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Herbicidal Potentiality of Fusel Oil

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1. Introduction

During the process of manufacturing sugar, various by-products are generated. Some, such as bagasse and vinasse, which are generated in large quantities, have the potential for use as fertilizers or soil conditioners and thus for reducing the environmental impact of sugar processing. Others, because they are produced in smaller quantities, are mixed with other materials and taken to the field or marketed as raw material for other processes, as is done with fusel oil.

In alcohol distilleries, fusel oil is a by-product produced during alcohol fermentation and is taken from the rectifying columns. Average production ranges from 0.1 to 0.5 liters per 100 liters of alcohol produced. Although there is no mention of its role in agriculture or distilleries, it has commercial value and is usually marketed according to the amount of isoamyl alcohol present.

Generally, the use of fusel oil is restricted to perfume industries, where it can be employed as a fixative in cosmetics manufacturing, and for preparing artificial flavors or flavoring.

A study from Azania (2003) suggested the possible use of this byproduct as a plant desiccant. When applied directly into the soil of pots planted with sugarcane, the plants wilted, progressively dried out and later died.

It is worth noting that up to this time, this work was unique, given the lack of studies using this approach.

2. Utilization of by-products in mills and distilleries

Reducing the cost of operations in the area of sugarcane reform can be substantial when by-products generated in the manufacturing of sugarcane are employed. Vinasse is the best known by-product in terms of reuse. Due to its pollutant potential and the large quantity in which it is produced, where vinasse is utilized merits attention.

There are several alternatives for vinasse reuse, but none is used to the same magnitude as fertigation. Fertigation of sugarcane may improve the physical, chemical and biological properties of the soil (Ferreira & Monteiro, 1987). Moreover, through fertigation, one can fully or partially replace mineral fertilization, increase the availability of macro and micronutrients and raise the pH of the soil. These effects, along with increased productivity

of sugarcane, may also contribute to an increase in the overall production of grains on former cane plantations.

Another by-product of manufacturing alcohol is flegmass, which is mixed with vinasse and applied in the field despite its effects on soil not being fully known. Flegmass is obtained from the rectifying column of phlegm during the process of alcohol production.

Fusel oil, another byproduct of this process, is a result of alcohol redistillation. It consists of a mixture of high-grade alcohols, usually stored in separate tanks. It is often used as a raw material with low commercial value for chemical industries recovering isoamyl alcohol, whose reuse in agriculture was not mentioned in the literature until a decade ago.

When a sufficient amount of by-product is accumulated in the storage tanks, it is sold to cosmetics or perfume companies or as a solvent, hydraulic fluid or defoamer (Patil et al., 2002). For Vauclair et al. (1997), the presence of high-grade alcohols increases the commercial value of fusel oil. However in Brazil, the sale price depends almost exclusively on the amount of amyl alcohol present, which is the largest constituent of fusel oil.

According to Nascimento et al. (2003), for each 1000 L of ethanol produced, about 2.5 L are fusel oil. Taking this estimate and the Brazilian production of 18 billion liters of alcohol in the harvest of 2005/2006 into account, approximately 42.5 million gallons of fusel oil were produced. According to data from Agrianual (2008), total production of ethanol from sugarcane in Brazil in the 2007/2008 harvest was approximately 21.3 billion gallons, which means that roughly 53.2 million liters of fusel oil were produced.

The data show that the trend for ethanol production is always increasing, and the production of fusel oil follows this trend as well. In the most current calculation by Conab (2010), the 2010/2011 crop will produce 28.5 billion liters of ethanol, which generates approximately 71 million gallons of fusel oil without direct use by production entities.

In an unpublished study, Azania (2003) mentioned a possible desiccant potential of fusel oil, indicating a possible use in the fields for chemical eradication of sugarcane to renew the sugarcane plantations because the product has contact action: it destroys the tissues of the plant surface. The only products that have contact action are acids, salts, oils and detergents (Deuber, 2003). Many oils can be highly phytotoxic, and some have been used as herbicides (Kissmann, 1985). This contact action is a result of the oil breaking down the tissues of the leaf surface and destroying the cells.

If studies demonstrate the economic feasibility of using fusel oil for weed control or eradication of sugarcane, this would be an option to reduce the expense of using certain herbicides, as it costs very little to produce fusel oil in the distilleries.

