

# Contamination of rice field water with sulfonylurea and phenoxy herbicides in the Muda Irrigation Scheme, Kedah, Malaysia

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**Abstract** The purpose of the present study was to investigate the potential risk of herbicide contamination (2,4-dichlorophenoxy (2,4-D), 2-methyl-4-chlorophenoxyacetic acid (MCPA), metsulfuron, bensulfuron, and pyrazosulfuron) in the rice fields of the Muda Irrigation Scheme, Kedah, Malaysia. The study included two areas with different irrigation water sources namely non-recycled (N-RCL) and recycled (RCL) water. Periodic water sampling was carried out from the drainage canals during the planting period of the wet season 2006/2007 and dry season 2007. The HPLC-UV was used to detect herbicide residues in the water samples collected from the rice fields. The results showed that the concentration of sulfonylurea herbicides such as bensulfuron and metsulfuron in the rice field was 0.55 and 0.51 µg/L, respectively. The potential risk of contamination depended on the actual dosage of each herbicide applied by farmers to their rice fields. The potential risk of water pollution by the five herbicides studied in the area with RCL water tended to be more widespread compared to the area with N-RCL water due to surface water runoff with higher levels of weedicides to the surrounding areas. During the two seasons, 50–73 % of the water samples collected from the area receiving RCL water contained the five herbicides studied at concentrations of more than 0.05 µg/L, and this percentage was higher than that from the areas

receiving N-RCL water (45–69 %). During the wet season, the overall total mean concentration of the eight herbicides found in the samples collected from the area with RCL water (6.27 µg/L) was significantly higher ( $P < 0.01$ ) than that from the area receiving N-RCL water (2.39 µg/L). Meanwhile, during the dry season, there was no significant difference ( $P > 0.05$ ) in the herbicide concentrations between the areas receiving RCL (6.16 µg/L) and N-RCL water (7.43 µg/L) water.

**Keywords** Herbicides · Non-recycled/recycled irrigation system · Water pollution · Contamination

## Introduction

The Muda Irrigation Scheme (which is under the Muda Agricultural Development Authority (MADA)) in Kedah is the largest rice granary area in Malaysia. It is the main area for rice production; hence, it is also known as the rice bowl of Malaysia. The sustainability of rice production in the Muda Scheme is attributable to the provision of irrigation facilities namely direct or non-recycled as well as recycled water to the rice agro-ecosystem and the implementation of double cropping of rice using the direct seeding crop establishment method (Ho 1998; Ayano et al. 2004).

Currently, direct seeding is the dominant rice crop establishment method in the rice field areas of the Muda Irrigation Scheme since the initiation of this cultivation method in 1970 (Ismail et al. 1998). Even more serious than pests and/or diseases, weeds are the most severe

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and widespread biological constraint to rice production. The direct seeding rice crop establishment technique requires a high level of herbicide inputs for effective weed management especially if water management is inadequate (Rajan 2002). Therefore, the control of weeds is an essential component for productive rice culture. Herbicides are an economical component for controlling weeds; thus, with proper selection and technical information, most farmers are able to use herbicides at costs lower than any other weed control option (Zoschke and Quadranti 2002). Chemical control using herbicides will still be considered as the main method of weed control in the twenty-first century (Harada 2001).

Pesticide products have been used in the rice fields of the Muda Irrigation Scheme since 1980, and it is estimated that approximately 1318 t of active ingredients of pesticides was applied in the year 1989 alone (Zanella et al. 2002). The total budget for pesticide expenditure in Malaysia increased from RM307 million in 2002 to RM504 million in 2007 with herbicides accounting for approximately 71 % (Anon 2009). Application of herbicides is still the main method practiced by farmers to effectively control the growth of weeds in rice fields.

The high weed population in direct-seeded rice fields necessitates the use of herbicides to control weed infestations. Pesticide use causes an adverse impact on the environment. Over 95 % of sprayed herbicides reach the target species, but the rest may be lost on non-target matter such as air, water, bottom sediments, and food (Miller 2004). Indiscriminate use of pesticides can cause undesirable effects to the rice ecosystem as well as the health of farmers where pesticide poisoning and environmental pollution are of major concern to the Muda Agricultural Development Authority (MADA) (Capel and Larson 2001).

The continuous use of agrochemicals in the Muda area has given rise to environmental pollution problems which in turn would influence the water quality of the agro-ecosystem. It was reported that pesticide pollution of surface and groundwater has become a growing concern in tropical countries (Blair et al. 1990; Ismail and Khalithasan 2002; Ismail et al. 2002). Monthly monitoring has indicated that the water resources in the Muda rice-growing areas contain pesticide compounds (Cheah and Lum 1998).

The environmental pollution from herbicide application is heaviest in water bodies. Pesticides in rice fields are carried by irrigation, drainage, and

runoff water sequentially from the rice fields to drainage canals, streams, and main rivers whereby they are widely dispersed through the water system (Bouman et al. 2002). The provision of the recycled irrigation system for improving the water resource efficiency may cause the reintroduction of pesticides into the irrigation canals, as new water sources for other rice field areas (Cheah and Lum 1994).

The highest pollution of the rice agro-ecosystem is estimated to occur during the planting period of each season (Ding et al. 2000). During this time, farmers intensively apply herbicides to control weeds in their fields. With the rice field area flooded by irrigation water or rainfall, there is high possibility that chemical residues after application may flow through the surface water runoff into the drainage canal system. If farmers have low awareness toward environmental contamination, they could be careless during cleaning of their spraying equipment or they could indiscriminately dispose of pesticide containers into the rice fields or nearby canals, thus posing a high risk of environmental contamination. Therefore, water bodies around rice cropping areas have the probability of containing high concentrations of pollutant materials.

