



Potential Influence of Quizalofop-P-Ethyl (A Herbicide) on Different Models: A Review

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ABSTRACT

Herbicide is a double-edge sword, plays crucial role in increasing crop production but it also causes some negative effects. Herbicide is a chemical compound which control and kill weeds or pests in both agricultural and non-agricultural setting. The indiscriminate use of herbicide in agriculture, justifies the evolution of toxicity. An attempt has been made to study the potential effect of quizalofop-p-ethyl to cause reproductive or developmental toxicity.

KEYWORDS: Quizalofop-p-ethyl, herbicides, phytotoxicity, reproductive toxicity, developmental toxicity

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INTRODUCTION

Food safety is an area of growing worldwide concern as it affects directly human health. The great concern among the consumers is the presence of harmful herbicide and pesticide residue in food. The increase in pollution and indiscriminate use of herbicides in agriculture has resulted in chemical toxicity. Chemicals of anthropogenic origin which cause environmental contamination are found in water, air and soil and are harmful for various organisms. Herbicides is one of common group of contaminants. Quizalofop is a selective phenoxy herbicide used for controlling perennial grass weeds in sugarbeets, peanuts, cotton, flax, potatoes and soyabeans. The indiscriminate use of herbicides in agriculture and the increase of pollution in ecosystems due to industrial development, results in the evolution of chemical toxicity [15, 6, 9, 16-19]. Quizalofop-ethyl is a chemical compound from the group of aryloxyphenoxypropionic - herbicides (a sub-group of derivatives of phenoxyacetic acid and of quinoxaline). Quizalofop-ethyl is a representative of quizalofop herbicides, structurally the ethyl ester of quizalofop, the free acid.

EXTRACTION

Quizalofop-ethyl can be obtained from propionic acid. This is chlorinated to 2-chloropropionic acid and then esterified with ethanol. The intermediate now reacts with hydroquinone and 2,6-dichloroquinoxaline to give the final product.

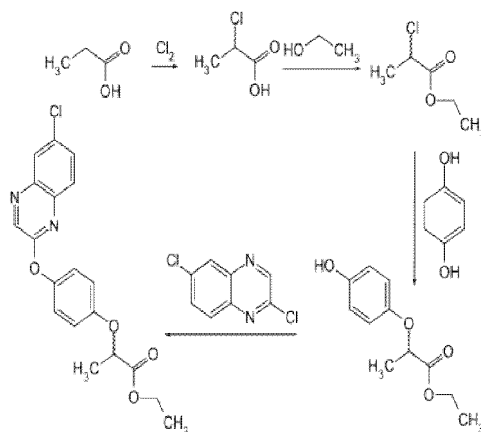


Fig.1: Quizalofop-ethyl

PROPERTIES

Quizalofop-ethyl is a colorless solid that is insoluble in water. It is unstable under the influence of light.

STEREoisomerism

Quizalofop-ethyl has one center of chirality and therefore can exist in two mirror-image forms, the (*R*) and the (*S*) isomer. The technical synthesis product represents a racemic mixture of both isomers. The more active (*R*) isomer is called quizalofop-P-ethyl.

EFFECT

The effect of quizalofop-ethyl is based on the inhibition of fatty acid - biosynthesis by engagement in the mode of action of the enzyme acetyl coenzyme A carboxylase .

USE AND APPROVAL STATUS

Quizalofop is a selective post-emergence - herbicide used against annual and perennial grasses, but not used against sedges and broadleaf weeds. The approval of the US took place in the late 1980s.

Quizalofop-P-ethyl was approved for use as an herbicide in the EU with effect from 1 December 2009. Crop protection products with Quizalofop-p-ethyl are only available in Switzerland, but not in Germany or Austria.

OATS

Quizalofop is directly applied to the surface of leaves i.e foliarly which selectively control grass weed in various vegetation. Petroleum oil adjuvant can increase the phytotoxicity of Quizalofop whereas vegetable oil adjuvants cannot enhance the phytotoxicity of quizalofop. The fatty acid methyl esters from vegetable oil is equally effective to petroleum oil in enhancing quizalofop phytotoxicity. In foliarly applied herbicide fatty acid methyl esters have enhanced the phytotoxicity.

Experiments were performed to examine the effect of triglycerides, free fatty acids and fatty acid methyl esters (FAME) on foliar absorption, delay of seed germination, inhibition in plant growth due to use of Quizalofop. In oats vegetation when quizalofop is applied with FFA and fatty acid methyl esters then absorption, translocation and phytotoxicity was increased. Triglycerides and FFA can also enhance quizalofop absorption and translocation only when they contain unsaturated and saturated fatty acid. Phytotoxicity in oats due to Quizalofop was greater when applied with sunflower oil fatty acid methyl esters and FFA than the linseed derivatives. Emulsifier lowers down the difference between linseed oil and sunflower oil in increasing the absorption, translocation and phytotoxicity of Quizalofop [15].

