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Review

The efficacy and safety of bromacil based herbicide for the control of the invasive bush species in South African rangelands

S. Dube[1]*, M. S. Lesoli[1] and A. O. Fatunbi[2]

[1]Livestock and Pasture Science Department, University of Fort Hare, PB x 1314, Alice 5700, EC, South Africa.
[2]Agricultural and Rural Development Research Institute (ARDRI), University of Fort Hare, PB x 1314, Alice 5700, EC, South Africa.

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The use of bromacil based herbicides in agriculture and environmental management is a growing practice with economic importance. Bromacil possesses broad toxicity to many plant species, although, different formulations exist that are used for different purposes in farming systems. There is increasing concern about its use for the control of invasive woody species on South African rangelands; especially its effects on non-target grasses, broad leaved plants and other biotic components of the rangeland ecosystem. This review outlines the importance of bromacil use, its nature and activities as an ingredient in herbicide formulation and the effects of its use on biotic and non-biotic components of rangeland ecosystems. The current use of bromacil based herbicides for the control of bush encroachment seems necessary to derive good productivity from encroached rangelands and reduce cost and drudgery associated with other methods of bush control. Bromacil is absorbed through the plant's root system and translocated upwards via the xylem vessels to the leaves, where it interferes with light harvesting complexes and disrupt the photosynthetic pathways of the plant. This kills the plant slowly; sometimes, it spans over two years. Bromacil could be persistent in the environment for the same length of time, depending on the application method, the target species and the soil properties at the application site. Bromacil has a very low mammalian toxicity, but is considered to be slightly toxic to fishes and amphibians. The effect of Bromacil on soil microbial population depends on the exact formulation, concentration and microbial species in question. Yet, bromacil is degraded by microorganisms in the soil and water, portions that escape into open water bodies are also degraded by photo-oxidation reaction. While bromacil provides for sustained weed control, its persistence in the environment and low degradation rates, is a cause for concern.

Key words: Bromacil, invasive species, rangeland encroachment.

INTRODUCTION

Encroachment of rangelands by shrubs and woody species has been observed globally. Often the encroaching species suppress the growth of palatable grasses and herbs, as they grow into impenetrable thickets (Wiegand et al., 2006). This often results in reduced grazing capacities in livestock farms. As a result, livestock farmers have regarded bush encroachment as a major problem and have resorted to various control measures. The causes of bush encroachment are not clearly understood but it is suffice to say that they are diverse and complex (Smit et al., 1999). Consequently, it is difficult to devise complete control measures for all encroaching species. Various control methods viz., cultural, mechanical and chemical uses have been tested. Burning, browsing with goats, cutting and application of herbicides are some of the methods that are widely used to control encroaching species. The uses of herbicides have however brought about various environmental concerns (EXTONET, 1993; Rosner et al., 1999; Singh et al., 2003; Zhu and Li, 2002). This has resulted in the need to investigate the effects of different types of herbicides on

*Corresponding author. E-mail: sdube@ufh.ac.za.

components of the ecosystem.

A number of herbicides in South African markets are currently being used in controlling encroaching species, of particular note are herbicides containing bromacil (5-Bromo-3-sec-butyl-6-methyluracil) as the active ingredient (a.i), for example Bushwacker SC(Enviro Weed Control Systems (Pty) Ltd), Bushwacker GG (Enviro Weed Control Systems (Pty) Ltd), Rinkhals 400 PA (Dow AgroSciences LLC) e.t.c. These herbicides differ mainly in their bromacil concentration, for instance Bushwacker SC contains 500 g bromacil per litre, Bushwacker GG contains 200 g bromacil per kilogram and Rinkhals 400 PA contains 400 g bromacil per kilogram. The different concentrations of bromacil determine the specific use of the herbicide, coupled with the concentration of other reactive ingredients. Herbicides are usually selective within certain application rates, environmental conditions, and methods of application (Masters and Sherley, 2001).