Herbicide products contain 2,4-dichlorophenoxy (2,4-D), 2-methyl-4-chlorophenoxyacetic acid (MCPA), pyrazosulfuron, bensulfuron, metsulfuron, and many other chemicals that are applied by farmers to control weeds in the rice fields of the Muda scheme. Therefore, these herbicide residues that are present in the surface water system of the rice agro-ecosystem are being investigated. Studies on the pollution levels of herbicides in the Muda area are to be carried out on two different types of irrigation water namely recycled and non-recycled water. To date, no reports on the level of pollution by pesticides have been documented particularly for the study area.

The objective of the present study was to investigate the contamination level of herbicide residues and the potential risk of herbicide pollution in the two rice field areas under recycled and non-recycled irrigation water systems. Periodically, water sample collection during the planting season was carried out to observe the presence and/or levels of herbicide residues. A large number of surface water samples were collected from the rice fields and canal systems of the two areas during the wet season 2006/2007 and the dry season 2007.

## Materials and methods

### Study areas

The study site was located in the central portion of the MUDA scheme near Alor Setar, the capital of Kedah. The study included two rice field areas with different irrigation water systems namely non-recycled (N-RCL) (N 6° 14' and E 100° 21') and recycled (RCL) (N 6° 09' and E 100° 20'). The water source for the N-RCL area was the Alor Changleh canal passing Alor Changleh left bund drain (ACLBD) 4-upper, and for the area with RCL water, the water came from the ACLBD 4-lower canal. When rainfall was late, water from the rivers and drainage canals which collected in a river at Alor Gunung was recycled and used as the irrigation water source for the area receiving water after passing ACLBD 4-lower.

Three sampling stations for collecting the water samples were selected at the drainage systems for areas with both the N-RCL and RCL water. In the area with N-RCL water, the water samples were taken from the drainage canals at Kampung Telaga Batu, Kota Rentang, and Pulo Kerengga. Meanwhile, in the area with RCL water, the water samples were taken from the drainage canals at Kampung Alor Gunung, Kampung Prumpung, and Kampung Mergung. A detailed map of the study sites of the areas supplied with N-RCL and RCL water can be seen in Fig. 1

### Water sampling activities

Field study activities were carried out during the wet season (October 2006–Jan 2007) and dry season (April–July 2007). The water sampling activities were conducted during the planting season from 25 September to 20 October 2006 for the wet season and from 20 April to 30 May 2007 for the dry season.

Water sampling activities were carried out regularly at each sampling station. “Grab water samples” were taken using 1-L Kemmerer<sup>®</sup> bottles (USA) from three depths, namely the bottom (5–20 cm from water surface), middle, and (5–15 cm from water surface) top (5–10 cm under the water surface). The water samples taken from the three different depths were combined together in a pail and then mixed thoroughly until homogeneous. A portion of the water (2.0–2.5 L) was poured into a 2.5-L amber bottle; then, concentrated 1 M H<sub>2</sub>SO<sub>4</sub> was added until pH 2 was obtained. The

bottle was covered with a Teflon cap and kept in an ice box maintained at temperature 4 °C. Water samples were also collected from the rice field near the sampling station. Each water sample was taken from ten points, combined in a pail, and then mixed thoroughly until homogeneous. A portion of the water (2.0–2.5 L) was poured into a 2.5-L amber bottle; then, concentrated 1 M H<sub>2</sub>SO<sub>4</sub> was added until pH 2 was obtained. The bottle was covered with a Teflon cap and kept in an ice box at a temperature of 4 °C. All water samples were stored in the cold room at 4 °C prior to analysis.

