## Assessment of buffer zone for aquatic organisms in pesticide application

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**Abstract:** In pesticide applications, the buffer zone helps to protect water sources against pesticide contamination. In 2014, in the Adana province, the percentage of herbicides used was approximately 12% in corn, sunflower, soybean and cotton. To control the weeds, fifteen active ingredients (a.i.) were used in these crops in 2014. These a.i. were acetochlor, aclonifen, benfluralin, bromoxynil, clethodim, dicamba, fluazifop-p-butyl, foramsulfuron, linuron, mesotrione, nicosulfuron, oxyfluorfen, prometryn, trifluralin and tritosulfuron. The aim of this study was to assess the risk of these herbicides on aquatic organisms and estimate buffer zone distances for the above agricultural crops in herbicide application. Risk index (RI) values were calculated according to German Drift Model (GDM) and Dutch Drift Model (DDM). Consequently, buffer zone needs for herbicide application of five a.i., namely acetochlor, benfluralin, linuron, prometryn, and trifluralin, were determined in this study. Results showed that acetochlor a.i. has the highest risk to aquatic organisms and needs a buffer zone distance of more than 57 meters in sunflower cultivation. It was assessed that buffer zone distances should be more than 1.32 m for linuron in soybean, 3.5 m for benfluralin in sunflower, 4.13 m for prometryn (1.5 kg a.i./hm<sup>2</sup>) in sunflower and 4.19 m for trifluralin in cotton and soybean, and 5.54 m for prometryn (2.0kg a.i./hm<sup>2</sup>) in cotton. There was no need for a buffer zone in corn. **Keywords:** buffer zone, pesticide, herbicide, risk index, cotton, sunflower, corn, soybean

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### **1** Introduction

Pesticides protect agricultural crops against pests such as insects, herbs, fungus, etc. If pesticides are applied under unsuitable conditions like hot weather, over dosage, incorrect application methods, etc., spray drift occurs. In particular, small droplets can move downwind and are easily transported to non-target crops. In Turkey, operators and farmers neither calibrate sprayers, nor know the details of meteorological condition values in pesticide applications<sup>[1]</sup>. Incorrect dosage of pesticide applications is one of the most prevalent reasons for

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exceeding maximum residue levels (MRL) of pesticides in the Indian environment<sup>[2]</sup>. Pesticides have negative effects on non-target organisms such as birds, bees, aquatic organisms, groundwater, etc.<sup>[3]</sup> Bozdogan<sup>[4]</sup> determined that three a.i. of fourteen a.i. in fungicide applications presented risks for aquatic organisms in wheat cultivation. Bozdogan and Yarpuz-Bozdogan<sup>[5]</sup> assessed that approximately 70% of pesticide used in peanut cultivation presented risks for aquatic organisms in insecticide and fungicide applications. Also, Silva et al.<sup>[6]</sup> detected 20 pesticides out of 29 in surface water in Portugal. Buffer zones defined as the distance between the last nozzle of spray equipment or field border and non-target organisms off-field are necessary for protecting aquatic organisms against spray drift in The widths of buffer zones pesticide applications. depend on application spray methods, type of nozzle, chemical properties of pesticides and sensitive non-targets, numbers of application, wind velocity, etc.<sup>[7-9]</sup>. Yarpuz-Bozdogan and Bozdogan<sup>[10]</sup> determined

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that percentage drift at 5 m was 15 fold less than that at 1 m in low drift 11003 nozzles whereas it was 12 fold in F11006, and 10 fold in hollow cone D4-45 nozzles.

According to Vercruysse and Steurbaut<sup>[11]</sup>, aquatic organisms in risk assessment are divided into three categories: fish, daphnia and algae. Miller<sup>[9]</sup> reported that buffer zones were used to protect surface water from exposure to spray drift. In France, 5 m wide vegetative filter strips are compulsory along all water resources<sup>[12]</sup>.

In Turkey in 2014, corn, sunflower, soybean and cotton were cultivated on 1.818 million hm<sup>2</sup> field<sup>[13]</sup>. In 2014, in the Adana province, the amount of herbicides used was approximately 1080 t, of which approximately 12% was used in corn, sunflower, soybean and cotton<sup>[14]</sup>.

