

THE LEACHING BEHAVIOR OF ALDICARB AMONG COMPLEX POLLUTION SYSTEM COMPOSED OF SURFACTANT SDBS AND ALDICARB*

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Abstract. The leaching behavior of aldicarb among the complex pollution system composed of aldicarb and surfactant – sodium dodecylbenzenesulfonate (SDBS) was studied by soil column. Distilled water was used to simulate rain in order to obtain the rainfall of 235 mm for each time. Three simulations were carried out successively to give 705 mm rainfall in all. The results of multi-step leaching experiment showed that compared with control column, SDBS can increase the vertical distance of aldicarb moving and accelerate the leaching. As the concentration of SDBS increased from 250 to 500 mg kg⁻¹ of soil, not only the leaching depth of aldicarb increased by 20 cm, but also below 10 cm depth in soil column the concentration of aldicarb at the same depth increased obviously. This will enhance the danger of groundwater pollution. SDBS affected the leaching behaviour of aldicarb in soil by influencing its water solubility, adsorption capacity and degradation process. The mechanism of this complex effect has been discussed in this article.

Keywords: aldicarb, complex pollution system, leaching, sodium dodecylbenzenesulfonates, soil

1. Introduction

Aldicarb [2-methyl-2-(methylthio) propionaldehyde O-(methyl carbomoyl) oxime], a systemic carbamate pesticide, has given excellent control of a wide range range of phytophagous insects, nematodes and mites. It was developed by Union Carbide Corporation in 1962 and has been used on numerous crops such as cotton, peanuts, corns, soybeans, broomcorns, beets, sugarcane, wheat, orange, potatoes and tobacco. As a broad spectrum insecticide, aldicarb has been registered for use on different crops in over 70 countries at present. In China, it has been registered for use on peanuts, cotton and tobacco since 1986.

Aldicarb and its two oxidation products, aldicarb sulfoxide and aldicarb sulfone, have very high water-solubility and toxicity. At 25 their solubilities in water are 0.6, 33 and 0.8%, respectively. Their acute oral LD50 values to mice are 0.9, 0.9 and 24.0 mg kg⁻¹, respectively. As one of the pesticides with the highest toxicity, its toxicity is 10 times of that of carbofuran.

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In general, aldicarb is applied to soil in a 5, 10 or 15% granular formulation. Because of its high water-solubility, aldicarb can eluviate downward to deep soil or through the soil into the groundwater with the movement of water in soil (Jones and Estes, 1995; Zhu *et al.*, 1993; Ma and Yun, 1986). At present aldicarb has been detected in groundwater in many countries around the world. For example, in 1979 aldicarb was found in drinking-wells on Long Island, New York, and subsequently in 12 other states (Zaki, 1982). In 1985 a number of wells in the states of Wisconsin and Maine were shut down as drinking water sources due to aldicarb contamination (U.S. EPA, 1987).

Surfactants, used in detergents for home laundry and institutional and industrial cleaning, have entered into the environment. Especially in rural areas, incalculable amounts of surfactants have been released into soil environment with the discharge of domestic sewage or irrigation with sewage. It was estimated that the concentration of surfactants in soil ranged from several decades to several hundreds mg kg^{-1} in many areas in China (Dong, 1999).

Surfactants have complex effects on the behavior of contaminants. Studies have shown that due to special surface properties nonionic and anionic surfactants can enhance water solubilization of pollutants and act as catalyzer during their degradation process (Haigh, 1996). There are many publications about the residue, degradation, movement and toxicity of aldicarb as a single pollutant (Jones and Estes, 1995; Zhu *et al.*, 1993; Ma and Yun, 1986; Jiao *et al.*, 1994; Cai *et al.*, 1995; Jones, 1988). But there is no report on aldicarb among a complex pollution system consisting of a surfactant and aldicarb. As the effective ingredient of detergents, sodium dodecylbenzenesulfonate (SDBS), an anionic surfactant, has entered into environment. There is a need to understand the interaction between SDBS and aldicarb to evaluate the risk of aldicarb on groundwater. This article studies the leaching behavior of aldicarb among the SDBS-aldicarb complex system by soil column simulation in the laboratory.

