Indian Journal of Agricultural Sciences **84** (5): 579–84, May 2014/Article

Effect of metsulfuron-methyl on water quality for fish culture using water quality index

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Received: 7 Feburary 2012; Revised accepted: 7 March 2014

ABSTRACT

Field and laboratory experiments were conducted to evaluate the effects of herbicide on water quality through water quality index (WQI). WQI was derived to see the suitability of water in term of its quality for fishery. The WQI proposed in this study was composed of eight measurable major environmental parameters, viz. herbicide residues, pH, total dissolve solids (TDS), dissolved oxygen (DO), biological oxygen demand (BOD), free ammonia, chloride and temperature. Concentrations of these eight variables were normalized on a scale from 0 (zero) to 100 and translated into statements of water quality (excellent, good, poor, very poor and unsuitable). Based on WQI, water quality of pond adjacent to wheat field was derived as category I (excellent) to category II (good), and found to be suitable for fish farming.

Key words: Metsulfuron-methyl, Persistence, Water quality, Water quality index (WQI)

Water quality of a pond is one of the major factors which determines the success or failure of a fish farming operation. Water Quality Index is a single numerical expression, which reflects the composite influence of physical and chemical parameters of water quality. Various water quality indices have been widely used to represents gradation in water quality of aquatic bodies (Elfmana *et al.* 2011). It indicates quality by an index number, which represents overall quality of water for any intended use. It is defined as a rating reflecting the composite influence of different water quality parameters on the overall quality of water (Harkins 1974). Herbicides which are used for control of weeds may have potential for causing water contamination through runoff and leaching. The application of herbicides near water sources can deteriorate water quality and may cause toxicity to fish (Sondhia 2008, Farombi *et al.* 2008, Lushchak *et al.* 2009). Some herbicides 2, 4-D, butachlor, mecoprop, dicamba, glyphosate and its major metabolite aminomethyl phosphonic acid (AMPA) were detected frequently in water samples (Iwafune *et al.* 2011, Glozier *et al.* 2011).

Environmental contaminants such as herbicides, heavy metals and insecticides are known to modulate antioxidant defensive systems and cause oxidative damage in the aquatic organisms by reactive oxygen species (ROS) production (Liu *et al.* 2006) and affect the reproduction and development of aquatic animals (Hanson *et al.* 2007).

For predicting suitability of water bodies near agricultural field, there is a need to develop an index that can categorize quality of water for diverse uses. Thus potential risk of water contamination due to use of herbicide near agriculture field can be assessed with the help of WQI. Among the various registered herbicides in India, metsulfuron-methyl (Fig 1), a sulfonylurea group of herbicides, is used for pre- and post-emergence control of broadleaved and grassy weeds in paddy, wheat, pasture, and plantation crops due to its selectivity (Sondhia 2009a,b). It is also used alone or as a mixture to control broad leaf weeds in paddy and wheat. Some authors suggested a potential risk of sulfonylurea herbicides, which are used at very low rate of application (Sondhia 2008, Sondhia *et al.*

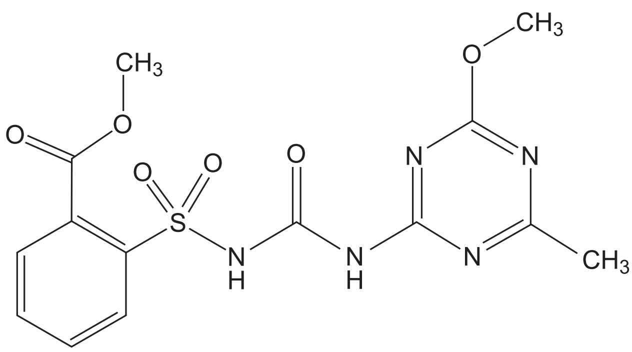

Fig 1 Chemical structure of metsulfuron-methyl ([Methyl 2-[[[[(4-methoxy-6-methyl-1, 3, 5-triazin-2-yl) amino] = carbonyl] amino] sulfonyl] benzoate

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2013). Thus in this study, water quality, risk of water contamination due to metsulfuron-methyl application, and bioaccumulation of residues in fishes were determined, using water quality indexes.

