Research Article

Pretilachlor and Oxadiargyl Residues in Surface and Ground Water in Rice Cultivated Areas in Peninsular India

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Abstract

A survey was conducted for two years in rice growing areas of Telangana state in Peninsular India, to study the persistence and entry pretilachlor an oxadiargyl into surface and subsurface water bodies during *kharif* seasons. In irrigation project command area, pretilachlor residues were detected in water samples collected from two drainage channels (0.052 and 0.081 µg/ml) and a minor irrigation tank (0.079 µg/ml) in the samples collected at 15 days after transplanting and in two samples in samples collected at 30 DAT (0.066 and 0.062 µg/ml). Field to field irrigation prevalent in the irrigation project canal command area might have resulted in accrual of pretilachlor residues in the water samples collected from the drainage channels. Oxadiargyl and pretilachlor residues were not detected in samples collected from aquifers surrounded by ground-water irrigated rice areas.

Keywords: Pretilachlor, Oxadiargyl, herbicide residues, irrigation water

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Introduction

Pretilachlor and oxadiargyl are the most commonly used pre-emergence herbicides in rice-growing regions of Telangana state, India. Consumption of pretilachlor and oxadiargyl was 1530 kilo-liters and 31 tons respectively during 2018 [1]. These pre-emergence herbicides are mixed with sand and normally applied as broadcast application at 3-5 days after transplanting (DAT). Among the rice pesticides, pretilachlor is one of the most applied in the flooded rice fields to control weeds through inhibition of photosynthesis [2].

The susceptible weeds for pretilachlor are *Echinochloa crus-galli, Echiniochloa colonum, Cyperus difformis, Cyperus iria, Fimbristylis miliacea, Eclipta alba, Ludwigia parviflora, Monochoria vaginalis, Leptochloa chinensis, Panicum repens*. Whereas oxadiargyl effectively controls *Echinochloa crus-galli, Echinochloa colonum, Cyperus iria, Cyperus difformis, Eclipta alba, Ludwigia quadrifoliata* [3].

Pretilachlor [2-chloro-2,6-diethyl-N-(2-propoxyethyl)acetanilide] is a chloroacetanilide herbicide which is widely used in transplanted and direct seeded rice (*Oryza sativa* L.) for the control of several grasses, broad-leaved weeds and sedges. Oxadiargyl (3-[2,4-dichloro-5-(2-propynyloxy)phenyl]-5-(1,1-dimethylethyl)-1,3,4-oxadiazol-2 (3H)-one), is an oxadiazolone class selective herbicide used in transplanted and direct seed rice for broad-spectrum control of weeds. Primary biochemical mechanism of action of chloroacetamide (pretilachlor) is linked to disruption in the formation of very long chain fatty acids located in plasma membranes of the plant cells. Loss of these very long chain fatty acids stops the biosynthesis and function of the plasma membrane, loss of cell integrity which leads to the death of the plant [4]. The herbicide activity of oxadiargyl lies in binding to the protoporphyrinogen oxidase IX as an inhibitor, preventing light-induced peroxidation and interrupting photosynthesis as a result. This herbicide has been mainly used in the prevention of certain perennial broadleaved and grass weeds during the pre-emergence of rice.

Presence of herbicide residues in surface water, soil leads to potential risk for aquatic plants. Paddy herbicides are of high-risk concern for aquatic plants, because they easily flow out from paddy fields into rivers, with toxic effects [5]. Residues of chloroacetanilide herbicides are extremely toxic to the aquatic organism caused the long-term adverse effects on the aquatic environment. Pretilachlor dissipated to below detectable limit at 10 DAA in flood water. The half-life of pretilachlor varied from 3.9-10.0, 3.4- 8.5, 0.87-1.52 days for soil, rice plant and flood water, respectively [6]. Pretilachlor has higher adsorption on the sediment suggest that pretilachlor disappearance from the water was mainly the result of degradation during the period of 18 to 27 days after pesticide application under field conditions [7]. Pretilachlor is a relatively non-persistent herbicide with 50% degradation time values of 3.5 and 7 to 10 days in paddy water and sediment, respectively [8].