2. Materials and Methods

2.1. APPARATUS

Gas chromatograph – M600D (Yong Lin Company, South Korea) with Hewlett Packard flame photometric detector equipped with 394 nm sulfur interference filter and stainless steel column (2 m long and 2 mm id) packed with 5% Carbowax 20 M on 100–120 mesh Chromosorb W-Hp. Adjust the injection port and the column oven temperatures to 240 and 210 °C, respectively. Nitrogen with the flow rate of 20 mL min^{-1} was used as carrier gas. Adjust the detector temperature to 220 °C and operate the hydrogen-rich flame of the photometric detector with a hydrogen flow rate of 80 mL min^{-1} and an air flow rate of 100 mL min^{-1} .

RE 52-C rotation evaporator with rotator, water bath and vacuum pump, THA-S shaker with regulated temperature, and LXJ 64-01 centrifugal machine were used

in experiment. A glassy chromatographic column (30 cm long and 10 mm inside diameter (id) with cotton plug was used to clean the sample. Erlenmeyer flasks (150 and 250 mL) and volumetric flasks (10 mL) with glass stoppers were used in process of soil sample treatment.

2.2. PESTICIDES

Analytical-grade aldicarb, aldicarb sulfone and a 5% granular formulation of aldicarb were provided by the Institute of Pesticide Industry, Tianjin. The purity of analytical grade chemical was better than 99%.

2.3. CHEMICALS

Acetone, dichloromethane, petroleum ether (boiling range 30–60 °C) were analytical grade and redistilled to purify. Sodium bicarbonate, anhydrous sodium sulfate and calcium chloride were analytical grade. The concentration of peracetic acid was 40%. Silica gel 200 mesh was used for column purification.

2.4. SOILS

Surface and subsurface soils used in this study were collected from suburban farmland, Tianjin. This site had no history of aldicarb application prior to the collection of the soil samples. According to the depth, soils were divided into three sections: upper soil (0–30 cm), middle-depth soil (30–80 cm) and deep-seated soil (80–120 cm). For each section, about 20 kg of soil was collected and taken back to the laboratory to be air-dried. Dry soils were then ground in a mill and sifted through a sieve of 18 mesh. The sifted particles were collected and used as broad filling in the bottom of soil column.

Selected properties of the soil used in this study are shown in Table I. The organic content was determined by potassium dichromate-sulfuric acid oxidation method, Soil water content was determined gravimetrically by drying overnight at 110°C in a convection oven. The soil-water content referred to hygroscopic water, i.e. the rest of total water in soil subtracted by free water and chemical bound water. Soil pH was determined by placing a combination glass electrode in a mixture containing equal weights of soil and a 0.005 M calcium chloride solution.

3. Procedure

3.1. PREPARATION OF SOIL COLUMN AND SIMULATION OF RAINFALL

3.1.1. *Short Column*

Perspex columns with 0.5 m long and 75 mm id were used. In the proportion of 100 g soil: 15 mL distilled water, upper soil, middle-depth soil and deep-seated soil

TABLE I
Selected soil properties

	pH	Organic matter content %	Soil water content %	Mechanical composition (%)			Specific gravity
				Sand	Silt	Clay	
Upper soil (0–30 cm)	7.93	2.47	3.66	76	11	13	2.24
Middle-depth soil (30–80 cm)	7.97	1.87	5.34	77	14	9	2.17
Deep-seated soil (80–120 cm)	8.15	1.79	6.31	81	11	8	2.13

(500 g each) were encased into column in turn. SDBS with a weight of 0.125 g was mixed into upper soil to give a concentration of 250 mg kg⁻¹ of dry soil. A weight of 0.6 g 5% granular formulation of aldicarb were applied to the surface of the soil column to give a concentration of 20 mg active ingredient per kg of dry soil. Following the application of aldicarb, 1 to 2 cm of soil was placed on top of the column to reduce the volatilization of the pesticide. Finally a piece of filter paper was put on the top of soil column to make the surface of soil accept rain equally. The soil column was placed in a ventilate room to simulate the field. Two hundred milliliters of distilled water, in a separatory funnel, was applied to the column at a rate of 3 to 4 drops per minute to simulate rainfall (Each simulation lasted about 24 hr). The 200 mL distilled water simulated 235 mm of rainfall in the field (Ma and Yun, 1986). Following the same procedures mentioned previously, another soil column without SDBS was prepared as a reference. Four replicas were applied for columns with and without SDBS.