MATERIALS AND METHODS

An experiment was conducted in 2009-10 in the experimental field of Directorate of Weed Science Research, Jabalpur, India. Eight ponds each with a dimension of 9.75 × 1.6 × 1.7 m^3 (L × W × H) were constructed adjacent to field plots each of 16 × 10 m^2 size where wheat was grown. Two meters distance was maintained between the plots and ponds. Fingerlings of freshwater fishes (*Catla catla* and *Labeo rohita*) 10-20 g weight were procured from local sources and released (200 nos.) in the each pond one month before application of herbicide into the wheat field. Fish specimens were subjected to a prophylactic treatment before release to pond by bathing twice in 0.05% potassium permanganate ($KMnO_4$) for two minutes to avoid any dermal infections. Fishes were feed regularly with recommended dose of fish feed containing egg and crop bran. Wheat crop was sown on 15/11/2009 in the plots adjacent to the pond. The physico-chemical properties of experimental soil were clay 35.47 %, silt 12.45 %, sand 52.09 %, 0.37% of organic carbon, EC 0.64 mS/cm and pH 7.66. After sowing of wheat, metsulfuron- methyl was applied at 4 g a.i. /ha on 12 December 2009 using flat fan nozzle to the wheat crop as post emergence application to control grassy and broad leaved weeds. A control plot was also maintained where no herbicide was sprayed. Crop was raised under irrigated conditions with recommended package of practices. Approximately 0.5% slope gradient of plots was maintained to allow runoff from plot to corresponding ponds. Soil samples were collected from wheat field at 0, 5, 10, 20, 30, 60 and 90 day after herbicide application. Samples from the control plots were collected before the herbicide treated plots for residue analysis. Water and fish samples were collected from ponds after second irrigation at 20, 30, 60, and 90 days after herbicide spray.

To evaluate persistence of metsulfuron in water, another set of experiment was also conducted under laboratory conditions in glass aquariums with three replications. Six glass aquariums with 0.6×0.3×0.3 m^3 (L×W×H) size were filled with 40 litres of well water and 5.31 μg/L of metsulfuron was applied to each tank which is equivalent to field application of 4g a.i./ha. Water samples were taken from each untreated and treated aquariums after metsulfuron application at 0, 10, 15, 30, 60 and 90 days, arranged in completely randomized design. Water quality and persistence of metsulfuron-methyl in the water was determined.

Water samples were collected at 0, 10, 15, 30, 60 and 90 from ponds to evaluate water quality according to the standard sampling methods and analysis (BIS 1966, APHA, 1998). Samples for estimating dissolved oxygen (DO) and biochemical oxygen demand (BOD) were collected separately in BOD (glass) bottles. Water temperature and pH were recorded at the sampling site. Total dissolved solid (TDS) and chloride were determined following the method of APHA (1998). Water sample were stored at 4°C, processed and analyzed within seven days for metsulfuron residues. Soil and fishes samples were stored at -10°C and analysis within seven days. Analytical standard of metsulfuron-methyl was purchased from ACCU standard, USA. Other laboratory chemicals were obtained from E-Merck, Germany. All analysis was conducted in residue laboratory of Directorate of Weed Science Research, Jabalpur, India.

Metsulfuron-methyl in water and fish samples was determined as described by Sondhia (2009a) using Shimadzu HPLC Chromatography consisting of LC-10 ATVP pump and SPD-1-AVvp Photo Diode Array. The HPLC was fitted with a Phenomenex C18 column4.6-mm-diameter × 25-cm-length. The analysis was carried out at 220 nm at ambient temperature using acetonitrile: water (70:30) as a mobile phase with flow of 1 ml/min. Quantification of metsulfuron-methyl residues was accomplished by comparing the peak area response for samples with peak area of the standards.

WQI was calculated to verify suitability of water for fish farming. Eight major physico-chemical parameters, namely pH, total dissolve solids, dissolved oxygen, biological oxygen demand, free ammonia, chloride, temperature and metsulfuron residues were used to calculate the WQI. Calculation of WQI was made using a weighted arithmetic index method given below (Brown *et al.* 1972) using the following steps,

For calculation of relative weight (wi) method of Prasad *et al.* (2009) was adopted. Based on eight parameters for this study, viz. metsulfuron methyl, DO, pH, TDS, BOD, free ammonia, chloride and temperature were assigned weight based on their correlation with respect to fish culture and the relative weight (w_i) was computed using following equation 1,

$$wi = wi / \sum_{i=1}^{i=n} Wi \qquad \text{(Equation 1)}$$

where w_i was the relative weight, W_i was the weight of each parameter and n is the number of parameters. Calculated relative weight (w_i) values of each parameter are presented in Table 1.