3. General characteristics of fusel oil

In general, fusel oil is a dark-colored liquid that may also have yellow and green tones. Its odor is unpleasant, distinctive and responsible for the characteristic taste and aroma of aguardentes (Lima, 1964). It is produced during the processing of amino acids by yeasts during fermentation in distilleries, and its components are high-grade alcohols (Botelho, 1945). According to Rasovsky (1973), its specific weight is 0.83, with a boiling point between 75 and 134°C. Fusel oil is flammable and burns with a bright blue flame. It mixes easily with other products such as alcohol, chloroform and ether.

Fusel oil is composed of a mixture of alcohols such as ethyl, amyl, isoamyl, propyl and butyl. According to Almazan et al. (1998), amyl alcohol, isoamyl alcohol, n-butanol and other compounds can be separated by another distillation process, which has some

economic advantages. However, this other distillation process is performed not by the distilleries, but by the companies that buy the product to market it. Besides the compounds listed above, Nascimento et al. (2003) report that sec-butanol, esters, alkanes and terpenes may also be present. Once separated and purified, these substances are useful in the preparation of artificial flavors or flavoring. Souza & Llistó (1978) reported that fusel oil may also contain hexyl, heptyl and octyl alcohols in small quantities.

However, the main constituent of fusel oil is isoamyl alcohol (Vauclair et al. 1997; Kuçuk & Ceylan, 1998; Pérez et al. 2001; Ceccato-Antonini & Silva, 2002; Azania, 2003, Nascimento et al. 2003), which comes from the decomposition of iso-leucine, an amino acid derived from the hydrolysis of proteins in yeast (Codistil, 1978). According to Nascimento et al. (2003), isoamyl alcohol has been investigated by chemical industries as a reagent in organic synthesis or as a solvent in the extraction of pharmacological compounds such as esters. According to Rasovsky (1973), fusel oil mostly consists of methanol, superior alcohols in the series of greases, isobutyl and propyl alcohols and 8-10% ethyl alcohol. Therefore, it is believed that the composition of fusel oil is dependent on the raw material used, the fermentation conductions and the process of distillation and decanting of the oil (Rasovsky, 1973).

In Brazil, the raw material used is sugarcane. In other countries, other types of raw materials also produce fusel oil as a byproduct. Accordingly, Brinker (2000) noted that alcohol distilled from potatoes has a greater amount of fusel oil, which is almost pure isoamyl alcohol, whereas alcohol produced from grain has more fusel oil than alcohol distilled from grapes. Grain fusel oil consists mainly of isoamyl alcohol, whereas the grapes have more butyl alcohol and other volatile fatty acids.

Table 1 describes the main components of fusel oil according to analysis using gas chromatography. Analyses performed in two different years showed higher percentages of isoamyl alcohol, followed by ethanol and butanol as principal products.

Components	**Fusel oil (%)**	
	2003	**2007**
Ethanol	11.70	14.46
n-propanol	0.83	1.69
i-butanol	8.47	10.30
n-butanol	0.21	0.67
i-amyl	28.66	61.60
n-amyl	0.12	0.49

Table 1. Chemical composition of fusel oil, analyzed by gas chromatography. (Azania, 2003 and 2007)

The fusel oil used by Azania (2003 and 2007) was from the same distillery but was collected in different seasons, which shows that its composition may vary according to time collected, method of conducting the process and characteristics of the raw material (Rasovsky, 1973). Kuçuk & Ceylan (1998) also showed this order of products in terms of percentage, but their results differ, as all of the values were lower than those of this work.

In the process of fusel oil production, Rasovsky (1973) states that the phase of oil extracted from the column is of paramount importance, without which there will not be a high quality product. To have properly-washed oil of good market value, one should measure the alcohol content of wash water, which should range between 8 and 12° GL (Codistil, 1978).

The most widely used system is the "settle-wash," in which crude oil is washed countercurrently with water, leaving the alcohol that was carried and deposited spontaneously, having then been extracted. When the fusel oil is not taken from the column, it is taken away by either flegmass or its own alcohol, which inevitably causes a fall in temperature at the base of the column (Codistil, 1978).