Yilmaz et al.<sup>[15]</sup> stated that organochlorine pesticides were detected in the Seyhan and Ceyhan Rivers which are very important for agricultural irrigation during the summer when pesticide is applied extensively in Adana. Bozdogan and Yarpuz-Bozdogan<sup>[16]</sup> observed that diuron a.i. had a high risk on aquatic organisms for defoliant application in cotton cultivation. Teklu et al.<sup>[17]</sup> estimated the high risk of chlorothalonil, deltamethrin, endosulfan, and malathion for aquatic organisms in Huber et al.<sup>[18]</sup> indicated that pesticide Ethiopia. pollution of surface waters depended on application rate of a.i., pesticide specifications and meteorological conditions. Vryzas et al.<sup>[19]</sup> detected high pesticide concentrations in surface waters in northeastern Greece within two months of pesticide application. Maloschik et al.<sup>[20]</sup> monitored water polluting pesticide in Hungary. From the measurements they made sure that there were one or more active pesticide ingredients above the detection limit in 209 samples. Papadakis et al.<sup>[21]</sup> recorded the highest concentration values of pesticides in the Strymonas River adjacent to agricultural land, mainly cultivated with corn and cotton, after pesticide applications. Tanabe et al.<sup>[22]</sup> indicated that the time of pesticide application in rice fields near the river influences the presence of pesticides in the river water. Therefore, monitoring of streams is important to establish the long-term effect of pesticides on aquatic organisms<sup>[23]</sup> and is useful for the implementation of pollution control and management policies<sup>[21]</sup>. Aquatic organisms can be

protected through improving spraying technologies such as sensors, chemigation, environmentally friendly sprayers, low drift nozzles and user technologies such as education, buffers and strategy integration<sup>[24]</sup>. Riparian zones, vegetative areas along ditches, have to be used to minimize pesticide contamination of aquatic organisms in pesticide application<sup>[24]</sup>. Van Eerdt et al.<sup>[25]</sup> indicated that aquatic risks can be reduced by voluntary measures of integrated pest management.

In pesticide application, the buffer zone helps to protect the water sources and environment against pesticide contamination. Bozdogan et al.<sup>[3]</sup> studied the relationship between environmental risk and pesticide application in cereal. They calculated a 30 m buffer Dunn et al.<sup>[26]</sup> zone for lambda-cyhalothrin a.i. indicated that the legislation mandates 10 m and 20 m buffers respectively for moderating sloped and steep sloped agricultural fields that border streams in Prince Edward Island in Canada. Generally, protection of aquatic organisms can be increased by using buffer zone distances<sup>[7]</sup>. Pesticide contamination in ditches depends on pesticide properties, application methods and rates, meteorological conditions etc.<sup>[18]</sup> Based on these assumptions, buffer zone distances protect aquatic organisms. Svversen and Bechmann<sup>[27]</sup> indicated that vegetative buffer zones have effective filters between field and surface waters in pesticide applications. However, a vegetated buffer zone is not the only solution for this problem due to run-off drift from on and in soil<sup>[28]</sup>. Yarpuz-Bozdogan and Bozdogan<sup>[10]</sup> indicated that %drift in Dutch Drift Model (DDM) was higher than in German Drift Model (GDM). Moreover, they determined that decreasing of %drift from 1 m to 5 m was nine fold for DDM and five fold for GDM. The reason for differences between drift models in buffer zone distance is explained below in Table 3. Teklu et al.<sup>[17]</sup> indicated that predicted environmental contaminations (PECs) of the same pesticide may differ significantly between their uses on different crops even when application rates are similar. Knewitz et al.<sup>[29]</sup> reported that in Germany, wide buffer zones protect water courses and aquatic organisms from pesticides. Carluer et al.<sup>[12]</sup> reported that buffer zones can be reduced by using proper