Experiment has been performed to control wild oats in peppermint field. Quizalofop is used in different combinations to increase its efficiency. Quizalofop was combined with many non-ionic surfactant such as methylated seed oil (MSO) or ammonium nitrate (UAN) liquid fertilizer . Methylated seed oil is more effective than non-ionic surfactant for enhancing quizalofop activity. The activity of quizalofop increases with both adjuvants when applied with ammonium nitrate. Effect of herbicide reduces when applied with proper adjuvant combination and also it increases weed control efficacy [23]. The experiment was conducted to examine the effect of Quizalofop-p-Ethyl at 10.8% EC in rape field. It was used to control the wild oats which was affecting the rape field. It has been seen that 10.8% EC of Quizalofop-p-Ethyl is used in 300L/hm² water and its foliarly applied to the wild oats. At the stage of 3-4 leaves, the controlling effect of wild oats reach from 66.24% - 95.75 %. So Quizalofop-p-Ethyl at 10.8% EC has proved that it has good controlling effects with long validity. Another experiment was conducted to see the control effects of Quizalofop-p-Ethyl at 15% EC and it has come out to be safe with good efficacy in controlling wild oats in rape field [26].

Allium cepa

The indiscriminate and excessive use of herbicide leads to very useful effect on human life and environment. It has been that Quizalofop-P-Ethyl decreases the mitotic index of *Allium Cepa*. Chromosomal aberrations like stickiness, bridges, ring chromosomes and micro nucleated were increased at different stages of cell cycle mainly in anaphase and telophase. Micro-nucleated cells were observed at different stages of cell cycle [22].

Allium Cepa is one of the most common plant indicators for environmental pollution. The meristematic roots of *allium cepa* were treated with Quizalofop-p-ethyl and cycloxydim at different concentration (0.5%, 1% and 1.5%) and as a result strong cytotoxic and genotoxic effects has been seen but in Quizalofop-p-Ethyl mitotic index decreases 30.2% (control) to 9.6% for the variant treated with 1.5% herbicide. In Quizalofop-p-Ethyl treated group strong mitodepressive effect with chromosomal aberration and nuclear alterations: stickiness, fragments, C-mitosis, lobulated nucleus, nuclear erosion

were observed both have strong potential so pollute the environment at concentration higher than 0.5% [19]. A field experiment was performed in Odisha in which Quizalofop-p-Ethyl and oxyfluorfen were foliarly applied and it was observed highest weed control efficiency (100%), plant height (60.63 cm), no. of leaves (8.80), leaf area (427.67 sq cm), average bulb weight efficiency (92.65 gm), total yield (315.76 q/ha) were seen when both herbicide were applied in combination [20].

CHICK PEA

Due to slow growth rate and limited leaf area development chick pea is a poor competitor to weeds. Due to wider crop spacing and slow growth rate, weeds give a tough competitor and due to this the yield and production of Kabuli Chickpea is reduced to 88 percent [4]. Excessive growth of weeds decline the crop quality. Due to extreme growth of weed it poorly affected the size of seed which is a important parameter in Kabuli Chickpea [10,11].

A field experiment was conducted to examine the effect of post emergence herbicide on growth and yield of chickpea. The plant height, pods growth, seed weight everything has been recorded with application of imazethapyr and quizalofop ethyl at 75 g/ha at 25 and 35 DAS resp. When higher dose of imazethapyr at 100g/ha is applied it has seen that it reduces the plant height and affects the growth of plant, pods, branches and root nodules and on the other hand seed weight has been increased. Application of post emergence herbicide i.e imazethapyr and quizalofop at lower dose i.e 50g/ha at 25 and 35 DAS was not sufficient to control the growth of weeds. But at higher rate of application of these herbicide at 75 g/ha and 100g/ha was totally effective on controlling weed growth but was phytotoxic on chickpea [12].

In each application of these herbicide at the dose rate of 75g/ha and 100 g/ha it reduces the grain yield and it was more at the 100 g/ha. It has been examined that both the post emergence herbicide are injurious to chickpea and injury increase with increase in the concentration of these herbicide. In case of imazethapyr phytotoxicity was more when compared to Quizalofop at all dose rates. It has been seen that at lower dose of application it was unable to control the growth of weeds and at higher concentration of imazethapyr and quizalofop it has declined the growth and yield of chickpea [15].

During rabi season in Varanasi a field experiment was performed to check effect of sowing dates, weed management, yield and nutrient uptake by weeds on chickpea when pendimethalin (1kg/ha pre-em) and Quizalofop-p-Ethyl (50g/ha post-em) was applied and it showed lowest density and dry weight of weeds. Crop sown earlier showed lowest nutrient depletion by weeds and high yield and nutrient uptake by chickpea [25].