The value of sub index of quality rating (qi) was calculated as described by Sisodia and Moundiotiya (2006) using the following expression.

$$qi = 100[(Vi - Vio) / (Si - Vio)] \qquad \text{(Equation 2)}$$

where qi, quality rating for the ith water quality parameter; Vi, estimated value of the ith parameter at a given sampling station; Si, standard permissible value of nth parameter; Vio, ideal value of *i*th parameter in pure water.

All the ideal values (Vio) were taken as zero for water except for pH=7.0 and dissolved oxygen=14.6 mg/L.

The quality rating for pH was calculated using the following relation:

$$qpH = 100\ [(VpH - 7.0) / (8.5 - 7.0)] \qquad \text{(Equation 3)}$$

where, VpH, observed value of pH during the study period.

Quality rating for dissolved oxygen (qDO) was calculated from following relation:

$qDO = 100\ [(VDO - 14.6)/\ (5 - 14.6)]$ (Equation 4)

where, *VDO*, measured value of dissolved oxygen.

In this study, the WQI was determined according to National Sanitation Foundation (NSF), USA using multiplicative and additive methods by using original equations proposed by Brown *et al.* (1972), Although the additive form of the index had been widely used, but an alternate multiplicative form, NSFWQI (M), was proposed subsequently to overcome the eclipsing, which occurs when a single parameter/pollutant variable shows extremely poor water quality.

$$\mathrm{NSFWQI(M)} = \sum_{i=1}^{n} \Pi q_i^{wi}$$

$$\mathrm{NSFWQI(A)} = \sum_{i=1}^{n} wiqi$$

RESULTS AND DISCUSSION

Water quality index was calculated to verify suitability of water for fish farming. Since selection of too many parameters might widen the water quality index, thus eight major physico-chemical parameters, namely pH, TDS, DO, BOD, free ammonia, chloride, temperature and metsulfuron residue were used to calculate the WQI. Calculation of WQI was made using a weighted arithmetic index method (Brown *et al.* 1972).

Water quality

Among various parameters, permissible values of pH, alkanity, TDS and DO are essential for pond fertility. Hence these parameters were routinely checked. Chloride content of pond water was found 65.7, 77.8, 65.4, 52.0, after 0, 10, 20 and 30 days which was increased to 80.0 and 91.8 mg/L after 60 and 90 days, respectively. pH and TDS of pond water were increased up to 60 days however, dissolved oxygen was decreased with passage of time in pond water. Dissolved oxygen varied from 8.0 to 7.6 during 0 to 90-days period. Fishes live the best in waters with a pH between 6.5 and 8.4. Fish are harmed if pH becomes too acidic (below 4.8) or too alkaline (above 9.2). Biological oxygen demand is an important measure of organic material. It can react with chlorine in water to form harmful disinfectant by-products. BOD of pond water was found 2.5 mg/L at 0 days which was found 1.5 mg/L after 90 days. Overall BOD of the ponds was found in acceptable limits. Change in temperature 22.8 to 22.7ºC of pond water was noticed between 0 to 90 days. TDS of water after application of metsulfuron was found 329 to 339 mg/L, between 0 and 90 days and found in acceptable and safe limits prescribed by Central Pollution Control Board (CPCB), India. pH was found almost stable and was in the range of 7.5 and 7.8 which was highly acceptable (Table 1).