Studies of European Commission [9] have shown that the DT_{50} of oxadiargyl in soil was 15, 25, 25, 9 days in Italy, UK, France and Spain respectively. DT_{90} values varied between 42 to 214 days in European nations. Studies on degradation of pretilachlor applied to rice at 1.0 and 2.0 kg i.e. /ha revealed that residues of pretilachlor persisted up to 40 days when applied at the recommended rate and up to 60 days when applied at double the recommended dose.

The soil-half-life of pretilachlor applied to rice varied from 11.9 days to 16.9 days at 1.0 and 2.0 kg application respectively [10]. Several experiments were conducted to determine the persistence of the pretilachlor in soils, rice straw and grain at various locations in India. However, data on the residue concentration of pretilachlor in surface/sub-surface aquifers is Telangana situation, where it is used very widely, has not been studied so far.

Methodology

This experiment was conducted for two years i.e. during *Kharif* seasons (June to October months) of 2014 and 2015. During the first year, water samples were collected from the aquatic bodies (open-wells, tanks, canals, field drains) located in rice growing areas under the Nagarjuna Sagar Project (NSP) left canal command area. All the sampling sites were located in the Nalgonda district of the Telangana state (**Table 1**). Samples were collected three times [at transplanting stage (01-09-2014), 15 days after transplanting (DAT) (15-09-2014) and 30 DAT (30-09-2014)]. In the year 2015, due to drought conditions, water was not released in NSP left canal command area. Hence, sampling was done in rice-growing regions in Karimnagar district of Telangana **(Table 2)**. During 2015, samples (22) were collected two times (10 DAT and 25-30 DAT stage) during crop growing season from tanks, open wells, bore wells etc.

Table 1 Sampling site details

S. No	Source of water sample	Location of the sampling site	GPS Coordinates
2014			
1.	Drain	Halia village	$16^0$47′32.9 ″ $79^0$20′ 06.6″
2	Bore well	Ibrahimpet village	$16^0$48′ 02.9″ $79^0$20′ 11.6″
3	Canal	Halia – Miryalguda Road	$16^0$48′ 05.3″ $79^0$20′ 30.5″
4	Irrigation Tank	Vengannagudem village tank	$16^0$49′ 46.4″ $79^0$24′ 27.7″
5	Canal	Mukundapuram village	$16^0$49′ 56.6″ $79^0$26′ 27.7″
6	Irrigation tank	Thummadam village	$16^0$47′ 46.3″ $79^0$25′ 48.2″
7	Borewell	Thummadam village (roadside)	$16^0$48′ 35.9″ $79^0$26′ 02.7″
8	irrigation tank	ARS, Kampasagar farm	$16^0$50′ 02.9″ $79^0$26′ 59.6″
9	Open well	ARS, kampasagar farm	$16^0$50′ 54.8″ $79^0$27′ 07.2″
10	Drainage Channel	Babusaipet village	$16^0$51′ 25.7″ $79^0$28′ 36.6″
2015			
1.	Irrigation tank	Gagireddipally village	$18^0$12′ 52.8″ $79^0$09′ 22.6″
2	Irrigation Tank	Indurthi village	$18^0$13′ 24.5″ $79^0$07′ 51.4
3	Borewell	Indurthi village	$18^0$13′ 50.8″ $79^0$08′ 28.2″
4	Irrigation Tank	Chigurumamidi village	$18^0$14′ 11.8″ $79^0$11′ 34.8″
5	Open well	Rekonda village	$18^0$14′ 18.2″ $79^0$14′ 05.7″
6	Bore well	Bommanpally village	$18^0$13′ 38.6″ $79^0$14 ′ 19.1″
7.	Bore well	Mahmadapur village	$18^0$09′ 46.3″ $79^0$14 ′ 24.1″
8.	Irrigation Tank	Koheda village	$18^0$09′ 51.2″ $79^0$05′ 40.0″
9.	Open well	Koheda village	$18^0$10′ 02.6″ $79^0$05′ 19.7″
10.	Bore well	Gotlamitta village	$18^0$12′ 11.3″ $79^0$07′ 21.8″
11.	Borewell	Narlapur village	$18^0$12′ 09.4″ $79^0$07′ 56.9″
12.	Open well	Vinjapally village	$18^0$12′ 20.3″ $79^0$05′ 28.4″
13.	Open well	Bhimdevarapally villag	$18^0$06′ 19.4″ $79^0$21′ 20.9″
14.	Open well	Vangara village	$18^0$07′ 15.1″ $79^0$20′ 37.7″
15.	Open well	Gagireddypally colony	$18^0$06′ 16.1″ $79^0$22′ 09.3″
16.	Open well	Mutharam village	$18^0$03′ 56.4″ $79^0$20′ 50.4″
17.	Open well	Kothakonda village	$18^0$02′ 23.5″ $79^0$18′ 23.3″
18.	Open well	Gatla Narayanpur	$18^0$04′ 40.0″ $79^0$19′ 18.0″
19.	Open well	Gandhi Nagar	$18^0$06′ 07.5″ $79^0$13′ 05.8″
20.	Irrigation Tank	Gandhinagar	$18^0$05′ 56.9″ $79^0$13′ 05.8″
21.	Open well	Akkannapet village	$18^0$02′ 39.6″ $79^0$12′ 48.0″
22.	Bore well	Anthakkapet village	$18^0$00′ 43.6″ $79^0$12′ 12.6″