### Analytical method for multi-residue herbicide determination

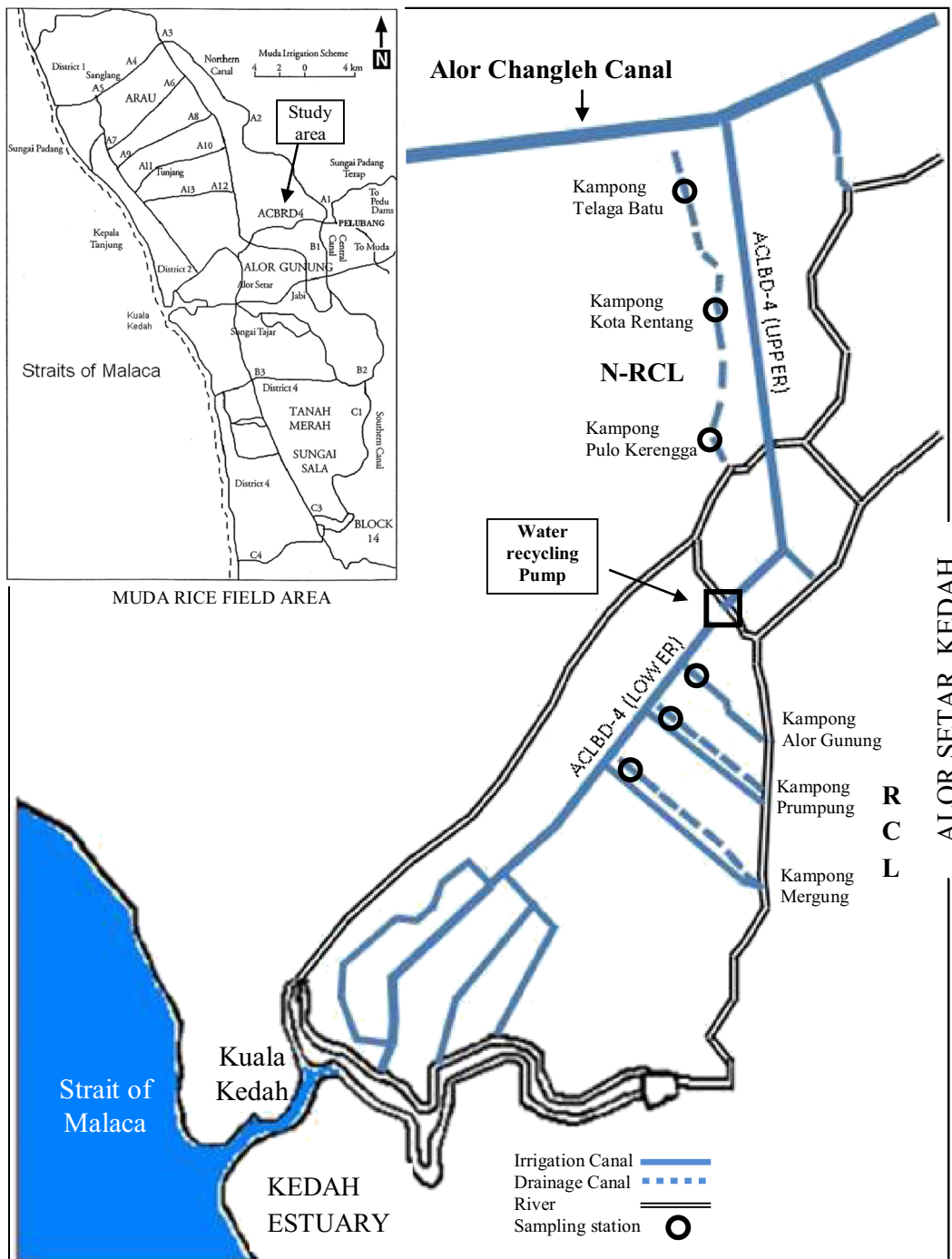
The determination of multi-residue such as 2,4-D, MCPA, pyrazosulfuron, metsulfuron, and bensulfuron was undertaken using HPLC-UV as suggested by Tran et al. (2007). The solid-phase extraction (SPE) method (with ISOLUTE<sup>®</sup> ENV<sup>+</sup> cartridge) was used to extract the herbicides in the filtered water samples.

### HPLC-UV condition

A Waters<sup>™</sup> HPLC Carbamate Analysis System model, CAS S/N MX6MM20099M with a dual-pumping system, controlled by Waters 600 Controller with E97600 460M series was used. The detector used was a Waters<sup>™</sup> Tunable Absorbance with UV wavelength of 230 nm. The column used was a Nova-Pak<sup>®</sup> C<sub>18</sub>, with 4.5- $\mu$ m particle size (150 mm  $\times$  3.9 mm i.d.), serial no. 1128373511, and part no. WAT086344 (obtained from Water Co., Milford, MA, USA). The systems were equipped with the In-line Degasser (serial E97ILD194M) to avoid bubbles in the mobile phase during analysis. The gradient elution of the mobile phase was conditioned at 1 % ACN/min from 20 to 50 % ACN in 30 min of running time and the pH of the buffer (NH<sub>4</sub>COOH) adjusted to the value 3.97. The volume of injection was 20  $\mu$ L. The above method resulted in the best resolution, and the group herbicides (2,4-D, MCPA, pyrazosulfuron, metsulfuron, and bensulfuron) were clearly separated.

### The method for herbicide extraction

The solid-phase extraction (SPE) procedure was used for the extraction of the herbicide compounds, and the recovery study as proposed earlier was used with slight



**Fig. 1** Study site of the areas receiving non-recycled (N-RCL) and recycled (RCL) water in the central portion of the Muda Irrigation Scheme, Kedah, Malaysia (the sampling station sites are circled)

modification (Gonzalo et al. 2003; Zanella et al. 2000). A SPE cartridge (ISOLUTE® ENV+ 6 mL) was used for the determination of the target herbicides in the study. This SPE cartridge was attached to a manifold which

was prewashed with 5 mL methanol and 10 mL Milli-Q water. The washing was then discarded. To a 500-mL water sample in a Schott bottle, 5 g sodium sulfate was added. The bottle was then fastened with a stopper and

put on the orbital shaker for 5–10 min to allow the contents to mix homogeneously. The stopper was then removed, and 5 mL of HCOOH was added drop by drop using the Thermolyne Nuova II stirrer plate to adjust the pH value to 3.7. The mixture was then filtered through ALBET<sup>®</sup> filter paper size 7–10  $\mu\text{m}$  to eliminate particulate matter and debris, prior to extraction. The SPE tubing was immersed into the mixture, and the aspirator was switched on. With the aspirator on, the water was drawn through the cartridge. The flow rate of the water through the SPE cartridge was controlled by a pressure knob in order to get the water to elute drop by drop. A preliminary study on the effect of loading water samples through the SPE cartridge had shown that the suitable flow rate was 8–10 mL/min. After the contents had been completely drawn through the SPE cartridge, the empty bottle was rinsed with 5 mL distilled water. The rinsing was also passed through the SPE cartridge. The cartridge was then vacuum-dried and the excess water removed by opening the knob and allowing air to pass through the SPE cartridge for 15 min. The herbicide absorbed in the cartridge was eluted with 5 mL of methanol, poured into a vial, and dried under a nitrogen stream to obtain a final volume of 1 mL. The solution was then filtered using the Minisart<sup>®</sup> membrane filter, 0.45  $\mu\text{m}$ . It was then kept in the freezer at a temperature of  $-4\text{ }^{\circ}\text{C}$  before being injected into the HPLC-UV.