By presenting a difference in the type of raw materials and processes used, the quantity of fusel oil produced varies greatly between producing units. In Brazilian literature, two references state that 2.5 L of fusel oil are produced for every 1000 L of ethanol produced (Nascimento et al. 2003) or between 0.1 to 0.5 L per 100 liters of alcohol (Codistil, 1978).

To understand the technological differences between countries, see Turkey as an example, where 5 liters of alcohol are produced for every 1,000 liters of alcohol distillation, and approximately 30 million gallons of fusel oil are produced per year (Kuçuk & Ceylan, 1998) from beets.

4. Results from research on the applications of fusel oil in agriculture

4.1 Application of fusel oil in sugarcane and effects on the soil

Until recently, there was no mention of fusel oil use in agriculture, for this potential was first described by Azania (2003) to test different products derived from alcohol (vinasse, flegmass and fusel oil) and their impacts on soil fertility in sugarcane plants and weeds. Sugarcane plants treated with fusel oil at four concentrations (12.5, 25.0, 50.0 and 100.0% v/v) applied at a volume corresponding to 150 m^3 ha^{-1} wilted in a progressive and irreversible process of drying of the leaves and branches in the first 24 hours after application.

One of the conclusions of this study pointed to a possible desiccant potential of the by-product toward the plants because the drying and death of the sugarcane plant was observed a short time after application of the by-product. In the soil, the chemical attributes were altered with increased levels of calcium, acid potential and aluminum.

4.2 Effects of fusel oil application in *Sida rhombifolia* and *Brachiaria decumbens*

The study was conducted under laboratory conditions by Azania et al. (2003) to evaluate the germination of *Sida rhombifolia* and *Brachiaria decumbens* after applications of vinasse, flegmass and fusel oil. These by-products at concentrations of 12.5, 25.0, 50.0 and 100.0% (v/v) and controls (water with pH and osmolality adjusted depending on the characterization of the by-products and their dilutions) were applied directly to 100 seeds in plastic boxes using paper as a substrate.

The seeds of *Sida rhombifolia* that were treated with fusel oil did not germinate and had reduced viability, especially with higher applications. *Brachiaria decumbens* seeds that were treated with a higher concentration of flegmass had reduced viability and germination speed index. In the presence of fusel oil, *Brachiaria decumbens* seeds did not germinate and were completely unviable.

In a similar work, Azania et al. (2004) evaluated the effects of fusel oil, compared to flegmass and vinasse, on the growth of plants (*Sida rhombifolia* and *Brachiaria decumbens*) grown simultaneously in the greenhouse. Concentrations of 12.5, 25.0, 50.0 and 100.0% (v/v) of each by-product and the control (water) were applied (at a rate equivalent to 150 m^3 ha^{-1}) in pots (22 L) containing 100 seeds of each weed. Fusel oil inhibited the emergence of *Sida rhombifolia* and *Brachiaria decumbens*. Vinasse and flegmass reduced the emergence and development of *B. decumbens* and *S. rhombifolia*.

4.3 Mixing fusel oil in the spray solution

After publication of the first results, several studies were conducted to understand better the way that by-product behaves, its characteristics and the application rates that were most effective in the eradication of sugarcane and weeds. However, one of the problems encountered during this research was how to blend the fusel oil spray because the product does not homogenize easily with water.

To remedy this problem, work was undertaken by Azania (2007), whose objective was to study the effectiveness of surfactants and/or adhesive spreaders and alcohol on the stability of the spray solution, which consisted of fusel oil and water. A range of products already used for this purpose were tried.

The results indicated that of all the products tested, a non-ionic wetting agent, trademarked Energic (226 g L of nonyl phenoxy poly (ethyleneoxy) ethanol + 226 g L of sodium salt of dodecyl benzene sulfonic acid to 548 g inert L) and a neutral detergent were those that presented the best results and were able to maintain the emulsion for 30 minutes without separation. Alcohol was unfeasible due to the amount that would be needed to achieve good results.

4.4 Application of fusel oil for the eradication of sugarcane plants

While Azania (2003) found a possible desiccant potential of fusel oil in sugarcane, the tests were performed by placing different concentrations of product directly into the potted soil. When used with manual spray application with the appropriate bar and nozzles, the isolated product was not satisfactory for use as a desiccant in any of the tested concentrations because the effects ranged from mild to moderate and some plants recovered (Azania, 2007).