pesticide applications. Pesticide contamination to ditches can be reduced by creating a 3 to 6 m margin<sup>[30]</sup>. Also, Kjaer et al.<sup>[31]</sup> reported that unsprayed buffer zones reduced deposition in hedgerows. In 2014, fifteen a.i. were used in sunflower, cotton, corn and soybean cultivation areas in Adana to control weeds. These a.i. were acetochlor (A), aclonifen (B), benfluralin (C), bromoxynil (D), clethodim (E), dicamba (F), fluazifop-p-butyl (G), foramsulfuron (H), linuron (I), mesotrione (J), nicosulfuron (K), oxyfluorfen (L), prometryn (M), trifluralin (N) and tritosulfuron (O). The main aim of this study was to assess the risk of these herbicides on aquatic organisms and buffer zone distances in the cultivation of major agricultural crops in Adana province.

#### 2 Materials and methods

In this research, the fifteen a.i. (A-O) mentioned above were used for weed control in sunflower, cotton, corn and soybean cultivation in Adana, Turkey, in 2014. The application rate of active ingredients, label dose and concentration for each crop are given in Table 1.

Table 1	Information	of a.i.	for	each	crop
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Code	Active ingredient (a.i.)	$\begin{array}{c} Concentration \\ /g \cdot kg^{\text{-l}} \end{array}$	Label dose /kg·hm <sup>-2</sup>	Application rate of a.i. /kg·hm <sup>-2</sup>	Crop
А	Acetochlor	840.0	2.00	1.68000	Sunflower
B1	Aclonifen	600.0	1.25	0.75000	Sunflower
B2	Aclonifen	600.0	2.00	1.20000	Sunflower
B3	Aclonifen	600.0	3.00	1.80000	Sunflower
С	Benfluralin	600.0	2.50	1.50000	Sunflower
D	Bromoxynil	225.0	1.50	0.33750	Corn
E1	Clethodim	116.2	0.75	0.08715	Cotton
E2	Clethodim	116.2	1.25	0.14525	Cotton
F	Dicamba	500.0	0.25	0.12500	Corn
G	Fluazifop-p-butyl	125.0	1.00	0.12500	Cotton, soybean
Н	Foramsulfuron	22.5	2.00	0.04500	Corn
Ι	Linuron	475.0	1.50	0.71250	Soybean
J1	Mesotrione	37.5	2.00	0.07500	Corn
J2	Mesotrione	37.5	2.50	0.09375	Corn
J3	Mesotrione	37.5	3.00	0.11250	Corn
K1	Nicosulfuron	60.0	1.00	0.06000	Corn
K2	Nicosulfuron	40.0	1.25	0.05000	Corn
K3	Nicosulfuron	15.0	2.00	0.03000	Corn
K4	Nicosulfuron	15.0	2.50	0.03750	Corn
K5	Nicosulfuron	15.0	3.00	0.04500	Corn
L	Oxyfluorfen	240.0	1.00	0.24000	Sunflower
M1	Prometryn	500.0	3.00	1.50000	Sunflower
M2	Prometryn	500.0	4.00	2.00000	Cotton
Ν	Trifluralin	480.0	2.30	1.10400	Cotton, Soybean
0	Tritosulfuron	250.0	0.25	0.06250	Corn

# 2.1 Determination of the risk index for aquatic organisms (RI<sub>a</sub>)

RI values for aquatic organisms were calculated by Equation  $(1)^{[32-34]}$ :

$$RI_{aquatic \ organisms} = \frac{(D \times \% drift \times n) / (d_{ditch} \times 1000)}{\min(NORM_w)}$$
(1)

where, *D* is the applied dose of a.i.,  $mg/m^2$ ; %*drift* is drift deposition of a.i. at a point downwind of the field, in %; *n* is the number of applied doses, default 1; *d*<sub>ditch</sub> is the depth of the ditch, default 1.5 m, and min(*NORM*<sub>w</sub>) is the toxicological reference on aquatic organisms, mg/L.