3.1.2. Long Column

UPVC plastic hollow columns, 2 m long and 110 mm id, were used to construct the long columns. A hole with 8 mm id was drilled as a sampling pore every 10 cm distance on the column. In the proportion of 100 g soil: 15 mL distilled water, upper soil, middle-depth soil and deep-seated soil (5, 5 and 4 kg, respectively) were encased into column in turn SDBS was mixed into upper soil to give a concentration of 250 mg kg⁻¹ for long column 1 and 500 mg kg⁻¹ for long column 2. A weight of 5.6 g of 5% granular formulation of aldicarb was applied to the surface of the soil column to give a concentration of 20 mg kg⁻¹ of dry soil. After covering with a soil layer of 1–2 cm thick and a piece of filter paper, as previously mentioned, distilled water with a volume of 430 mL (according to the difference between short column id and long column id) simulated 235 mm of rainfall in the field. Two replicas were applied for columns with and without SDBS.

3.2. SAMPLING

In order to avoid contamination of the low concentration sampling site with the high concentration site, the samples were collected from bottom to top. For the short column, soil samples were taken at 6 points one week after the end of rain simulation. The distance between two neighboring points was 5 cm. For each sampling point, 20 g of soil was collected. For the long column, simulation of rain was carried out three times. Each sampling was carried at the completion of the rainfall simulation and sampled again after one week. Sampling occurred at 8 sites (10–80 cm deep) for the first and second simulation, but at 15 sites (10–15 cm deep) for the third simulation. Each sample contained 20 g of soil.

3.3. SAMPLE EXTRACTION AND CLEANUP

Soil samples were placed into 250 mL Erlenmeyer flasks and 100 mL 3:1 (v/v) acetone-distilled water mixture was added. The flasks were placed in a shaker to extract for 1 hr at 25 °C. For each sample the mixture of soil and extraction solvent was centrifuged at 3000 rpm for 15 min. The supernatant was transferred to a 250 mL round bottom flask and the soil was extracted with 50 mL 3:1 (v/v) acetone-distilled water mixture again. After a second centrifugation, the supernatant was transferred to the same round bottom flask. The extracts were evaporated to 50 mL with rotation evaporator at 50 and 0.05 kpa vacuum. Then 5 mL of 40% peracetic acid was added to oxidize the extracts and stirred continuously for 20 min. A 10% (w/v) aqueous sodium bicarbonate solution was carefully added to each flask with continued stirring. The extracts were stirred for an additional 20 min to neutralize the excess acid and to evict the air bubbles. The extracts were then transferred to 250 mL separatory funnels and the flasks were rinsed with 50 mL portions of dichloromethane, transferring the rinsings to the separatory funnels. The funnels were shaken for 30 sec, venting to release carbon dioxide pressure, and the lower solvent layers were flowed into 250 mL round bottom flasks. The aqueous layers were additionally extracted two times as preceding. After the third extraction the round bottom flasks were immersed in a 40–50 °C water bath and evaporated to less than 5 mL for cleanup.

Cleanup columns were prepared by placing a plug of glass wool in the bottom of each column, adding exactly 5.0 g anhydrous sodium sulfate and 10.0 g silica gel, tapping the column to settle the adsorbent and prewetting each column with 15 mL of dichloromethane. When the solvent level reached the top layer of the adsorbent, the oxidized sample was transferred to the column and allowed to elute dropwise. The sample flask was rinsed with 50 mL 3:2 (v/v) petroleum-dichloromethane mixture and the rinsings were then transferred to column and allowed to elute dropwise. When the solvent level reached the top of the adsorbent layer, the stopcocks were closed and receivers changed. The first two eluates were discarded. One hundred mL of a 1:1 (v/v) acetone–dichloromethane mixture was added to the column, eluted dropwise, and collected in 250 mL round bottom flasks. The flasks were

TABLE II
The recovery of sample treatment

Aldicarb	(mg kg ⁻¹)	0.05	0.1	0.2	0.4	0.5	0.6	0.8	1.0
Recovery	(%)	81.7	83.1	102.3	86.0	85.9	78.7	80.6	93.2

then immersed in a 40–50 °C warm-water bath and the eluates were evaporated to dryness with a gentle stream of dry air. The residues were then redissolved in 5 mL acetone for the GC-FPD analysis.

