degradation of the pesticide aldicarb to a moderate extent. Degradation primarily occurs in the liquid solution state, degradation rate in the solution state being several time greater than that in the sorbed state.

The relative contributions of the two phases to the total degradation were therefore dependent on both the sorption and the relative degradation rate constants for the dissolved and sorbed chemicals. In the study, the soil sample with low porosity was found to have high concentration of aldicarb and lower concentration of the daughter products sulfoxide and sulfone at the points under study while the soil sample with high porosity (clayey soil) showed lower saturation value for aldicarb concentration and higher values for daughter products.

Porosity inhibits sorption of the chemical thereby increasing its bioavailability and hence increasing its degradation rate. Degradation rate of sulfoxide was also affected by the porosity of soil sample.

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