%*drift* was calculated by Equation (2) for German Drift Model (GDM) and Equation (3) for Dutch Drift Model (DDM)<sup>[34]</sup>.

$$\% drift = A \times z^B \tag{2}$$

In GDM Equation, z is the distance between the field border and a point downwind of the field, m; A and B are coefficients<sup>[34]</sup>. There are three categories which are early fruit application, late fruit application and field crops. All crops were taken as field crops according to drift model. Therefore, coefficients were taken as 2.7593 for A, and -0.9778 for  $B^{[34]}$ .

$$\% drift = A_0 e^{-Z.A_2} + B_0 e^{-z.B_1}$$
(3)

In DDM Equation, *z* is the distance between the last spray nozzle and a point downwind of the field, m;  $A_0$ ,  $B_0$ ,  $A_1$  and  $B_1$  are coefficients that depend on the crop categories which are bare soil, sugar beets, potatoes, cereals, leaf and leafless fruit trees<sup>[34]</sup>. Crops were taken into account as a bare soil category. For this reason, coefficients were taken as 25 for  $A_0$ , 1.5 for  $A_1$ , 1.54 for  $B_0$  and 0.133 for  $B_1^{[34]}$ .

In this research,  $\min(NORM_w)$  was calculated as toxicological reference by Equations (4), (5) and (6)<sup>[34,35]</sup>. Fish was used as the toxicological reference due to the lowest  $\min(NORM_w)$  for aclonifen, benfluralin, clethodim, foramsulfuron, mesotrione, nicosulfuron, oxyfluorfen, and tritosulfuron a.i. (Equation (4)). Daphnia was used for bromoxynil, dicamba, and fluazifop-p-butyl a.i. (Equation (5)), and algae was used for acetochlor, linuron, prometryn, and trifluralin a.i. (Equation (6)).

 $\min(NORM_w)$  for Fish =  $LC_{50}/100$  (4)

$$\min(NORM_w) \text{ for Daphnia} = EC_{50}/100$$
 (5)

 $\min(NORM_w)$  for Algea = NOEC/100 (6)

Toxicity data for each a.i. of herbicides on aquatic organisms are listed in Table  $2^{[36]}$ . Toxicity data were used for determination of risk indices (RI) (Table 2).

Table 2	Toxicity	data f	or	each	a.i. <sup>[36]</sup>
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Code	$\begin{array}{c} \min(\text{NORM}_{\text{water}}) \\ /\text{mg} \cdot \text{L}^{\text{-1}} \end{array}$	$\frac{LC50_{fish}}{/mg \cdot L^{-1}}$	$\frac{EC50_{daphnia}}{/mg \cdot L^{-1}}$	NOEC <sub>algae</sub> /mg·L <sup>-1</sup>
А	0.000059	0.360	8.600	0.00059
B1	0.006700	0.670	1.200	nd
B2	0.006700	0.670	1.200	nd
В3	0.006700	0.670	1.200	nd
С	0.000810	0.081	100.000	nd
D	0.125000	29.200	12.500	3.13000
E1	0.250000	25.000	100.000	nd
E2	0.250000	25.000	100.000	nd
F	0.410000	100.000	41.000	25.00000
G	0.006200	1.410	0.620	0.30000
Н	1.000000	100.000	100.000	100.00000
Ι	0.001000	3.150	0.310	0.01000
J1	1.200000	120.000	900.000	nd
J2	1.200000	120.000	900.000	nd
J3	1.200000	120.000	900.000	nd
K1	0.657000	65.700	90.000	100.00000
K2	0.657000	65.700	90.000	100.00000
K3	0.657000	65.700	90.000	100.00000
K4	0.657000	65.700	90.000	100.00000
K5	0.657000	65.700	90.000	100.00000
L	0.002500	0.250	0.720	2.00000
M1	0.000690	5.500	12.660	0.00690
M2	0.000690	5.500	12.660	0.00690
Ν	0.000500	0.088	0.245	0.00500
0	1.000000	100.000	100.000	nd

Note: nd: not determined.

### 2.2 Determination of buffer zone

For aquatic organisms, according to Equation (1), if RI value is higher than 1, it indicates high risk and needs a buffer zone. If RI is equal to or lower than 1, it means minimum risk and indicates a safe situation. Therefore, the buffer zone protects aquatic organisms against drifted spray and was determined by  $Z_{RI=1}$  according to %*drift* in Equation (1). There is no need for a buffer zone if RI<1, and it requires a buffer zone if RI>1. RI=1 is critical value for determining the minimum distance of the buffer zone ( $Z_{RI=1}$ ).