Slight increase in free ammonia content after application of metsulfuron was noticed and it varied from 0.05 at 0 day to 0.17 mg/L after 90 days. Free ammonia content of the pond was found below the safe limit (1.2 mg/L) during 90 days period (Table 1 and 2). Total dissolved solids are a measure of material that is suspended in the water. Ammonia is a source of nitrogen, an important nutrient for plants and algae. Ammonia occurs in a harmless form but at higher temperatures or higher pH, ammonia changes to a gas, which is harmful to fish and other aquatic life. Excess ammonia tends to block oxygen transfer from the gills to the blood and can cause damage to gill and nuclear membrane, reduce external slime coat and damage the internal intestinal surface. Temperature, pH, TDS, DO, BOD and chloride of pond water were found within the safe limits for water suitable for fishery as described by Central Pollution Control Board, India (Table 1).

Table 1 Assigned Weight for different parameters

Parameter	Standard value	Recommending agency	Unit weight (Wi)	Relative weight (wi) ***
pH	6.5-8.5	CPCB*, India	5	0.13
DO (mg/L)	4-5	CPCB, India	8	0.22
BOD (mg/L)	2-3	CPCB, India	1	0.02
Herbicide residue (mg/L)	0.01	WHO	6	0.16
Total Dissolved solid (mg/L)	500	WHO	3	0.08
Temperature (ºC)	20	CPCB, India	4	0.11
Free ammonia (mg/L)	1.2	CPCB, India	7	0.19
Chloride (mg/L) (mg/L)	250	BIS**10500:1991 (reaffirmed in September 2003).	2	0.05
		Total = 36		Total = 0.96 (1)

*CPCB- Central pollution control board, **BIS-Bureau of Indian Standard; *** Weight assigned for current study

Metsulfuron-methyl residues in water and fishes

Metsulfuron- methyl residues were 0.091µg/L in water at 0- days which further dissipated to 0.062, to 0.001µg/L after 10 to 90 days respectively under laboratory conditions. While under field conditions, 0.0015 and 0.0013 µg/L residues were detected from pond water of 20 and 30 days after spray of metsulfuron, respectively. However, metsulfuron-methyl residues were found below detectable limits (<0.001 µg/L) in pond water after 60 days under field conditions.

Herbicides may cause sub lethal effects with biochemical and histopathological alteration in fish tissues with long term exposure (Neškovic *et al.* 2009). Fish can serve as bio-indicators of environmental pollution and can play significant roles in assessing potential risk associated with contamination in aquatic environment since they are directly exposed to chemicals resulting from agricultural production via surface run-off or indirectly through food chain of ecosystem (Lakra and Nagpure 2009). Residues of

Table 2 Water quality parameter values of metsulfuron treated pond water at various days

Days	Temperature (°C)	pH	Chloride (mg/L)	TDS (mg/L)	DO (mg/L)	BOD (mg/L)	Free ammonia (mg/L)	Herbicide residue(µg/g)
0	22.8	7.7	65.7	329	8.0	2.5	0.05	0.00
10	19.8	7.9	77.8	320	8.1	1.6	0.04	0.00
20	22.5	9.0	65.4	330	7.0	2.8	0.08	0.0015
30	21.8	8.9	52.0	348	7.4	2.9	0.10	0.0013
60	22.6	8.6	80.0	350	7.5	2.7	0.15	<0.001
90	20.7	7.7	91.8	339	7.6	1.5	0.17	<0.001

metsulfuron in fishes were found 0.017, 0.013 and 0.006 µg/g at 20, 30 and 60 days under field conditions. Bioaccumulation of metsulfuron in fish under field conditions and persistence of metsulfuron in water under laboratory and field conditions are presented in Table 3.

Metsulfuron-methyl residues in soil

In the soils, 0.2950 and 0.01030 µg/g metsulfuron residues were detected at 0 and 5 days and by 10, 20 and 30 days residues were declined to 0.0930, 0.0570 and 0.0254 µg/g, respectively. Residues were continuously degraded with passage of time and by 90 days residues of metsulfuron were found below 0.001 µg/g in soil (Table 3). Sondhia (2009) also reported rapid dissipation of sulfosulfuron residues in field conditions. Degradation of sulfonylurea is pH dependent (Sondhia 2008, Sondhia *et al*. 2013). The field soil had clay content (35 %) that might have also favoured degradation of metsulfuron in the soil thus less amount of herbicide was moved from adjoining plots to the pond. The pH of the experimental soil was slightly alkaline (7.6) which allowed less adsorption of the metsulfuron in the soil and hence facilitated lateral movement of metsulfuron through runoff and hence residues were detected from pond water after second and third irrigations only.