The herbicide concentration (in  $\mu\text{g/L}$ ) in the spiked water samples was calculated by comparing the peak area response between the sample and the standard herbicide. A series of the two mixtures of standard solutions, comprising the five standard herbicides 2,4-D (purity 98.8 %), MCPA (99.1 %), metsulfuron (99.1 %), bensulfuron (95.8 %), and pyrazosulfuron (98.8 %) of Dr. Ehrenstorfer standards, Germany, with concentrations ranging from 0.01 to 10  $\mu\text{g/mL}$  were used for the recovery study of the compounds in the water samples. For each concentration, there were three replicates. These standard solution mixtures were spiked with 500 mL of water from rice fields free of herbicide residues, in 500-mL Schott bottles. The fortified water samples then underwent current extraction for determination of the herbicide residue by HPLC-UV as explained earlier. The percentage recovery was calculated by comparing the peak areas between the spiked water samples divided by that of the actual standard herbicides.

## Data analysis

The data obtained was analyzed using the SPSS 11. The comparison means of the concentration of herbicide compound variables were between the N-RCL and RCL water and the wet and dry seasons.

## Results and discussion

### Analytical performance

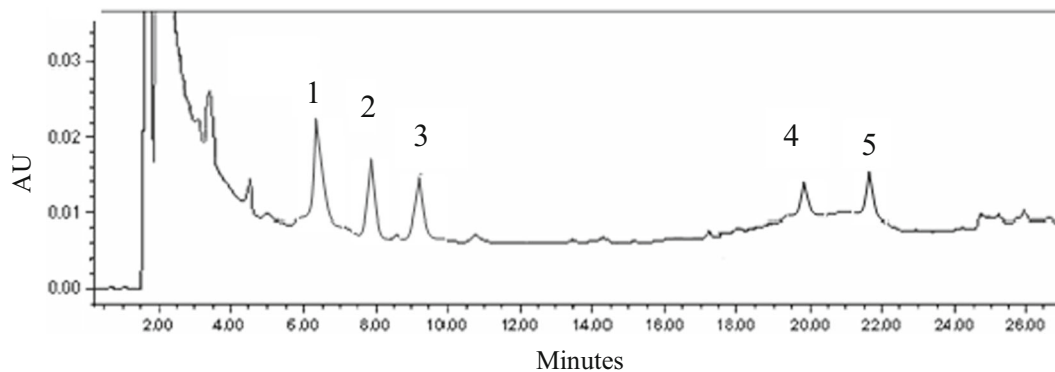
Effective water pollution control requires analytical methodology that allows for the correct identification and measurement of the low concentrations of herbicide residues in water samples. There are many methods for determination and quantification of herbicides in water samples using the HPLC or GC systems after the SPE using various types of cartridges (Wells and Yu 2000; Cerejeira et al. 2003).

The herbicides in a mixture solution containing herbicides such as 2,4-D, MCPA, metsulfuron, bensulfuron, and pyrazosulfuron were clearly separated using the HPLC-UV system with the retention times of 6.695, 8.093, 9.323, 20.144, and 21.990 min for 2,4-D, MCPA, metsulfuron, bensulfuron, and pyrazosulfuron, respectively (Fig. 2).

The calibration curves for the five herbicides studied were linear for the concentration range of 0–0.10 mg/L with the correlation coefficient being higher than 0.998 for all the herbicides studied. The limit of detection (LOD) using these methods was 0.025  $\mu\text{g/L}$  for 2,4-D, MCPA, metsulfuron, bensulfuron, pyrazosulfuron, and 0.05  $\mu\text{g/mL}$  for metsulfuron-methyl. The average recovery rate for all the live herbicides in the rice field water samples ranged from 88.1 to 101 %.

The results of the study are similar to those of other research studies in that the method of extraction using SPE and determination using the HPLC or GC systems were optimized to determine the herbicide compounds in rivers and other natural water sources, where 2,4-D and MCPA were at low concentrations ranging from 0.02 to 0.25  $\mu\text{g/L}$  and the percentage recovery ranged from 70 to 120 % (Ding et al. 2000; Pena and Silveira 1997; Tran et al. 2007; Vink and Poll 1996). The sulfonylurea group which includes bensulfuron and pyrazosulfuron could be determined from natural water samples at low concentrations of 0.01–0.1  $\mu\text{g/L}$  with percentage recovery ranging from 70 to 120 %





**Fig. 2** Typical HPLC-UV chromatographic peaks of 2,4-D (1), MCPA (2), metsulfuron (3), bensulfuron (4), and pyrazosulfuron (5), extracted from the water samples spiked at the fortification level of 0.5  $\mu\text{g/L}$  of the standard mixture solution

(Deschamps et al. 2003). Therefore, the procedure and methods which were carried out in the present study were good, reproducible, and accurate for determination and quantification of the five herbicides studied from water samples taken from the rice fields of MADA.

#### Field conditions of the study sites

Field study activities were carried out from 25 October 2006 to 20 January 2007 for the wet season 2006/2007 and from 20 April to 30 May 2007 for the dry season. Rice cultivation methodology in the study area was dominated by direct seeding. The seeding activity carried out by farmers started from September to October 2006 for the wet season and from April to May 2007 for the dry season. The whole study area was cropped by 11 October 2006 for the wet season and 8 May 2007 for the

dry season (Table 1). It should be noted that there were more areas using RCL water than those with N-RCL water.

The seeding schedule between areas using N-RCL and RCL water for the wet season was not different. Meanwhile, for the dry season, areas with N-RCL water started planting earlier due to the shortage of irrigation water caused by the delay of rainfall. The planting activities at the study area followed the scheduled time of water distribution.