### **3** Results and discussion

RI values of downwind distance at one meter for aquatic organisms  $(RI_{a,1})$  were calculated at label dose of

herbicides according to Equation (1). For each crop cultivation, RI values at one meter ( $RI_{a,1}$ ) and buffer zone distances at RI=1 ( $Z_{RI=1}$ ) for aquatic organism are given in Table 3.

Table 3	RI <sub>a,1</sub> values for aquatic organisms and approximate
	buffer zone distances ( $Z_{RI=1}$ ) for crops

Celle	RI	RI <sub>a,1</sub>		<sub>=1</sub> /m	0
Code	GDM	DDM	GDM	DDM	- Crop
А	52.380	97.535	>57	>25	Sunflower
B1	0.329	0.383	-	-	Sunflower
B2	0.494	0.613	-	-	Sunflower
В3	0.206	0.920	-	-	Sunflower
С	3.407	6.343	>3	>4	Sunflower
D	0.005	0.009	-	-	Corn
E1	0.001	0.012	-	-	Cotton
E2	0.001	0.020	-	-	Cotton
F	0.001	0.001	-	-	Corn
G	0.037	0.069	-	-	Cotton, Soybean
Н	0.000	0.000	-	-	Corn
Ι	1.311	2.441	>1	>2	Soybean
J1	0.000	0.000	-	-	Corn
J2	0.000	0.000	-	-	Corn
J3	0.000	0.000	-	-	Corn
K1	0.000	0.000	-	-	Corn
K2	0.000	0.000	-	-	Corn
K3	0.000	0.000	-	-	Corn
K4	0.000	0.000	-	-	Corn
K5	0.000	0.000	-	-	Corn
L	0.177	0.329	-	-	Sunflower
M1	3.999	7.446	>4	>5	Sunflower
M2	5.332	9.929	>5	>7	Cotton
Ν	4.062	7.563	>4	>5	Cotton, Soybean
0	0.000	0.000	-	-	Corn

As shown in Table 3,  $RI_{a,1}$  values in DDM were calculated as 1.86 fold higher than in GDM if RI<sub>a,1</sub>>1. Schampheleire et al.<sup>[34]</sup> calculated that for cereals crops, DDM value at 1 m for aquatic organisms was 5.28 fold higher than GDM.  $Z_{RI=1}$  value of acetochlor a.i. was approximately 57 m in GDM, and 25 m in DDM, however,  $RI_{a,1}$  value in DDM was higher than in GDM. As shown in Table 3, Z<sub>RI=1</sub> for acetochlor a.i. was calculated as >25 m for DDM and >57 m for GDM. Comparing percentage drift values in these models, we observed that decreasing of %drift in 15 m was 25.36 fold for DDM, and 14.12 fold for GDM. It can be calculated that decreasing of %drift in DDM was 1.79 fold higher than GDM in 15 m downwind. Therefore, approximately 15 m downwind, decreasing of %drift value in DDM is equal to GDM's value. Based on this assumption, buffer zone distances up to 15 m in DDM were wider than GDM's. It was assessed that buffer zone distances in DDM after 15 m downwind were narrower than GDM's.  $Z_{RI=1}$  for benfluralin, linuron, prometryn (M1 and M2) and trifluralin a.i., in DDM was higher than GDM's because of  $Z_{RI=1}$ <15 m for these a.i.

As seen from Table 3, buffer zone in herbicide



application is not necessary in corn cultivation. Other crops need buffer zones in herbicide application. The widest distance of buffer zone was assessed in sunflower as >57 m for GDM, and >25 m for DDM ( $Z_{RI=1}$ ).

RI values for several distances were determined according to Equation (1). These values are shown in Figure 1. Exact  $Z_{\text{RI=1}}$  according to GDM and DDM can be calculated based on Figure 1.





By using Figure 1, Equations (7-18) were developed for determining exact  $Z_{RI=1}$ . Equations (7-18) were used for RI values of a.i. in GDM (Equations (7-12)), and in DDM (Equations (13-18)).