When the product hit the leaves, a yellow color appeared in the location of the drops in just a few hours, and the tissue generally began wilting and posterior necrosis. In this study, were used XR Teejet 110.02 VS nozzles for the preliminary results. However, the results were not satisfactory, so another application was made, this time with TT 110.02 nozzles, which provided better spreading of the product.

Based on previous research results, Azania (2007) evaluated the effect of fusel oil, glyphosate and a mixture of the two products in the eradication of sugarcane. Due to the lack of knowledge about the use of fusel oil in agriculture, it became necessary to test different dosages compared to glyphosate. Dosages for fusel oil application were determined by the cost of the individual products, so that the final cost would not exceed that of the glyphosate application (4 L ha^{-1} commercial dose) usually used by farmers for sugarcane eradication.

The experiment was conducted in 22 L pots maintained until 60 days after treatment (DAT). The treatments were (1) 4 L ha^{-1} glyphosate; (2) 150 L ha^{-1} fusel oil; (3) glyphosate 2.5 + 6.25 L ha^{-1} fusel oil; (4) glyphosate 2.0 + 25.0 L ha^{-1} fusel oil; (5) glyphosate 1.5 + 43.75 L ha^{-1} fusel oil; (6) glyphosate 1.0 + 62.50 L ha^{-1} fusel oil; (7) 100 L ha^{-1} fusel oil; (8) glyphosate 1.50 + 18.75 L ha^{-1} fusel oil; (9) glyphosate 1.0 + 37.50 L ha^{-1} fusel oil; (10) 75.0 L ha^{-1} fusel oil; (11) glyphosate 1.0 + 12.50 L ha^{-1} fusel oil; and (12) 50.0 L ha^{-1} fusel oil applied with pressurized backpack equipment, fitted with four Teejet 110.02 Turbo TT nozzles, at a pressure of 30 lb $in.^2$ (2.1 kgf cm^2) and spray volume of 200 L ha^{-1}. Also, 0.2% neutral detergent was added to all treatments involving fusel oil to facilitate mixing.

For application, the developmental stage of the culture was considered, which was an average of 28 cm in height measured from the first visible ligule to the ground. Moreover, the plants were in full vegetative development and not subjected to any kind of stress.
The fusel oil alone did not promote drying of sugarcane. In treatments with a mixture of glyphosate and fusel oil, the injuries were not as severe initially but were enough to dry out the main tiller until 60 DAT. Another important factor was the sprouting of suckers, which may mean that the results were not satisfactory from an agronomic point of view, as the expected result would be that the whole plant suffered stress resulting in the desiccation process. Overall, the soil chemical properties did not suffer alterations with the application of glyphosate, fusel oil or a mixture of the two.

4.5 Application of fusel oil in late post-emergence in a natural community of weeds

Azania et al. (2008) evaluated the effectiveness of fusel oil applied singly or in combination with desiccant herbicides during the late post-emergence stage in a natural community of weeds.
The experiment was conducted in the field in 3x3 m plots. The least satisfactory results of the experiment were those in which only the fusel oil was applied. In the treatments (1.50 + 43.75, 1.00 + 62.50, 1.50 + 18.75, 1.00 + 37.5, 1.00 + 12.5 L ha^{-1} glyphosate and fusel oil, respectively) that contained glyphosate, fusel oil allowed a reduction of the herbicide dosage and provided maximum control over a natural community of weeds consisting of *Amaranthus spp., Brachiaria spp.* and *C. echinatus*, but not *Commelina* and *Cyperus* genera. These species, even with yellow spots, showed tolerance to the products and did not desiccate (Figure 1).

4.6 Application of fusel oil for weed management in no-till farming

Osipe et al. (2009) proved the effectiveness of fusel oil for weed management in no-till systems, for they obtained positive results in controlling *Digitaria insularis* and *Commelina benghalensis*.
The authors concluded that fusel oil was effective in controlling weeds in the doses tested (220, 440, 660 and 880 L ha^{-1}) and that it has the potential to become a product for use in no-till management. However, they stressed that further studies are necessary to design an application technique that reduces the volume of product applied per hectare.