3.4. DETERMINATION OF RECOVERY RATE

Eight aliquots of 20 g soil were weighed into 8 Erlenmeyer flasks and an aqueous aldicarb solution was added to give a concentration of 0.05, 0.1, 0.2, 0.4, 0.5, 0.6, 0.8 and 1.0 mg kg⁻¹ of dry soil. Distilled water was then added to give a ratio of 100 g soil:15 mL water. After some time these samples were extracted by the same method as previously mentioned. This process was repeated twice and the average recovery rate was determined.

4. Results

4.1. TOTAL TOXIC RESIDUE RECOVERY DATA

Aldicarb is rapidly oxidized to aldicarb sulfoxide, which, in turn, is slowly oxidized to aldicarb sulfone in soil. Aldicarb sulfoxide and aldicarb sulfone have a toxicity similar to that of their parent compound, aldicarb. The term ‘total toxic residue’ (TTR) was often used to include the three toxic compounds (Woodham *et al.*, 1973). In this experiment peracetic acid was used to oxidize aldicarb sulfoxide into aldicarb sulfone and the sum of the concentrations of these three compounds was regarded as total toxic residue of aldicarb. TTR expressed as mg aldicarb per kg dry soil can be calculated with the following formula:

$$\text{TTR} = C * V * 0.856 \text{ m}^{-1} \quad (1)$$

where C is the concentration of aldicarb sulfone in final 5 mL acetone calculated from the standard curve (mg L⁻¹), V is the final volume of solution (5 mL), 0.856 is the conversion coefficient from aldicarb sulfone to aldicarb, m is the dry weight of soil sample (17 g).

Table II shows the recoveries for total toxic residues ranged from 78.7 to 102.3%.

TABLE III
Total aldicarb residues (mg kg^{-1}) in the short columns

	Concentration of SDBS (mg kg^{-1})	Soil depth (cm)					
		5	10	15	20	25	30
Short column 1	0	84.48	93.71	0.95	0.067	– ^a	–
Short column 2	250	76.94	88.25	4.83	1.68	1.20	0.83

^a – = Not detected.

4.2. EXPERIMENT OF SHORT SOIL COLUMN LEACHING

The properties of soil column such as porosity, compactibility and uniformity had an effect on leaching. Prior to regular experiment three replicas were applied for columns with and without SDBS. The aim of doing so was to observe the effect of SDBS on the leaching of aldicarb and to obtain satisfied soil columns to eliminate the interference of these factors. In these three replicas the effect that SDBS accelerated the leaching of aldicarb was observed.

Because of high water-solubility, aldicarb, aldicarb sulfoxide and aldicarb sulfone can eluviate downward to deep soil with the movement of water. In the short column experiment, aldicarb carbamate residue was detected in the 20 cm deep soil after a single simulated rain event. Ma and Yun reported that aldicarb residues can move through a 30 cm thick soil layer and in a long time leaching experiment the maximum leaching depth can exceed 1.5 m (Ma and Yun, 1986; Mo *et al.*, 1997).

Surfactant SDBS has a strong influence on the leaching of aldicarb in soil (Table III). In the short column 2 containing 250 mg kg^{-1} SDBS more than 1 mg kg^{-1} of aldicarb leached to a 25 cm depth. In contrast, less than 1 mg kg^{-1} of aldicarb was detected at 15 cm in the short column containing no SDBS. Aldicarb was not detected in the soil below 25 cm.

4.3. EXPERIMENT OF LONG SOIL COLUMN LEACHING

On the basis of short column experiment two long soil columns containing different level of SDBS were assembled to evaluate this complex effect. Because of the reason mentioned in Section 3.2 prior to regular experiment one replica was applied to observe the effect of SDBS on leaching of aldicarb and to eliminate the interference of column effect.