In NSP command area, irrigation to paddy fields is characterized by conventional irrigation system or "flow-through" system, wherein water is usually supplied mostly field to field, starting from the top of the basin to the lower end of the basin ending in a field drain. Whereas in Karimnagar district most of the paddy fields are irrigated from

tube-wells, open wells and in some case by water drawn from irrigation tanks. The field to field irrigation was not noticed in the second year of sampling.

Water samples were collected from various sources (open wells, tube wells, irrigation tanks, drainage channels, irrigation canals) adopting all the precautions required for the collection of representative samples. Samples were collected in HDPE sterile sample bottles of one-liter capacity. Collected water samples were stored in a deep freezer to prevent chemical decomposition, photo-decomposition and biodegradation of the herbicides and the samples were brought to room temperature at the time of analysis.

Samples were analyzed for residues of pretilachlor using the procedure given by [11]. Oxadiargyl residues were analyzed using the protocol outlined as in [12].

Results and Discussion

Recovery of pretilachlor in the water samples varied from 82.4 to 88.2 %. Oxadiargyl recovery varied from 78.2 to 82.4%. Limit of quantification (LOQ) for pretilachlor and oxadiargyl were 0.05 and 0.025 mg/l respectively.

First Year – 2014 (NSP Command Area)

At the time of first sampling, field preparation (puddling) and transplanting were in progress in most of the NSP command area. None of the samples collected were found to contain residues pretilachlor or oxadiargyl irrespective of the source. the pH of the water samples was neutral and samples were non-saline. The farmers have not completed the application of pre-emergence herbicides in the command area which might have resulted in non-detection of herbicide residues in the water samples.

In the samples collected during the second time (15 DAT), oxadiargyl residues could not be detected in any of the water samples (**Table 3**) irrespective of the source. Studies European commission (2002) had shown that the hydrolytic degradation half-life of oxadiargyl was 7.3 days and photolytic degradation half-life was 25.5 hours and the oxadiargyl in water rapidly moves from water to soil/sediments. These attributes of oxadiargyl might have resulted in its rapid degradation in water and its adsorption onto sediment/ soil which resulted in complete absence of oxadiargyl in water samples. Pretilachlor residues were detected in three water samples (sample 1, 8 and 10) in the water samples collected at 15 DAT. Pretilachlor residues could be detected in water samples collected from both the drainage channels (0.052 and 0.081 mg/l) and one tank (0.071 mg/l in small irrigation tank which collects drainage water from the rice fields in the upper reaches). pH and EC of the water samples did not differ significantly compared with the first sampling. In a survey conducted (13) a wide distribution pattern with more than 79% of the water samples with pretilachlor residues was noticed in Malaysia. Pretilachlor residue concentration ranged from 0.05 to 5.00 µg/L was observed in water samples collected during two years of study. The highest residue level reached was 25-50 µg/L.