Water quality index

Sub-index and sub index additive (qi × wi) values of metsulfuron-methyl treated pond water between 0 to 90

Table 3 Persistence of metsulfuron in water, soil and its bioaccumulation in fishes

Days after metsulfuron application	Sampling date	Residues (µg/g)*			
		Field conditions		Laboratory conditions	
		Water	Soil	Fish	Water
0	12/12/2009		0.2950±0.0152**		0.0911±0.012
5	16/12/2010		0.1030±0.0055		0.0620±0.0069
10	21/12/2010		0.0930±0.0060		0.0310±0.0082
20	2/01/2010	0.0015±0.0003	0.0570±0.0097	0.0169±0.0054	0.0201±0.0045
30	11/01/2010	0.0013±0.0003			
	0.0254±0.0049				
	0.0131±0.0030	0.0100±0.0046			
60	11/02/2010	<0.0010	0.0092±0.0010	0.0060±0.0015	0.0090±0.0010
90	11/3/2010	<0.0010	<0.001	<0.0010	<0.0010

*Average of four replications, **Standard deviation

Table 4 Sub-index values for NSF multiplicative Water Quality Index of metsulfuron-methyl treated pond water

Parameters	0-day		10-day		20-day		30-day		60-day		90-day	
	qi	(qi ^{wi})	q_n	(qi^{wi})	qi	(qi ^{wi})	qi	(qi ^{wi})	qi	(qi ^{wi})	qi	(qi ^{wi})
pH	47	1.65	60	1.70	133	1.89	127	1.87	107	1.83	47	1.65
DO (mg/L)	72.5	2.57	73	2.57	84	2.65	79	2.61	79	2.61	77	2.60
BOD(mg/L)	100	1.09	64	1.09	112	1.09	116	1.09	100	1.10	60	1.08
TDS(mg/L)	65.8	1.40	64	1.39	66	1.40	69.6	1.40	70	1.40	120	1.40
Temperature (ºC)	114	1.68	99	1.26	112.5	1.68	109	1.67	113	1.68	150	1.66
Free ammonia(mg/L)	4.16	1.31	3.33	0.77	6.67	1.43	8.33	1.49	12.5	1.61	11	1.65
Chloride (mg/L)	26.2	1.17	31.12	1.00	26.16	1.17	20.8	1.16	32	1.19	36.7	1.20
Metsulfuron residue (µg/g)					15	1.54	13	1.5	10	1.44	10	1.44
NSF WQI(m)		16.76		13.89		33.08		32.24		28.7		30.6

Table 5 Sub-index values for NSF additive Water Quality Index of metsulfuron-methyl treated pond water

Parameters	0-day		10-day		20-day		30-day		60-day		90-day	
	qi	qi × wi	qi	qi × wi	Qi	qi × wi	qi	qi × wi	qi	qi × wi	qi	qi × wi
pH	47	6.11	60	7.80	133	17.3	127	16.5	107	13.9	47	6.11
DO (mg/L)	72.5	16.0	73	16.0	84	18.5	79	17.4	79	17.3	77	16.9
BOD (mg/L)	100	2.00	64	1.28	112	2.24	116	2.32	100	2.16	60	1.2
TDS (mg/L)	65.8	5.30	64	5.12	66	5.28	69.6	5.56	70	5.6	120	5.42
Temperature (°C)	114	11.5	99	10.9	112.5	12.4	109	11.9	113	12.4	150	11.4
Free ammonia (mg/L)	4.16	0.79	3.33	0.63	6.67	1.26	8.33	1.58	12.5	2.37	11	2.67
Chloride (mg/L)	26.2	1.32	31.1	1.50	26.2	1.30	20.8	1.04	32	1.6	36.7	1.82
Metsulfuron residue (µg/g)					15	2.4	13	2.2	10	1.6	10	1.6
NSF WQI(a)		44.05		43.33		60.62		57.81		57.05		47.12

days is presented in Table 4. High Sub index (qi × wi) values of DO, TDS and temperature were found between 0 to 90 days (Table 3 and 4). WQI values of pond at various days were found between 16.76 to 33.0 on the basis of using two indices WQI (M) (Multiplicative) whereas it was found 50.3 to 69.9 on the basis of WQI (A) (additive). Pond water was characterised as excellent quality from 0-10 days and at 20-90 days pond water was found as good quality according to WQI (M). However, on the basis of WQI (A) pond water was characterised as good to poor quality from 0-60 days and after 90 days water was found as good category (Table 6).