The experimental results of two long soil columns are listed in Tables IV and V. The data in these two tables show that the leaching distance of aldicarb residue was a function of the quantity of rainfall and concentration of SDBS. With the additional simulated rainfall and the increase of the concentration of SDBS the leaching depth increased. At the end of first rain, aldicarb leached to a 10 cm depth and the concentration was very low which indicates that most of the aldicarb was

still retained above 10 cm. One week later aldicarb can be found at 20 cm in column 1 and at 30 cm in column 2. At the end of second rain, aldicarb reached 40 cm depth in column 1 and 60 cm depth in column 2. At the end of the third rain aldicarb had reached the 90 cm depth in column 1 and 110 cm in column 2. One week after the third rain the depth of aldicarb leaching in column 1 and column 2 is 110 and 130 cm, respectively.

In Tables IV and V, the first, third and fifth time sampling occurred at the end of the first, second and third rain, respectively. The second, fourth and sixth time sampling was carried out one week after the end of the first, second and third rain, respectively. It was worth noting that each datum in these two tables only represent the concentration of certain sampling depth, not a mean value of aldicarb residues in soil above the depth. For instance, the concentration of aldicarb residues at sampling pore 2 referred to the concentration of the 20 cm depth, not an average from 10 to 20 cm deep.

Because the concentration of SDBS in column 2 is greater than that in column 1, the leaching depth of aldicarb in column 2 is greater by 20 cm than that in column 1 and the concentration of aldicarb is higher than that in column 1 at the same depth below 10 cm. For most samplings at 10 cm the soil concentration of aldicarb in column 2 was lower than that in column 1. The reason is estimated that aldicarb in column 2 moved downward faster than in column 1.

The extent to which groundwater contamination can occur as a result of normal crop application depends on a variety of factors: the type of pesticide used, how the pesticide is applied (application method, frequency, and quantity), the characteristics of the soil, and the geology of the area. These factors, working singly or in combination, will determine how quickly the pesticide will move through the soil and how fast it will break down. The primary driving force for movement of pesticides in soil is the movement of water. Because aldicarb, aldicarb sulfoxide and aldicarb sulfone are soluble in water, aldicarb residues move with soil water in both the unsaturated and saturated zones. In the root zone, aldicarb residues move downward with water from rain or irrigation. Conversely, plant transpiration of water will retard downward movement of aldicarb residues. Evaporation of soil moisture from the land surface may result in upward movement of aldicarb residues within the root zone, although this movement is usually insignificant under normal agricultural conditions. Movement of aldicarb residues in the lower strata of the unsaturated zone is generally in a vertically downward direction.

SDBS may have affected the leaching behavior of aldicarb in soil by influencing the water solubility and adsorption capacity as well as the degradation process of aldicarb in soil. Jawitz *et al.* (1997) stated that a surfactant could form microemulsions, a special state between emulsion and colloid solution, and microemulsions can increase the water solubility of some organic chemicals. In another experiment it has been reported that SDBS can increase the water solubility of aldicarb from 6000 to 12 000 mg L⁻¹ (Dai, 1999). This solubilization of aldicarb in water may be the factor that increased the downward mobility of aldicarb. At the same time

TABLE IV
Total aldicarb residues (mg kg^{-1}) in the long columns following the first and second simulated rainfalls

		Soil depth (cm)								
		10	20	30	40	50	60	70	80	
Long column 1 (250 mg kg^{-1} SDBS)	First time sampling ^a	0.76	-	-	-	-	-	-	-	-
	Second time sampling ^b	177.74	0.089	-	-	-	-	-	-	-
	Third time sampling ^c	351.53	1.79	0.092	0.066	-	-	-	-	-
	Fourth time sampling ^d	178.59	4.52	1.13	0.12	0.11	0.096	0.066	0.023	
Long column 2 (500 mg kg^{-1} SDBS)	First time sampling ^b	1.27	-	-	-	-	-	-	-	-
	Second time sampling ^b	163.31	0.14	0.065	-	-	-	-	-	-
	Third time sampling ^c	334.65	2.85	0.89	0.81	0.039	0.015	-	-	-
	Fourth time sampling ^d	174.60	7.29	2.57	1.47	0.28	0.16	0.090	0.098	

- = Not detected.