Table 2 Other details of the sampling locations

1. Season and year	*Kahrif* -2014	*Kahrif* -2015
2. Dominating weed species	*Echinocloa colona, Echinocloa crusgalli, Cyperus iria, Eclipta alba, Ammania baccifera*	*Echinocloa colona, Echinocloa crusgali, Cyperus iria, Eclipta alba, Scirpus supinus*
3. Herbicide applied	Pretilachlor or oxdiargyl	Pretilachlor or oxdiargyl
(a) Method of application	Sand mixed broadcast	Sand mixed broadcast
(b) Dose and time of application	Pretilachlor : 0.625 kg a.i. /ha Oxadiargyl : 0.100kg a.i./ha (3-5 days after transplanting)	Pretilachlor : 0.625 kg a.i. /ha Oxadiargyl : 0.100kg a.i./ha (3-5 days after transplanting)
(c) Spray volume and nozzles used	Herbicide is mixed with sand broadcasted in the field	Herbicide is mixed with sand broadcasted in the field
(d) Control efficiency	More than 70 % compared unused plots up to 30 DAS	More than 80 % compared unused plots up to 30 DAS

In the third spell of sampling, water samples collected from two sources viz., sample 8 and 10 have shown the presence of pretilachlor residues and residues could not be detected in all other eight sources. However, the residue concentration decreased compared to the second spell of sampling (0.056 and 0.061 mg/l respectively). Oxadiargyl residues in all the water samples were BDL. In the third spell of sampling also other water properties (pH and EC) did not change significantly. In a laboratory microcosm, [14] found that 10 days after the treatment, 57.0% of the initially

applied pretilachlor was still present in the surface water and 20.5% in the soil surface (0–2 cm). These amounts remained almost constant until 30 days after the treatment, showing that no degradation occurred at that time.

Second Year – 2015 (Karimnagar District)

Transplanting and herbicide application was completed 7-10 days before the first spell of sampling in most of the sample collection area in Karimnagar district. None of the samples drawn from the irrigation tanks, open wells or bore wells were found to contain residues pretilachlor or oxadiargyl irrespective of the source (Table 4) . Samples collected from none of the sources were saline and the pH of the water samples was neutral to moderately alkaline. In the samples collected during the second sampling also pretilachlor or oxadiargyl residues were below the detection limit.

Table 3 Analytical details of water samples collected during 2014

Sample No	Source of water sample	First sampling				Second sampling				Third sampling			
		pH	EC (dS/m)	PR	OR	pH	EC (dS/m)	PR	OR	pH	EC (dS/m)	PR	OR
1	Drainage Channel	7.22	0.21	BDL	BDL	7.12	0.32	0.052	BDL	7.11	0.33	BDL	BDL
2	Bore well	6.98	0.13	BDL	BDL	7.02	0.11	BDL	BDL	6.94	0.09	BDL	BDL
3	Canal	6.87	0.05	BDL	BDL	6.92	0.04	BDL	BDL	6.98	0.05	BDL	BDL
4	Irrigation Tank	7.08	0.12	BDL	BDL	7.12	0.21	BDL	BDL	7.11	0.26	BDL	BDL
5	Canal	6.85	0.06	BDL	BDL	6.99	0.05	BDL	BDL	7.12	0.05	BDL	BDL
6	Irrigation tank	7.14	0.11	BDL	BDL	7.16	0.19	BDL	BDL	7.21	0.23	BDL	BDL
7	Borewell	6.91	0.12	BDL	BDL	7.02	0.11	BDL	BDL	7.11	0.14	BDL	BDL
8	Irrigation tank	7.42	0.34	BDL	BDL	7.55	0.41	0.079	BDL	7.58	0.40	0.066	BDL
9	Open well	6.95	0.09	BDL	BDL	6.86	0.11	BDL	BDL	7.21	0.13	BDL	BDL
10	Drainage Channel	7.21	0.22	BDL	BDL	7.23	0.25	0.081	BDL	7.19	0.28	0.062	BDL