A field experiment was performed on chickpea (2015-2016) in Junagadh to see the efficacy of different pre and post emergence herbicide. The pre-em used were Pendimethalin (0.90 kg/ha) and oxyfluorfen (0.18 kg/ha) at 40 DAS and post-em were pre mix of Imazamox and Imazethapyr at 0.03kg/ha and Quizalofop-p-Ethyl at 0.04 kg/ha at 20 and 40 DAS. The results revealed that Oxyfluorfen (0.18kg) as pre-em and pre mix of Imazamox, Imazethapyr and Quizalofop-p-Ethyl as post-em were more effective on yield attributes and quality of chickpea as compared to others [20]. Chickpea, being slow in its early growth and short stature plant, is highly susceptible to weed competition and causes 75% yield loss [9]. Among all weed control treatment, highest yield of chickpea has recorded in Quizalofop-p-Ethyl at 50g/ha at 30 DAS. However second hand weeding at 30 and 60 days after sowing (DAS) gave 20.2% higher grain yield than Quizalofop-p-Ethyl. All doses of Quizalofop-p-Ethyl at 40 and 50g/ha applied at 20 and 30 DAS gave higher values of yield as compared to imazethapyr [13].

SOYABEAN

Pesticide which are used these days to control the pests have some serious effects on human life as well as environment [18]. Plant growth regulators, pesticides, herbicide are excessively used in agriculture, the use of these pesticide have become a basic parameter to control the pests and to enhance yield and quality of crop. But continuous and indiscriminate use of these pesticide leads to undesirable conditions in culture plants. Pesticides are used individually or in combination from different range of class during cultivation or in post harvest storage to protect crops against pests/fungi or to preserve the quality and quantity of crop.

Anatomical and morphological experiments were conducted and quizalofop concentration taken was 0.4 M and 0.8 M Quizalofop-P-Ethyl was foliarly applied in 2-3 leaf stage. From morphological and anatomical experiments phytotoxicity due to Quizalofop-P-Ethyl has been seen. Due to exposure of Quizalofop-P-Ethyl there is decrease in amount of carotenoid and chlorophyll b pigments except chlorophyll a. Due to increase in concentration of Quizalofop-P-Ethyl the length of root and seedling has been decreased and also it affects the quality of seed [1]. Field experiment was performed during kharif season in Nagpur and Quizalofop-p-Ethyl was foliarly applied at dose of 62.5 g/ha at 20 DAS and 30 DAS and hoeing, weeding were done simultaneously. The highest seed yield (1160kg/ha) and straw yield (1973kg/ha) was

obtained after the chemical treatment, hoeing and hand weeding at 20 and 40 DAS. The highest weed control efficacy (96.8%) and lowest weed biomass were recorded with 2 hoeings and 2 hand weeding at 20 and 40 DAS [3]. Another field experiment was conducted in Patnagar to examine bio-efficacy of haloxyfop (10 EC) at 75, 100 and 125g/ha. Quizalofop-p-Ethyl 50g/ha, fenoxaprop 100g/ha and hand weeding at 30 and 45 DAS. The dose 125g/ha was found better than 75g/ha and no phytotoxic effect was seen. Application of fenoxaprop and Quizalofop-p-Ethyl recorded comparable weed density with haloxyfop at 100 and 125g/ha [24, 25]. The metabolism of Quizalofop-p-Ethyl was examined in soyabean and cotton plants. This herbicide was applied at dose of 4 oz of AI/acre. No detectable ^{14}C residues (<0.01 ppm) were found in mature beans or pods, but on the other hand mature fibre and seeds of cotton plant contain 0.08 and 0.09 ppm total ^{14}C residue respectively [12].

HELIANTHUS

Helianthus belongs to a daisy family Asteraceae and common name is sunflower and it is an sessile organism which has survived various ecological niches. Toxic substances enter the environment in various forms like acid rain, toxic gases, herbicide, pesticide etc. In modern agriculture the use of herbicide has become the necessity and it is foliarly applied and then these toxic substances enter the plant from cuticle or stomata then reacts physiologically and anatomically. Post emergence phenoxy herbicide is foliarly applied to helianthus annuus at dose rate of 0.3 to 3.1 Mm. On 1st, 5th, 10th and 15th day of treatment various activities has been recorded and it has been seen that peroxidase activity (POD) increase in all days of treatment and ascorbate peroxidase activity increases on the 5th and then continuously decreases whereas the amount of malondialdehyde (MDA) has increased in all days of treatment. The values of chlorophyll, carotenoids and total phenolic content fluctuates with the application of herbicide at different time interval. Salicylic acid plays an important role in protecting plant from phytotoxicity [2]. In sunflower root growth tests, roots were treated with 0.75 (EC50/2), 1.5 (ec50) and 3 mg/L concentration of Quizalofop-p-Ethyl for 24, 36, 48h. Morphological, mitotic abnormalities and effects in somatic chromosome has been seen. Mitotic concentration decreases with increase in herbicide concentration at each exposure time. Disturbed prophase, c-mitosis, stickiness, laggard chromosome and chromatid bridges were seen [9].