^a Sampling occurred at the completion of the first rainfall simulation, i.e., 1 day after application of aldicarb.

^b Sampling occurred one week after the first rainfall simulation, i.e., 8 day after application of aldicarb.

^c Sampling occurred at the completion of the second rainfall simulation, i.e., 9 day after application of aldicarb.

^d Sampling occurred one week after the second rainfall simulation, i.e., 16 day after application of aldicarb.

TABLE V
Total aldicarb residues (mg kg^{-1}) in the long columns after the third rainfall

		Soil depth (cm)														
		10	20	30	40	50	60	70	80	90	100	110	120	130	140	150
Long column 1 (250 mg kg^{-1} SDBS)	Fifth time sampling ^a	97.64	12.76	2.99	0.89	0.53	0.19	0.077	0.036	0.022	-	-	-	-	-	-
	Sixth time sampling ^b	90.57	12.77	3.02	0.79	0.66	0.33	0.069	0.044	0.031	0.017	0.007	-	-	-	-
Long column 2 (500 mg kg^{-1} SDBS)	Fifth time sampling ^a	95.36	13.41	2.98	1.66	0.55	0.45	0.20	0.12	0.076	0.034	0.019	-	-	-	-
	Sixth time sampling ^b	96.58	13.73	3.01	1.82	1.03	0.79	0.28	0.20	0.110	0.055	0.023	0.020	0.009	-	-

- = Not detected.

^a Sampling occurred at the completion of the third rainfall simulation, i.e., 17 days after application of aldicarb.

^b Sampling occurred one week after the third rainfall simulation, i.e., 24 days after application of aldicarb.

this solubilization can decrease the amount of aldicarb adsorbed onto soil organic matter, which increased the amount of aldicarb moving freely in soil. SDBS can also affect the degradation rate of aldicarb in soil, but more systematic study is needed to explain this complex effect. In addition, SDBS can reduce the surface tension of soil water. As a result the mobility of soil water can be enhanced, which also contributed to the downward movement of aldicarb.

In the environment, aldicarb is applied in granular form and released by soil moisture; degradation begins immediately. The first step in degradation appears to be the oxidation of aldicarb to aldicarb sulfoxide, some of which is further oxidized to aldicarb sulfone. These three species also concurrently hydrolyze to form non-carbamate oximes and nitriles which can continue to be degraded to aldehydes, acids and alcohols (Lightfoot *et al.*, 1987). At last all of these chemicals can be mineralized in organic degradates. After application, most pesticides are retained in surface soil above 20 cm depth. Degradation occurs mainly in surface soils. This has been reported in literatures (Ma and Yun, 1986; Mo *et al.*, 1997). Therefore the concentration of aldicarb residues in surface soil became low after some time. As the time elapsed the amount of aldicarb residues in soil will decrease.

In the leaching experiment the inside diameter of soil column has a remarkable influence on leaching rate. In general, the leaching rate increased while the id of column decreased. In this experiment this has been proved by the difference of leaching distance between short column and long column after rain. Compared with others, the id of soil column in this experiment is larger than that of others, so the maximum leaching depth in this experiment is smaller than that in others' experiments (Ma and Yun, 1986; Mo *et al.*, 1997). This may be the result of an edge effect. The smaller diameter column had a greater edge effect than the larger diameter column.

In this experiment the overall simulated rainfall for the long soil column was equal to 705 mm actually and the experimental time lasted for approximately one month. This accorded with the actual status in summer in China. Abundant rainfall during summer can make aldicarb move to the deep soil or even enter into groundwater. Sufficient attention should be paid to this.

5. Conclusions

SDBS can accelerate the leaching of aldicarb in soil. As the concentration of SDBS increased from 250 to 500 mg kg⁻¹ of soil, the leaching depth of aldicarb increased by 20 cm and below 10 cm depth in soil column the concentration of aldicarb at the same depth increased. SDBS affected the leaching behavior of aldicarb in soil by influencing its water solubility, adsorption capacity and degradation process.