4.7 Eradication of sugarcane with application of fusel oil spray and soil treatment and evaluation of subsequently-planted sunflowers

The eradication of sugarcane ratoon was also studied by Azania et al. (2010a) to test different concentrations of fusel oil which were pulverized and applied to the soil, as well as the development of subsequently-planted sunflowers.
The rationale for performing this work was that in the reform of a sugarcane plantation, the use of fusel oil could be another option for producers, which consequently would have economic and environmental benefits because there would be less application of desiccant herbicides. However, the use of fusel oil should be studied further because the residue only highlights its desiccant potential.
The planting of sugarcane, which is costly and consumes considerable amounts of herbicides that may even harm the environment, could benefit from the use of this

byproduct. From this standpoint, Pérez et al. (2001) thought that the low commercial value of fusel oil coupled with high production volume of crops are factors that should encourage proposals to develop technology to use fusel oil. Consequently, the choice of desiccant herbicides for of sugarcane reform is essential for the selection of both the sugarcane and the species that can be cultivated after eradication of the ratoon.

The cultivation of legumes (Bolonhezi, 2007), sunflowers and peanuts (Ramos et al., 2009) is common after ratoon eradication and before new sugarcane planting. However, Pires et al. (2003) stated that it is essential that there be no herbicide residues that are selective for these plants in the soil to ensure the development of new plants.

Sunflowers are cultivated to obtain green mass to be incorporated into the soil to improve the physical and chemical properties. In the case of fusel oil, it is interesting to identify portions that enable the development of sunflowers or other crops after eradication of sugarcane ratoons.

Therefore, to highlight the use of fusel oil, the objective was to test the hypothesis that fusel oil applied by spraying or directly into the soil promotes the eradication of the ratoon without harming the development of successive sunflower plantings.

The authors found that fusel oil applied by spraying the sugarcane did not eradicate the ratoon. However, applying fusel oil directly to the soil was effective in eradication of ratoons, and it did not alter the chemical attributes of the soil that are essential for plant development (except phosphorus values, which were less than those of the control due to the 0.1 m^3 ha^{-1} of fusel oil). It also did not jeopardize sunflower development afterward. The failure of fusel oil to alter the majority of soil chemical properties, which was found in the work of Azania (2003 and 2007) and corroborated by the results of this research, is a positive signal to continue this type of research. One should not forget that agro-industrial residues such as fusel oil are generally chemically unbalanced and should be applied in the environment with caution.

4.8 Efficacy of herbicide management in association with fusel oil on species of weeds

In a more recent publication on the subject, Pizzo et al. (2010) warned that it is common for producers to mix different herbicides directly into the same spray tank in the field, with standard formulations for two or more molecules, according to Rodrigues & Almeida (2005). However for technical purposes, studies that demonstrate the efficiency of control of two or more herbicides mixed in a single application are important for the subsequent possibility of registering new standard formulations.

Considering the technical need to verify the effectiveness of the mixtures made directly in the tank, the herbicide potential and low commercial value of fusel oil, Pizzo et al. (2010) evaluated the efficiency of herbicide control in combination with fusel oil on *Panicum maximum*, *Amaranthus deflexus*, *Ipomoea quamoclit*, *Euphorbia heterophylla* and *Brachiaria decumbens*.

The treatments consisted of: diuron + hexazinone (1170 + 330 g ha^{-1}); diuron + hexazinone (1170 + 330 g ha^{-1}) + fusel oil (25.0 L ha^{-1}); diuron + hexazinone (819 + 231 g ha^{-1}) + fusel oil (25.0 L ha^{-1}); metribuzin (1920 g ha^{-1}); metribuzin (1920 g ha^{-1}) + fusel oil (25.0 L ha^{-1}); metribuzin (1344 g ha^{-1}) + fusel oil (25.0 L ha^{-1}); amicarbazone (1400 g ha^{-1}); amicarbazone (1400 g ha^{-1}) + fusel oil (25.0 L ha^{-1}); amicarbazone (980 g ha^{-1}) + fusel oil (25.0 L ha^{-1}) and no

herbicide. The treatments were applied with a pressurized backpack sprayer at a volume corresponding to 250 L ha-1 in post-crop emergence (30 cm) and weeds (up to 20 cm).
The herbicides diuron + hexazinone, metribuzin and amicarbazone isolates were effective in controlling all species, but full dosage and 70% of the dose plus fusel oil only showed satisfactory control in species of *I. quamoclit* and *E. heterophylla*.