Different herbicide were used with different active ingredients as pre-plant, pre emergence and post emergence i.e Benfluralin, pendimethalin, alconifen, Quizalofop-p-Ethyl and Imazamox. Imazamox decreases plant height of both Clearfield hybrid. Pendimethalin decreases the no. of days to flowering of linoleic sunflower hybrid. Benfluralin showed the highest seed yield whereas Quizalofop-p-Ethyl decreases seed yield/hectare and also decreases significantly days to the flowering and seed oil content and Quizalofop-p-Ethyl gave the lowest plant height [17].

ZEBRAFISH

Quizalofop-P-Ethyl at different concentrations i.e 0.2, 20, 200 ug/L given for 30 day and it has been observed that it disturbs the endocrine system of zebrafish in sex-specific manner and then this herbicide increases the estrogen axis activity in males and decreases the same in females. And sex-specific manner explains that this herbicide regulates steroidogenesis and activates estrogen receptors [30].

Zebrafish embryo were exposed to different herbicide including Quizalofop-p-Ethyl from blastoderm stage to 4 days post fertilization. Quizalofop-p-Ethyl exposed embryos displayed cardiac dysfunction at LD₅₀, concentration slightly higher LD₅₀ resulted in 100% mortality, other abnormalities like curved spine, shortened body axis, lack of motility and abdominal edema were spotted. Quizalofop-p-Ethyl showed many teratogenic effects (King et al; 2019). Structure of zebrafish estrogen receptor was modelled by homology modelling. Aryoxy-phenoxy propionate (APP) herbicide have estrogenic effects on zebrafish. Interactions between APP herbicide and zebrafish estrogen receptor increases due to same size of substituents and polarity [28]. Zebrafish was exposed to Quizalofop-p-Ethyl with different concentration and high performance liquid chromatography was utilized to detect actual concentration of Quizalofop-p-Ethyl in water after 0h, 24h, 48h, 72h, 96h. Median lethal concentration was calculated and poisoning symptoms were seen. Quizalofop-p-Ethyl was judged as highly toxic for aquatic life according to classification standard of herbicide [30].

RATS

Pharmacokinetic and distribution of enantiomer of Quizalofop-Ethyl and its metabolite quizalofop acid has been examined in Sprague-Dawley male rats. Oral dose of Quizalofop-Ethyl was given at 10mg/kg and quick metabolism of Quizalofop-Ethyl to Quizalofop acid has been observed. Quizalofop-Ethyl is not detected in brain due to blood-brain barrier but it can be detected in many other organs even within 120 hrs. When concentration has been increased in rats then it has been observed that it lower downs the

food consumption, body weight, organ weight and increase in the organ coefficient of brain, lung, liver, kidney were observed at the dose of 1300 mg/kg [8].

Quizalofop-P-Ethyl in wistar rats given orally at a dose of (59.2 mg/kg) for 120 days shows significant increases in total leukocyte count, neutrophil, eosinophil, lymphocyte, cholesterol and potassium. Significant increase in lungs and decrease in weight of ovary. Swelling of intestine and in liver tissue has been seen [5].

HUMANS

Quizalofop-P-Ethyl is phenoxy herbicide belong to the group of aryloxyphenoxy propionic acid. Quizalofop-P-Ethyl is slightly poisonous and irritates the skin and eyes as well [29, 30]. This was the first reported case in humans causing cholestatic/hepatocellular toxicity due to continuous use of Quizalofop-P-Ethyl. It has been seen that the patient foliarly applies this chemical to his crop by spraying method. Due to Quizalofop-P-Ethyl exposure there were increase in serum level, bilirubin, a 2-fold increase in alkaline phosphatase and a 5-fold increase in γ -glutamyl transferase. Serum level of alanine and aspartate aminotransferase also increase.

CONCLUSION

A brief review of results on different models indicate that use of Quizalofop-p-ethyl caused a potential danger to the genetic material of exposed living organisms and cause damage to plants. Use of this herbicide for control of weeds is also a potential threat to *H. annuus*, *Allium cepa* and also other higher plants. Quizalofop-P-Ethyl has toxic influence on living organisms causing developmental and reproductive toxicity and showed many teratogenic effects and repeatedly shown to affect liver. Studies also indicate correlation between chromosome abnormalities and mutagenic activity in root-tip systems and in mammalian cell systems. Hence judicious use of this herbicide is recommended.

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CONFLICT OF INTEREST

No conflict of interest

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