Appendix A-1Total aldicarb residues (mg kg^{-1}) in the short columns

		Soil depth (cm)					
		5	10	15	20	25	30
Short column 1 (no SDBS)	Replica 1	85.36	90.68	1.09	0.071	–	–
	Replica 2	85.03	94.19	0.92	0.062	–	–
	Replica 3	85.09	94.28	0.89	0.066	–	–
	Replica 4	84.48	93.71	0.95	0.067	–	–
Short column 2 (250 mg kg^{-1} SDBS)	Replica 1	77.13	87.96	4.86	1.581	1.29	0.79
	Replica 2	74.69	90.21	4.65	1.74	1.16	0.71
	Replica 3	80.31	86.89	4.92	1.77	1.21	0.80
	Replica 4	76.94	88.25	4.83	1.68	1.20	0.83

Appendix A-2Total aldicarb residues (mg kg^{-1}) in the long columns (regular experiment)

Sampling		Soil depth (cm)							
		10	20	30	40	50	60	70	80
Long column 1	First time	0.76	–	–	–	–	–	–	–
	Second time	177.74	0.089	–	–	–	–	–	–
	Third time	352.53	1.79	0.092	0.066	–	–	–	–
	Fourth time	178.59	4.52	1.13	0.12	0.11	0.096	0.066	0.023
Long column 2	First time	1.27	–	–	–	–	–	–	–
	Second time	163.31	0.14	0.065	–	–	–	–	–
	Third time	334.65	2.85	0.89	0.81	0.039	0.015	–	–
	Fourth time	174.60	7.29	2.57	1.47	0.28	0.16	0.090	0.098
Sampling		Soil depth (cm)							
		10	20	30	40	50	60	70	80
Long column 1	Fifth time	97.64	12.76	2.99	0.89	0.53	0.19	0.077	0.036
	Sixth time	90.57	12.77	3.02	0.79	0.66	0.33	0.069	0.044
Long column 2	Fifth time	95.36	13.41	2.98	1.66	0.55	0.45	0.20	0.12
	Sixth time	96.58	13.73	3.01	1.82	1.03	0.79	0.28	0.20
Sampling		Soil depth (cm)							
		90	100	110	120	130	14	150	
Long column 1	Fifth time	0.022	–	–	–	–	–	–	–
	Sixth time	0.031	0.017	0.007	–	–	–	–	–
Long column 2	Fifth time	0.076	0.034	0.019	–	–	–	–	–
	Sixth time	0.110	0.055	0.023	0.020	0.009	–	–	–

Appendix B-1Total aldicarb residues (mg kg⁻¹) in the long columns (preparative experiment)

Sampling		Soil depth (cm)							
		10	20	30	40	50	60	70	80
Long column 1	First time	0.82	–	–	–	–	–	–	–
	Second time	175.31	0.077	–	–	–	–	–	–
	Third time	350.08	2.01	0.076	0.056	–	–	–	–
	Fourth time	176.35	4.37	1.20	0.17	0.08	0.0076	0.058	–
Long column 2	First time	1.42	–	–	–	–	–	–	–
	Second time	162.06	0.21	0.053	–	–	–	–	–
	Third time	332.79	3.15	0.94	0.87	0.032	0.011	–	–
	Fourth time	173.59	6.98	2.69	1.60	0.19	0.18	0.062	0.055

Sampling		Soil depth (cm)							
		10	20	30	40	50	60	70	80
Long column 1	Fifth time	96.39	11.82	3.17	1.06	0.74	0.22	0.069	0.045
	Sixth time	91.48	12.31	3.24	0.91	0.69	0.28	0.056	0.041
Long column 2	Fifth time	96.02	13.59	4.01	1.89	1.03	0.99	0.31	0.086
	Sixth time	94.68	15.47	4.36	2.15	1.01	1.10	0.39	0.13

Sampling		Soil depth (cm)						
		90	100	110	120	130	140	150
Long column 1	Fifth time	0.016	–	–	–	–	–	–
	Sixth time	0.023	0.012	0.005	–	–	–	–
Long column 2	Fifth time	0.087	0.021	0.011	–	–	–	–
	Sixth time	0.087	0.036	0.034	0.014	0.007	–	–

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