4.9 Fusel oil applied in early and late post-emergence of weeds

Azania et al. (2010b) studied the response of weeds to doses of fusel oil applied in early and late post-emergence. For this study, the species *Ipomoea hederifolia*, *Ipomoea quamoclit*, *Euphorbia heterophylla*, *Digitaria spp*. *Cenchrus echinatus* and *Panicum maximum* were used. Fusel oil was applied in early and late post-emergence at doses of 50, 125, 250, 375 and 500 L ha^{-1} plus the untreated control. The plots were made of polyethylene pots with a capacity of 3 L and contained soil from the topsoil of a fallow field. The percentage of intoxication at 7 and 30 days after application (DAA) were visually observed.
These species were only susceptible to the use of 500 L ha^{-1} of fusel oil applied in early or late post-emergence. *Digitaria spp*. was susceptible, *E. Heterophylla* was tolerant, and all of the other species were moderately tolerant to fusel oil applied in early post-emergence. *E. heterophylla* was susceptible, *Digitaria spp*., *C. echinatus* and *P. maximum* were moderately tolerant and *I. hederifolia* and *I. quamoclit* were tolerant to fusel oil applied in late post-emergence.

4.10 Influence of fusel oil on the development of peanut crops planted in rotation with sugarcane

Azania et al. (2009) evaluated the influence of by-products (vinasse, flegmass and fusel oil) that had previously been applied to sugarcane on the chemical attributes of the soil and the development of peanut crops (*Arachis hypogaea*) in a greenhouse.
The experiment was set up in 22 L pots with treatments of a combination of the three by-products at four concentrations (12.50, 25.00, 50.00 and 100.00% v/v), as well as a control that was irrigated with water and fertilized. Forty days after treatment, the pots that the sugarcane was taken from were planted with seeds of the peanut cultivar Tatu vermelho at 10 seeds per vase, and two plants were maintained per pot after thinning (20 days after planting – DAP).
Fusel oil at 50.0 and 100.0% reduced the soil pH and increased the levels of toxic aluminum. The vinasse increased the pH, freeing up more nutrients. The initial development and subsequent peanut production were influenced by the fusel oil at the two highest concentrations (50.0 and 100.0%), where there was little plant development.

4. Conclusion

The residuals and/or by-products generated by different industrial processes most often have no practical application, and when stored, they may contaminate the environment. Research dedicated to exploring possible uses for these materials is of great importance. In this way, research so far shows that the fusel oil applied in combination with herbicides or herbicide alone has potential, and it only needs to be further explored scientifically to adjust doses and expand application technology.



Fig 1. A) Weed community before the application of treatments; B) lack of control of *Cyperus* sp. and *Commelina benghalensis* (1.50 + 43.75, 1.00 + 62.50, 1.50 + 18.75, 1.00 + 37.5, 1.00 + 12.5 L ha^{-1} glyphosate and fusel oil, respectively); C) *Commelina benghalensis* with yellow leaves and D) total control of weeds (1.50 + 43.75, 1.00 + 62.50, 1.50 + 18.75, 1.00 + 37.5, 1.00 + 12.5 L ha^{-1} glyphosate and fusel oil, respectively). Ribeirão Preto, Brazil, (Azania, 2007).

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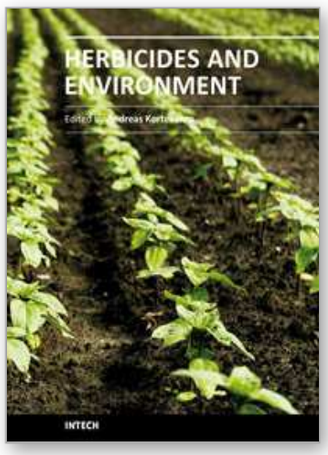
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Herbicides are much more than just weed killers. They may exhibit beneficial or adverse effects on other organisms. Given their toxicological, environmental but also agricultural relevance, herbicides are an interesting field of activity not only for scientists working in the field of agriculture. It seems that the investigation of herbicide-induced effects on weeds, crop plants, ecosystems, microorganisms, and higher organism requires a multidisciplinary approach. Some important aspects regarding the multisided impacts of herbicides on the living world are highlighted in this book. I am sure that the readers will find a lot of helpful information, even if they are only slightly interested in the topic.

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