Based on WQI indexing by Mishra and Patel (2001), WQI value of pond water in the present study was found 17 to 33 between 0 to 90 days (Table 6). Various water quality indices have been used in India but not as extensively as the tool deserves. Except for the first reported Indian WQI (Bhargava 1985), other indices have been mostly weighted sum-indices apparently inspired by Brown's multiplicative WQI. Brown *et al.* (1972) developed a water quality index similar to Horton's index (1965) but with much greater rigor in selecting the parameters, developing a common scale, and assigning weights for which elaborate Delphic exercises were performed. This index is also referred as NSFWQI. WQI of various ponds and rivers were also determined by some other worker using various water quality parameters. Dwivedi *et al.* (2007), evaluated quality indices of Mandakini river, Chitrakoot on the basis of various water quality parameters for pre, post-monsoon and winter season at six sampling sites. Their investigations showed

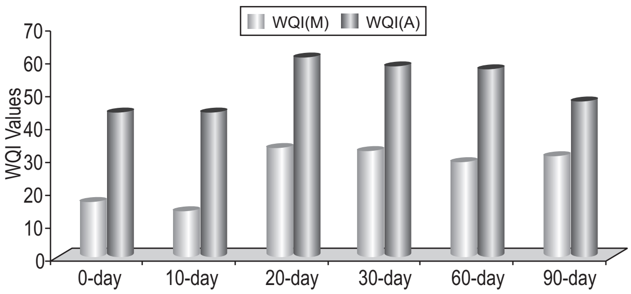

Fig 2 Multiplicative and additive Water quality index (WQI) of metsulfuron treated pond water

Table 6 Status of water quality based on WQI for fish culture based on Mishra and Patel (2001), WQI Index

Water Quality Index	Category	Status
0-25	I	Excellent
26-50	II	Good
51-75	III	Poor
76-100	IV	Very poor
100 and above	V	Unsuitable for fish culture

that all the six sampling sites had slight to moderate water pollution and water can be used for drinking purposes after proper treatments. Avvannavar *et al.* (2007) found that the water quality of Netravathi River varied from excellent to marginal range using Bhargawa WQI method and excellent to poor range by Harmonic Mean WQI method. They found that the main cause of deterioration in water quality was due to the lack of proper sanitation, unprotected river sites and high anthropogenic activities. Roy *et al.* (2007) evaluated WQI of PK-1 Coal mine of *Pathakhera*, Betul, India and WQI was found 65.50 that was good for fisheries, and irrigation. They found that water was not suitable for human consumption due to high nitrate content and faecal coliforms.

Variation in various categories based on WQI (M) and WQI (A) was due to the fact that while computing WQI values, using WQI (A), change in one parameter had significant influence on WQI sub-indices values (qi × wi) as it was added to the total values and giving higher WQI values thus pond water characterized as excellent to good quality. Whereas in WQI (M), computing of WQI sub indices (*qi* × *wi*) depend on multiplicative method and did not affect much on total WQI values. Due to high sub-indices values (*qi* × *wi)* of DO and temperature, pond water was characterized as good to very poor quality in WQI(A) as compared to WQI(M) where water was characterised as excellent to good quality (Fig 2).

CONCLUSION

Over all multiplicative values of pond at 0 to 90 days were found between 17-33, and according to quoted classification, pond water was characterized as category (excellent) I to category II (good) and can be considered suitable for fish farming. This study demonstrated that application of metsulfuron-methyl near the agricultural field did not alter water quality significantly that may cause significant deleterious effects on fishes. Though eight major parameters were found effective to deduce WQI of aquatic ponds near agricultural field, there is a scope of inclusion of more parameters which can also be accommodated to deduce WQI of different aquatic sources.

ACKNOWLEDGEMENT

Authors are greatly thankful to Director, Directorate of Weed Science Research, Jabalpur, India for allowing us to conduct this study.

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