The water pumping activities for irrigation with RCL water started operating due to the occurrence of delayed rainfall especially during land preparation, weed control, and fertilizing. The source of the water was from rivers and water discharged from the rice fields at the upper site areas as well as the water from the N-RCL area through the canal system. The water was stored in a

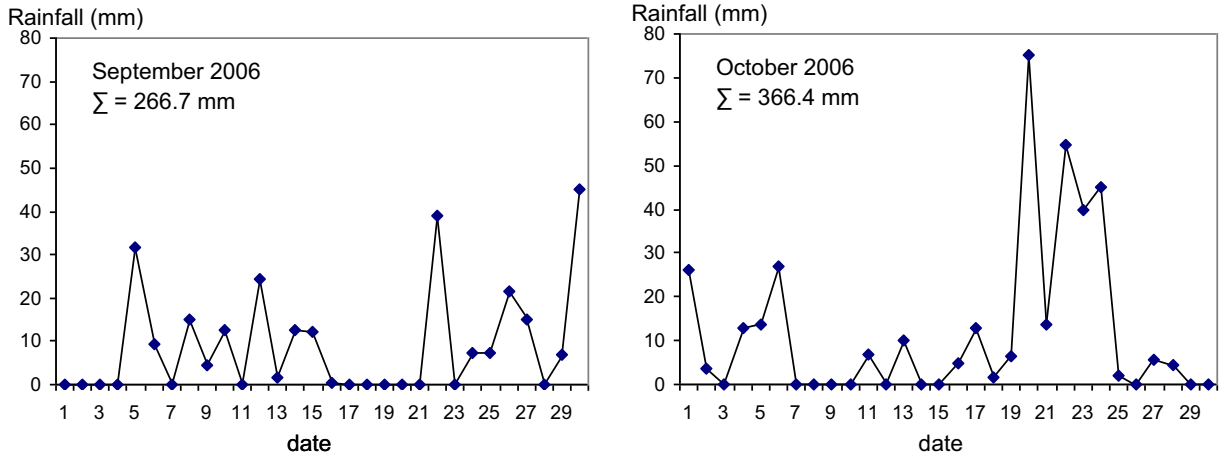
**Table 1** The percentage area planted at different months in the wet season 2006/2007 and the dry seasons 2007

Location	Area (ha)	Sept 06		Oct 06		April 07		April/May 07	
		19 (%)	27 (%)	3 (%)	11 (%)	17 (%)	24 (%)	30 (%)	8 (%)
Non-recycled water	457.5								
Telaga Batu	na	5	45	97	100	45	74	98	100
Kota Rentang	na	5	45	97	100	37	65	94	100
Pulo Kerengga	na	5	45	98	100	50	90	95	100
Recycled water	699.9								
Alor Gunung	226.4	7	40	70	100	4	33	79	100
Prumpung	331.7	2	7	78	100	12	36	65	100
Mergung	141.8	10	10	60	100	20	40	90	100

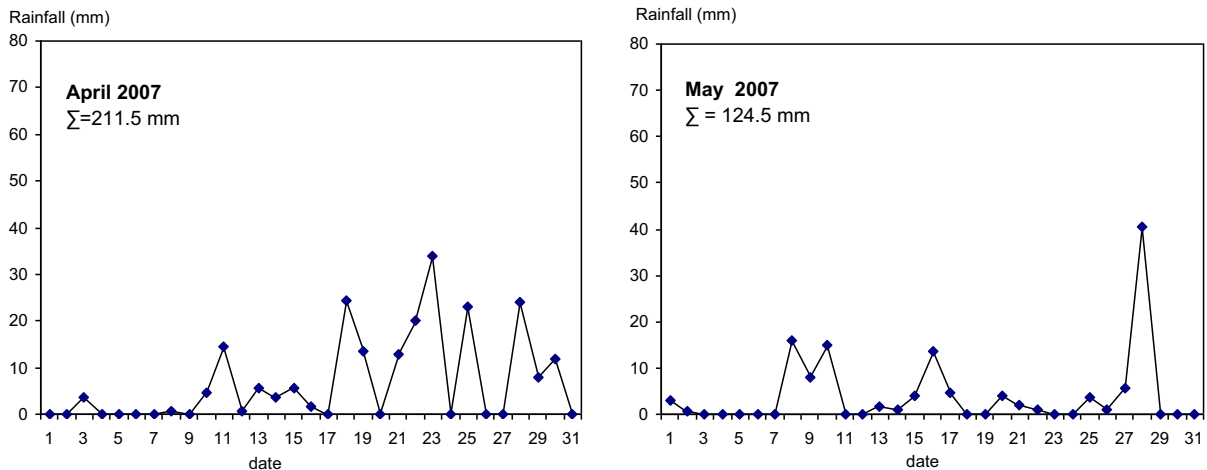
Data source: farmer's organization at Kuala Sungai and Kepala Batas

na data not available

### Wet Season 2006/2007



### Dry Season 2007



**Fig. 3** Daily rainfall during planting activities at the study site (source: Climate Station Kuala Sungai, Kedah, Malaysia)

river and then pumped back to the fields passing through the ACLBD 4-lower canal at Kampung Alor Gunung, as the water source for the areas supplied with of RCL water. During the seeding season, the total rainfall was 633.1 mm (Sept–Oct 06) for the wet season which had much higher rainfall compared to 336.0 mm (April–May 07) in the dry season. Daily rainfall data from the meteorological station in Kuala Sungai showing the difference in the amount of rainfall for the two seasons can be seen in Fig. 3.