Bromacil belongs to the uracil family of herbicides (Arteca, 1994). It can be used to selectively control annual and perennial weeds, broad leaved and woody plants on cropland and non-cropland areas (EXTOXNET, 1993; Meister, 1998; Zhu and Li, 2002). It is also widely used for selective weed control in pineapple and citrus crops (EXTONET 1993). Bromacil works by interfering with the photosynthetic pathway of plants (EXTOXNET, 1993). One herbicide that is gaining importance in bush control in South Africa is Bushwacker SC. It has been reported to be an effective herbicide for general weed and bush controls in agricultural and non-agricultural areas (Zhu and Li, 2002). This herbicide can be sprayed on the plants or spread dry. It quickly dissolves in soil water and may stay in the soil for several years (EXTOXNET, 1993). Its application is usually done just before the active growth stage of plants thus, before the wet season stabilizes. Bromacil is readily absorbed through the root system (Gangstad, 1989) and is a specific inhibitor of photosynthesis. In the soil, there is little adsorption of bromacil to soil colloids therefore it moves (leaches) through the soil and it can contaminate groundwater (EXTOXNET, 1993); however, it is highly susceptible to microbial degradation (Arteca, 1994). When used as a selective herbicide it can persist in the soil for one year, however if it is applied at high concentrations it can persist for more than one year (Arteca, 1994).

There is the speculation that bromacil can destroy some grasses if it stays too long on the upper horizon of the soil profile. Grasses are assumed to extract water from the top soil layer (0 - 15 cm) due to their shallow rooting characteristics, while trees and bushes derive their nutrients from the lower layers (Wiegand et al., 2006). The movement rate of bromacil when applied is therefore important to its economic use and ecological suitability. There is the perception that phytotoxicity could occur when animals ingest plants that may have taken up bromacil from soil water. Furthermore, the relative effects of bromacil on soil microbial activity and dynamics need to be investigated.

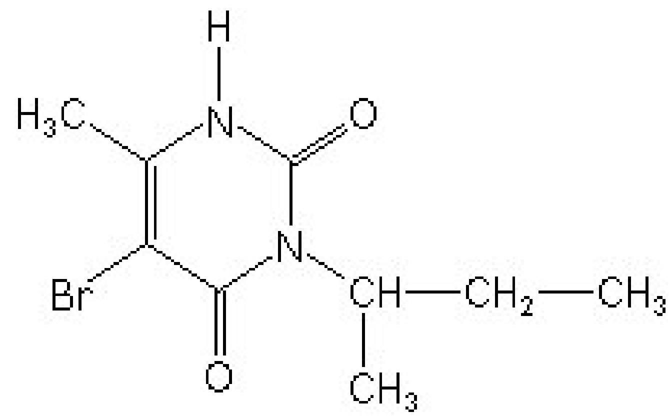

Figure 1. Bromacil (5-bromo-3-sec-butyl-6-methyluracil). Adapted from the International Organization for Standardization (ISO).

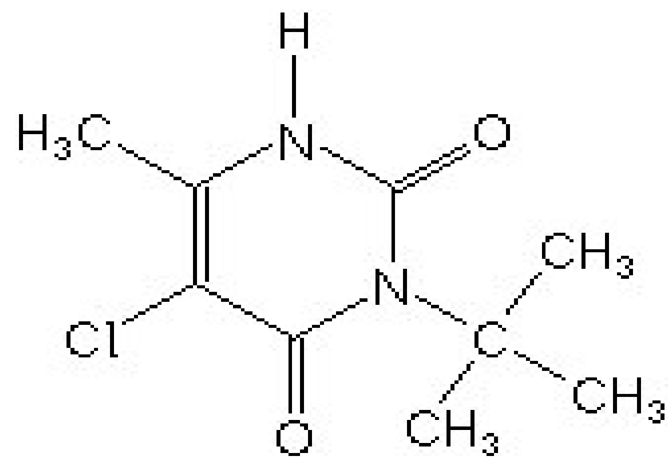

Figure 2. Terbacil (3-tert-butyl-5-chloro-6-methyluracil). Adapted from the International Organization for Standardization (ISO).

The aim of this paper is to clear doubts about the effectiveness and safety of the use of bromacil for the control of invasive species in South African rangelands. We also aim to identify areas that require further study in order to retain a useful perspective of the subject. Although the focus of the paper is South African rangeland, the authors admit the flexibility of citing reported work from other parts of the world.

PROPERTIES OF BROMACIL

Bromacil (Figure 1) falls under the substituted uracil family; other members of the family include terbacil and isocil (Figures 2 and 3). Terbacil is an effective herbicide for the control of annual and perennial weeds. The general characteristic of the uracil family is the presence of a methyl group located at the sixth position on the ring. The members of the substituted uracil herbicide family