$RI_{Acetochlor} = 52.3800 \cdot Z^{-0.978}$	$R^2 = 1.00$	(7)
$RI_{Benfluralin} = 3.4065 \cdot Z^{-0.978}$	$R^2 = 1.00$	(8)
$RI_{Linuron} = 1.3107 \cdot Z^{-0.978}$	$R^2 = 1.00$	(9)
$RI_{Prometryn(M1)} = 3.9990 \cdot Z^{-0.978}$	$R^2 = 1.00$	(10)
$RI_{Prometryn(M2)} = 5.332 \cdot Z^{-0.978}$	$R^2 = 1.00$	(11)
$RI_{Trifluralin} = 4.06175 \cdot Z^{-0.978}$	$R^2 = 1.00$	(12)
$RI_{Acetochlor} = 53605 \cdot Z^{-3.38}$	$R^2 = 0.99$	(13)
$RI_{Benfluralin} = 5.6475 \cdot Z^{-1.104}$	$R^2 = 0.98$	(14)
$RI_{Linuron} = 2.295 \cdot Z^{-1.193}$	$R^2 = 0.99$	(15)
$RI_{Prometryn(M1)} = 6.4093 \cdot Z^{-1.061}$	$R^2 = 0.99$	(16)
$RI_{Prometryn(M2)} = 8.5458 \cdot Z^{-1.061}$	$R^2 = 0.99$	(17)
$RI_{Trifluralin} = 6.5098 \cdot Z^{-1.06}$	$R^2 = 0.99$	(18)

In these equations, where RI equals 1, is the buffer zone distance ( $Z_{RI=1}$ ). In this situation, for example acetochlor a.i., we can rewrite Equation (7) as follows (Equation (19)) for GDM.

 $Z_{\text{RI=1(Acetochlor)}} = 52.3800^{1.0225} = 57.26 \text{ m}$ (19)

Based on this assumption,  $Z_{RI=1}$  value for each a.i. can be calculated by using Equations (7-18).  $Z_{RI=1}$  values are given in Table 4.

As seen in Table 4,  $Z_{RI=1}$  values in DDM were higher than in GDM except for acetochlor a.i. Increases of  $Z_{RI=1}$  were between 36.46%-52.27%. However, in acetochlor a.i.,  $Z_{RI=1}$  in GDM was higher than in DDM (56.15%).

Table 4 Calculated exact buffer zone distances  $(Z_{RI=1})$  forcrops

a.i.	Buffer zone distance $(Z_{RI=1})/m$		Difference between drift models	Crops		
	GDM	DDM	/%			
Acetochlor	57.26	25.11	-56.15	Sunflower		
Benfluralin	3.50	4.80	+37.14	Sunflower		
Linuron	1.32	2.01	+52.27	Soybean		
Prometryn (M1)	4.13	5.77	+39.71	Sunflower		
Prometryn (M2)	5.54	7.56	+36.46	Cotton		
Trifluralin	4.19	5.85	+39.62	Cotton, Soybean		

### 4 Conclusions

It can be derived from this study:

1) Buffer zones should be required for three a.i.,

acetochlor, benfluralin, and prometryn (M1), in sunflower cultivation, two a.i., linuron and trifluralin a.i. in soybean cultivation, and two a.i., prometryn (M2) and trifluralin, in cotton cultivation. There is no need for a buffer zone in corn cultivation.

2) It means that in Adana approximately 30% of herbicides used in these cultivations present risks for aquatic organisms.

3) To protect the environment in Turkey, drift reducing techniques such as low drift nozzles, air-induction nozzles, adjuvants, vegetative and no-spray buffer zones, etc., have to be mandatory in pesticide applications. Moreover, rivers in Adana province should be monitored to determine pesticide effects on aquatic organisms. Electrostatic pesticide applications and GPS-controlled patch spraying can be used in weed control to overcome pesticide contamination in aquatic organisms.

4) Moreover, contact meetings about the effect of pesticides on aquatic organisms including drift reduction techniques such as nozzle and sensor technology, buffer zones, calibration of sprayers etc., should be arranged with farmers in villages adjacent to rivers in Adana.

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