The direct seeding method of crop establishment resulted in very high weed population, and it was also difficult to control the weeds. The high weed population in the direct-seeded rice fields necessitated the use of

more herbicides to control the weed infestations compared to the transplanting method where farmers hardly used herbicides to control weeds. Based on interviews conducted with the farmers, herbicide spraying of pre-emergence herbicide started within 4 DAS followed by postemergence herbicide spraying until the initial flowering stage. In general, farmers sprayed herbicides twice, but some farmers sprayed more often depending on the intensity of the weed infestation in the rice fields. Generally, motorized sprayers with the capacity of 20–25 L per tank were used for the spraying of herbicides.

In general, farmers only knew the commercial name of the herbicide products that they used but did not know the chemical name and content of the active

**Table 2** Herbicide concentration detected in the rice field water of areas receiving N-RCL and RCL irrigation water during the wet season 2006/2007 and the dry season 2007

Herbicides	Wet season 2006/2007			Dry season 2007		
	<i>n</i>	Minimum ( $\mu\text{m/L}$ )	Maximum ( $\mu\text{m/L}$ )	<i>n</i>	Minimum ( $\mu\text{m/L}$ )	Maximum ( $\mu\text{m/L}$ )
<b>N-RCL</b>						
2,4-D	38	nd	8.55	50	nd	322.65
MCPA	38	nd	2.28	50	nd	236.12
Pyrazosulfuron	38	nd	4.13	50	nd	7.82
Bensulfuron	38	nd	5.08	50	nd	3.78
Metsulfuron	38	nd	1.75	50	nd	9.57
<b>RCL</b>						
2,4-D	50	0.11	103.99	56	nd	329.42
MCPA	50	nd	82.75	56	nd	354.28
Pyrazosulfuron	50	nd	63.22	56	nd	3.60
Bensulfuron	50	nd	60.76	56	nd	5.03
Metsulfuron	50	nd	32.69	56	nd	14.92

nd not detected= $<0.05 \mu\text{g/L}$ , *n* number of samples

ingredients. Based on the manner of application, there were two types of herbicide products used by farmers namely the preemergence and postemergence herbicides. Commercial herbicide products containing of 2,4-D, MCPA, pyrazosulfuron, bensulfuron, and metsulfuron, respectively, are known as postemergence herbicides, and butachlor, oxadiazon, and oxadiargyl are known as preemergence herbicides. These herbicides were applied on to the rice fields under flooded water conditions ( $<15 \text{ cm}$ ) around the third week after seeding.

#### Herbicide residue levels in rice field water

Table 2 shows the herbicide residue levels observed in the rice field water for areas using N-RCL and RCL water during the wet season 2006/2007 and dry season 2007. The potential residue levels in areas using N-RCL and RCL water were different for the two seasons. The areas receiving N-RCL water, during the wet season, were seen to have herbicide residue concentrations much lower compared to those during the dry season. Meanwhile, for areas receiving RCL water, high residue concentrations were observed for both the seasons. The potential concentrations of weedicides of the sulfonylurea group, namely pyrazosulfuron, bensulfuron, and metsulfuron, were low. The maximum concentrations observed were as follows: 63, 61, and

33  $\mu\text{g/L}$  for pyrazosulfuron-ethyl, bensulfuron-methyl, and metsulfuron-methyl, respectively, in the areas with RCL water during the wet season, while it ranged from 9.57 to 3.78  $\mu\text{g/L}$  for areas receiving the N-RCL water.

Meanwhile, the sulfonylurea herbicides were used at low dosages ranging from 0.004 to 0.05 kg a.i./ha, and this accounted for the low concentrations of sulfonylurea compounds detected. These herbicides are commonly used by farmers at maximum dosage to control *Echinochloa crus-galli*, *Leptochloa chinensis*, and *Cyperus* spp., as it was observed that these grasses and sedges were dominant in the rice fields of the studied area. It was also reported that the growth of these weeds was dominant in most of the Muda rice field areas (Machado et al. 2006; Pane et al. 1998).

The weedicides 2,4-D and MCPA showed high residue concentration in the rice field water due to the higher-dosage application and also because the sampling was done soon after spraying, whereas the active ingredient residues of the weedicides such as pyrazosulfuron, bensulfuron, and metsulfuron showed lower concentrations, as the dosage used was considerably low. During the wet season, heavy rainfall after herbicide spraying could possibly have diluted the herbicide residue content in the rice field water.

The concentration levels of herbicide residues in the rice field water were hardly affected by the herbicide



and the volume of standing water at application time when sampling was done. During the wet season, the levels of residue in the rice field water for areas with the N-RCL water were much lower compared to those in areas with RCL water. The locations of the areas with N-RCL water were at the upper section compared to the areas receiving RCL water. When there was surplus water supply due to intensive rainfall, the excess water will easily flow out from the rice fields, thereby transporting the herbicide residues away from the rice fields. On the other hand, the areas with RCL water were in a bad condition due to improper drainage. When the overflow of water occurred after heavy rainfall, it was difficult to drain the water out of the rice fields. This condition may have caused high residue concentration levels of all the herbicides studied including the sulfonylureas in the rice fields. The residues of sulfonylurea herbicides such as pyrazosulfuron, bensulfuron, and metsulfuron were high during the wet season (see Table 2). According to Hamilton et al. (2003), the highest concentration observed in rice field water was immediately after application, at the day of spraying.

Herbicide concentration levels in drainage water

During the wet season of 2006/2007, the number of water samples collected was 58 and 70 from the areas with N-RCL and RCL water, respectively. About 62–97 % of the

collected water samples from the areas receiving N-RCL water contained 2,4-D, pyrazosulfuron, and metsulfuron, and only 36–41 % contained MCPA and bensulfuron with concentrations of more than 0.05 µg/L. Meanwhile, for the areas with RCL water, all of the five herbicides studied could be found in 49–86 % of the collected water samples. The spread of the herbicide pollutants in the average percentage of water samples which contained herbicide residues for areas with RCL water (73 %) was relatively higher compared to the areas supplied with N-RCL water (69 %) (Table 3).