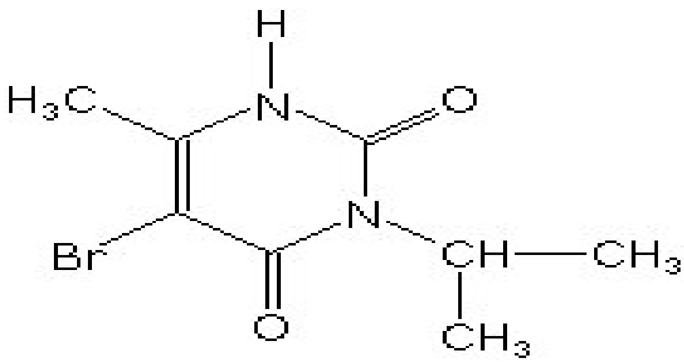

Figure 3. Isocil (5-bromo-3-isopropyl-6-methyluracil). Adapted from the International Organization for Standardization (ISO).

differ one from another by substituents at the third or fifth position of the ring, or both. The bromacil molecule consists of a uracil nucleus containing bromine, methyl and a secondary butyl substituent.

The family as a whole possesse a broad toxicity to many plant species, however specific compounds differ significantly in their toxicity to plants, solubility in water, persistence in soil and other economically significant characteristics. Firstly introduction of this family of herbicides was intended for general vegetation control, mainly because the different compounds have broad spectrum activity over a wide range of plant species and they also persist long in the soil, therefore, having long residual activity for weed control in industrial areas. The principal use of these herbicides are the selective control of many annual and perennial weed species in certain crops and general weed control in non-crop areas, such as railroads, highways, pipeline right-of-ways, lumber-yards, storage areas and industrial sites. The uracils are formulated as both wettable powders and as water soluble preparations. All of the uracil herbicides in pure form are white, crystalline solids and are temperature stable up to their melting point of 335℃. The uracils are characteristically low in mammalian toxicity and are nonvolatile. Their long persistence in soil, however, does create problems in crop rotations.

MODE OF ACTION

The mode-of-action is the overall manner in which an herbicide affects a plant at the tissue or cellular level. Bromacil is a powerful mobile inhibitor of photosynthesis (Prostko, 2001). The target plant must be undergoing active photosynthesis for the herbicide to be effective. It is readily absorbed through the root system (Gangstad, 1989); the leaves and stems can also absorb some bromacil. It is translocated upward via the xylem to foliage and interferes with light-harvesting complexes (Prostko, 2001). It inhibits photosynthesis by blocking the photo-system II reaction; thereby preventing the conversion of sunlight into chemical energy (Prostko, 2001), thus it blocks the photosynthetic electron transport (Prostko, 2001). Bromacil blocks electron transport from QA to QB in the chloroplast thylakoid membranes by binding to the D-1 protein at the QB binding niche. The electrons that are blocked from passing through photosystem II are transferred through a series of reactions to other reactive toxic compounds. These compounds disrupt cell membranes and cause chloroplast swelling, membrane leakage, and ultimately cellular destruction (Tu et al., 2001). Inhibition of photosynthesis thus results in slow starvation of the target plant and eventual death.

Bromacil is readily absorbed through the plant root system (Bovey, 2001; Gangstad, 1989). Little or no bromacil moves from the apex downward toward the base of a treated leaf via the phloem. The early symptom of bromacil kill activities in a plant is leaf chlorosis concentrated around the veins, this is often noticed at the lower leaves and it gradually moves up the plant. The structure of the leaves' chloroplasts is altered while further cell wall development will cease. Chlorosis will then appear first between leaf veins and along the margins which is later followed by necrosis of the tissue and eventual death of the plant (Prostko, 2001).

USES AND IMPORTANCE OF BROMACIL

The control of undesirable species in rangelands is a basic maintenance activity in livestock production. This could be carried out using methods that range from cultural, biological, chemical and a combination of these methods. The amount of drudgery involved in administering these methods makes some of them practically undesirable. Bromacil has many benefits in this case; it is used as an herbicide for general weed or bush control in non-croplands; it is also particularly useful against perennial grasses (Meister, 1998). The current use of bromacil in agriculture is necessary so as to sustain high productivity, reduce cost and drudgery and give high profit margins. It is used on rail road rights of way and other industrial, non-cropland areas. Bromacil is one of the most commonly used herbicides to control weeds in citrus orchards. It is used in citrus and pineapple fields for selective control of weeds (Turner, 2003). Bromacil is also effective in the control of deep-rooted perennial broadleaf and grass weeds. Other commonly used herbicides are glyphosate, diuron, diquat, simazine, linuron, terbuthylazine and terbumeton (Gomez-Barreda et al., 1991).