PR: pretilachlor concentration in water (mg/kg), OR : Oxadiargyl concentration in water (mg/kg)

Table 4 Analytical details of water samples collected during 2015

Sample No	Source of water sample	First sampling				Second sampling			
		pH	EC	PR	OR	pH	EC	PR	OR
1	Irrigation tank	7.89	1.12	BDL	BDL	7.92	0.96	BDL	BDL
2	Irrigation Tank	7.92	1.41	BDL	BDL	7.85	1.11	BDL	BDL
3	Bore well	7.65	0.54	BDL	BDL	7.54	0.42	BDL	BDL
4	Irrigation Tank	7.84	0.86	BDL	BDL	7.78	0.65	BDL	BDL
5	Open well	7.25	0.24	BDL	BDL	7.42	0.11	BDL	BDL
6	Bore well	7.54	0.65	BDL	BDL	7.61	0.54	BDL	BDL
7	Bore well	7.71	0.45	BDL	BDL	7.54	0.32	BDL	BDL
8	Irrigation Tank	8.12	0.55	BDL	BDL	8.24	0.21	BDL	BDL
9	Open well	7.25	0.51	BDL	BDL	7.25	0.32	BDL	BDL
10	Bore well	7.41	0.21	BDL	BDL	7.25	0.26	BDL	BDL
11	Bore well	8.12	0.42	BDL	BDL	8.51	0.31	BDL	BDL
12	Open well	7.54	0.21	BDL	BDL	7.32	0.26	BDL	BDL
13	Open well	7.42	0.21	BDL	BDL	7.45	0.31	BDL	BDL
14	Open well	7.56	0.31	BDL	BDL	7.51	0.41	BDL	BDL
15	Open well	7.32	0.41	BDL	BDL	7.23	0.25	BDL	BDL
16	Open well	8.12	0.25	BDL	BDL	8.56	0.18	BDL	BDL
17	Open well	8.06	0.18	BDL	BDL	8.26	0.11	BDL	BDL
18	Open well	7.55	0.32	BDL	BDL	7.44	0.26	BDL	BDL
19	Open well	8.21	0.15	BDL	BDL	8.19	0.09	BDL	BDL
20	Irrigation Tank	7.12	0.12	BDL	BDL	7.45	0.25	BDL	BDL
21	Open well	7.25	0.25	BDL	BDL	7.26	0.68	BDL	BDL
22	Bore well	7.65	0.84	BDL	BDL	7.44	0.77	BDL	BDL

PR: pretilachlor residue concentration in water (mg/kg), OR : Oxadiargyl residue concentration in water (mg/kg)

Analytical results of the pretilachlor and oxadiargyl residue analysis in water samples collected from the rice-growing areas in NSP left canal command area and Karimnagar districts showed that oxadiargyl residues were not detected in water samples collected during both the years. However, pretilachlor residues could be detected during second and third sampling during 2014. Presence of pretilachlor residues in water samples collected from canal command areas (during the first year) indicated that, in the canal command areas where field to filed irrigation is customary, there is a possibility for herbicide residues originating from a field to be transmitted to downstream fields through irrigation water or leaching. Such transportation might have resulted accrual of pretilachlor residues in the water reaching the field drains. This hypothesis is corroborated by the observed pretilachlor residues in water samples only from field drains rather than in samples collected from other aquifers in NSP left canal command area. Absence of field to field irrigation and prevalence of small contiguous areas under rice (which act as a source of herbicide residues) resulted in the non-appearance of herbicide residues in water samples collected in Karimnagar district. Results of [7] showed pretilachlor concentration in the paddy water decreased by more than 90% during the first three weeks after the treatment. The amount of herbicide in the paddy water gradually fell to levels below the sensitivity of the analytical method when water circulation was re-established.

Conclusion

Results of the present study indicate the possible contamination of surface aquifers (such as irrigation tanks and field drains) by pretilachlor residues in the canal command areas where field to field irrigation is practiced. Oxadiargyl residues were not found in surface and sub-surface aquifers.

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