The highest and average concentrations of herbicide residues in water samples collected from areas with N-RCL water were 14.74 (average 0.69), 5.73 (2.94), 3.59 (0.91), 3.16 (0.51), and 0.95 µg/L (0.11) for MCPA, 2,4-D, pyrazosulfuron, metsulfuron, and bensulfuron, respectively. Meanwhile, the highest and average concentrations for the areas with RCL water were 13.56 (average 3.79), 3.90 (1.32), 3.48 (0.38), 2.77 (0.45), and 1.14 µg/L (0.32) for 2,4-D, pyrazosulfuron, bensulfuron, MCPA, and metsulfuron, respectively (Table 3). The overall total mean of the five herbicide concentrations for the areas with RCL water (1.252 µg/L) was significantly higher ( $P>0.01$ ) compared to the areas receiving N-RCL water (1.032 µg/L) (Table 3).

During the dry season of 2007, the number of water samples collected was 78 and 120 for the areas receiving

**Table 3** Herbicide residue concentrations (µg/L) and percentage residue detected in drainage water samples of the areas receiving N-RCL and RCL water during the wet season 2006/2007

Herbicide	<i>n</i>	Min (µm/L)	Max (µm/L)	Mean	Samples detected (%)
N-RCL					
2,4-D	58	nd	5.73	2.94	97
MCPA	58	nd	14.74	0.69	41
Pyrazosulfuron	58	nd	3.59	0.91	79
Metsulfuron	58	nd	3.16	0.51	83
Bensulfuron	58	nd	0.95	0.11	36
RCL					
2,4-D	70	nd	13.56	3.79	80
MCPA	70	nd	2.77	0.45	49
Pyrazosulfuron	70	nd	3.90	1.32	74
Metsulfuron	70	nd	1.14	0.32	83
Bensulfuron	70	nd	3.48	0.38	51
<i>P</i> value				$P<0.01$	

nd not detected= $<0.05$  µg/L, *n* number of samples

**Table 4** Herbicide concentrations ( $\mu\text{g/L}$ ) and percentage residue detected in drainage water samples from areas supplied with N-RCL and RCL water during the dry season 2007

Herbicides	<i>N</i>	Min ( $\mu\text{m/L}$ )	Max ( $\mu\text{m/L}$ )	Mean	Detected samples (%)
N-RCL					
2,4-D	78	nd	12.52	1.72	54
MCPA	78	nd	32.41	3.17	51
Pyrazosulfuron	78	nd	1.76	0.26	31
Metsulfuron	78	nd	0.85	0.07	19
Bensulfuron	78	nd	7.23	0.54	32
RCL					
2,4-D	120	nd	14.49	1.70	45
MCPA	120	nd	25.86	1.99	47
Pyrazosulfuron	120	nd	2.04	0.32	32
Metsulfuron	120	nd	1.34	0.16	22
Bensulfuron	120	nd	9.58	0.55	28
<i>P</i> value				<i>P</i> =0.195	

nd not detected= $<0.05 \mu\text{g/L}$ , *n* number of samples

N-RCL and RCL water, respectively. The spread of the five herbicides studied in the areas with N-RCL and RCL water during the dry season was 37.4 and 34.8 %, respectively (Table 4), and these percentages were lower compared to the percentages during wet season (see Table 3). In the drainage water samples collected from both areas receiving RCL and N-RCL water, 2,4-D and MCPA could be found in 45–54 % of the water samples collected, while for the sulfonylurea group, bensulfuron and metsulfuron were found in fewer water samples (19–31 %) (Table 4).

The highest and average concentrations of herbicide residues in the water samples collected from the areas receiving N-RCL water were 32.41 (average 3.17), 12.52 (1.72), 7.23 (0.54), 1.76 (0.26), and 0.85  $\mu\text{g/L}$  (0.07) for MCPA, 2,4-D, bensulfuron, pyrazosulfuron, and metsulfuron, respectively. Meanwhile, for the areas with RCL water, the highest and average concentrations were 25.86 (average 1.99), 14.49 (1.70), 9.58 (0.55), 2.04 (0.32), and 1.34  $\mu\text{g/L}$  (0.16) for MCPA, 2,4-D, bensulfuron, pyrazosulfuron, and metsulfuron, respectively. However, the overall total mean concentrations of the five herbicides studied for the areas with N-RCL and RCL water were 1.15 and 0.94  $\mu\text{g/L}$ , respectively, which was not significantly different ( $P>0.05$ ) (Table 4).

The potential risk of herbicide contamination for areas receiving the N-RCL and RCL water was different depending on the season. During the wet season, the situation in both rice field areas was the same with

excess water. The intensity of rainfall could carry the herbicide residues from the rice fields through surface runoff to the drainage canals. The five herbicides studied were detected in most of the water samples collected (69–73 %) from areas with both types of irrigation water. Geographically, the areas with RCL water were flatter compared to the areas receiving N-RCL water. The excess water in the areas supplied with N-RCL water could be easily released through the drainage system, while the excess water remained stagnant in the areas receiving RCL water due to inadequate drainage. Therefore, the concentration of herbicides in the drainage water of the areas receiving RCL water was significantly higher than that of areas receiving N-RCL water due to the inadequate drainage in these areas.

On the other hand, during the dry season, the situation was different compared to the wet season, when there was a lack of water due to delayed rainfall in both areas. Hence, farmers especially from the N-RCL area used the standing water in the drainage canal as their water supply. Therefore, no water was allowed to be drained out from the rice fields to the RCL area. This may result in an accumulation of pesticide residues in the drainage water of the N-RCL area which was higher than the RCL area, although only 45–50 % of the drainage water samples collected from both areas had average concentrations of the five herbicides studied. It should be noted that 2,4-D and MCPA were the ubiquitous contaminants, as these compounds could be

detected in 51 to 54 % of all water samples collected as shown in Table 4.

According to Huber et al. (2000), herbicide residues in the water bodies of rice fields can be transported by surface water runoff through drainage canal systems to small and large rivers, whereby effecting wide dispersion throughout the water systems. The potential risk of herbicide residue contamination depends on the runoff rate. The runoff rates differ depending on environmental conditions such as rainfall and the amount of pesticides used. Farmers' awareness on the handling of pesticides and cleaning of spraying equipment as well as the disposal of pesticide containers is also very important in reducing environmental pollution.

Runoff has been shown to be a major non-point source of pesticide transportation to surface waters in agricultural areas (Kuivila and Foe 1995) and is dependent on the method of application and physico-chemical properties (such as the solubility, half-life, and  $K_{OC}$ ) of the pesticides, catchment variables of the surrounding area (Capel and Larson 2001; Merkle and Bovey 1974), environmental conditions such as rainfall and temperature, amount used per unit area, and the water management system (Kolpin et al. 2000). The catchment variables influencing runoff include the gradient of the terrain on which pesticides have been sprayed, crop type, organic carbon content of the soil, the size of the crop area, and the vegetation type (Cole et al. 1997).

The occurrence of intensive rainfall after herbicide spraying would increase the spread of herbicide pollutants through surface water runoff. The results of the present study revealed that the average number of collected water samples which contained herbicide compounds in the wet season was higher than that during the dry season. During the two seasons, the areas supplied with RCL water showed higher pollution spread compared to that of areas supplied with N-RCL water. It was assumed that the intensity of rainfall during the two seasons was not significantly different for both the areas with N-RCL and RCL water. Therefore, the geographic conditions and water management systems are the factors that influenced the potential risk of contamination of the two areas. The location of the area with N-RCL water is in the lower site of the RCL area, where the excessive water which contained herbicide pollutants can easily be drained out from this area passing through the drainage canal system to the river. Therefore, the high pollutant content in the water bodies can be easily washed away and its concentration decreased by the rain

water. Meanwhile, the spread of pollutants in the water bodies of the canals in the area with RCL water was due to the inadequate drainage, as this area was very flat. The location of the area with RCL water is in the downstream area where flooding frequently occurred after heavy rainfall and the water could not easily be drained out. It should be noted that the irrigation scheme is well connected between the area with N-RCL and RCL water.

In the current study, the contamination levels of 2,4-D and MCPA were higher compared to those of the other weedicides such as pyrazosulfuron, bensulfuron, and metsulfuron. The high level of contamination with these compounds was due to the higher dosage used compared to that of the sulfonylurea groups (pyrazosulfuron, bensulfuron, and metsulfuron). Field observations showed that pesticide containers were dumped in the canals, and this situation could trigger high contamination levels of pesticide residues in the surrounding rice fields.

It has been also reported that intensive rainfall would encourage preferential flow and consequently contaminate the environment through surface runoff. Monthly monitoring that took place from November 1992 to December 1993 showed the presence of herbicide residues in the Muda rice field areas. In the present study, pesticide residues were detected in most of the water samples at levels ranging from <0.005 to 25.5  $\mu\text{g/L}$ . However, the presence of 2,4-D, paraquat, and molinate residues was evident, but the occurrence of these herbicides was seasonal (Machado et al. 2006). Herbicide concentration in river water was closely related to herbicide application rates at nearby rice fields, the levels of which were high around rice seeding time. A study done in Japan indicated that the concentrations of ten herbicides in river water were high during the months of May/June of each year from 1978 to 1984 (Lee et al. 2004). The highest concentration of molinate reached 100  $\mu\text{g/L}$  in 1978, while the other herbicides such as thiobencarb, simetryn, and butachlor were around 10  $\mu\text{g/L}$  and the others such as oxadiazon, chlomitrofen, chlomethoxyfen, and simazine ranged from 0.5 to 2  $\mu\text{g/L}$  (Ueji and Inao 2001).

## Conclusion

The potential risk of pollution by the five herbicides studied in the areas supplied with RCL water compared

to those with N-RCL water showed that rice field areas tended to contaminate the surrounding areas through the water systems. The potential risk of contamination depended on the applied dosage of the herbicides used by farmers in their rice fields.

During the two seasons, the wet season (October 2006–Jan 2007) and dry season (April–July 2007), the number of water samples collected from the areas supplied with RCL water 67.4 and 34.8 %, respectively, contained more than 0.05 µg/L for each of the five herbicide compounds studied and was higher compared to that from the areas supplied with N-RCL water (67.2 and 37.4 %).

During the wet season, the overall total mean concentration of the five herbicides in the water samples collected from the RCL area (1.252 µg/L) was significantly higher ( $P < 0.01$ ) than that from the N-RCL area (1.032 µg/L). Meanwhile, during the dry season, there was no significant difference between the herbicide concentrations for the areas supplied with RCL (0.944 µg/L) and N-RCL water (1.152 µg/L).

The average concentration of 2,4-D and MCPA was 3.79 and 3.17 µg/L, respectively. Meanwhile, the sulfonylurea herbicides such as bensulfuron and metsulfuron were found in concentrations of 0.55 and 0.51 µg/L, respectively.

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