EFFECTIVENESS OF BROMACIL APPLICATION METHODS

Bromacil can be applied in a variety of ways. Application can be made as broadcast, band or spot treatments (Gangstad, 1989). The most appropriate application method is determined by the weed being treated, the herbicide being applied, the skills of the applicator and the application site (Tu et al., 2001). The bromacil application method is of considerable importance; since it determines the extent of contact with the target plant and its movement within the soil. Three conventional methods of application are known, these are aerial spraying with the use of an aircraft and direct application to the soil near the target plant with the use of a backpack sprayer (liquid application) or the placement of the granular form at a close proximity to the target plant.

Bromacil can be applied on its own as a selective herbicide or it can be applied in mixture with other herbicides to control a broad spectrum of weeds (Gomez de Barreda Jr. et al., 1998). Generally bromacil is applied at rates of 2 - 4 kg/ha (Meister 1998), depending on soil properties and persisting environmental conditions. In citrus, pineapple, and non-crop areas, Bromacil can be applied at rates of 5 - 7, 1.5 - 3, and 1.5 - 5 kg/ha respectively (Rao, 2000). Differences in soils could affect the overall performance of bromacil and these differences must be taken into consideration, i.e. soils with low clay or organic matter content and lower application rates must be used so as to avoid high rates of leaching of the chemical (Gangstad, 1989). The type, diversity and height of the vegetation are also important factors to be considered for the effective application of bromacil (Gangstad, 1989). Other methods of bromacil application are the foliar application, where bromacil is directly applied to the leaves and stems of a plant (Tu et al., 2001). Bromacil can be applied with a backpack sprayer or a hand-held bottle to the basal bark of the target plant (Tu et al., 2001).

EFFECTS OF BROMACIL ON THE ENVIRONMENT

Bromacil toxicity to mammals and birds is described by its LD_{50}, which is the dose received either orally or dermally that kills half the population of study animals. The LD_{50} is typically reported in grams of bromacil per kilogram of animal body weight (Tu et al., 2001). Tests conducted by the United States Environmental Protection Agency (USEPA) for bromacil mammalian toxicity revealed an LD_{50} of 3998 mg kg^{-1} when administered on acute oral basis; this showed that bromacil is practically non toxic to mammals. A similar result was obtained for birds (LD_{50} of 2250 mg kg^{-1}) and reptiles.

Bromacil's toxicity to aquatic organisms is quantified with LC_{50}, which is the concentration of the herbicide in water that is required to kill half of the study animals. The LC_{50} is typically measured in micrograms of bromacil per liter of water (Tu et al., 2001). The USEPA test with rainbow trout and bluegill sunfish resulted in an LC_{50} of 36 and 127 ppm of the ai. This suggests that bromacil is slightly toxic to rainbow trout and non-toxic to the bluegill sunfish. Consequently, bromacil is viewed to be slightly toxic to fishes and amphibians. Determining the implication of this toxicity on the secondary component of the aquatic food chain will constitute an interesting endeavor.

Bromacil is mainly degraded by micro-organisms in the soil and several forms of micro-organisms are involved in the process such as the bacteria *Psuedomans* spp. which can use bromacil as a source of carbon (Chaudhry and Cortez, 1988). Bromacil has varying effects on soil microbial populations depending on herbicide concentrations and the microbial species present. Low residue levels can enhance populations while higher levels can cause population declines (Tu et al., 2001).

Water bodies can be contaminated by direct overspray, or when herbicides drift, volatilize, leach through soils to groundwater or are carried in surface or subsurface runoffs. Amounts of leaching and runoff are largely dependent on total rainfall in the first few days after an application (Tu et al., 2001). Most environmental fate and impact concerns linked to the use of herbicides are related to offsite movement into aquatic ecosystems (Zhu and Li, 2002). Bromacil rapidly moves through the soil, as a result it has the potential to be a groundwater contaminant (Gomez de Barreda Jr. et al., 1998). Bromacil may degrade in natural waters through microbial degradation and photo-sensitized degradation. Bromacil is moderately soluble in water (0.815 gl^{-1} at 25°C) (Gomez de Barreda Jr. et al., 1998; Zhu and Li, 2002). Bromacil is one of the most commonly found herbicides in groundwater; it is usually detected at higher concentrations than those of terbuthylazine and simazine (de Paz and Rubio, 2006).

Bromacil in the atmosphere is mainly degraded by light, in a process known as photo-oxidation. The hydroxyl radicals and superoxide radicals are the primary oxidizing species in the photocatalytic oxidation process of bromacil (Singh et al., 2003). Oxygen has no pronounced effect on the initiation of the photolytic process of bromacil, as compared to that of metribuzin where oxygen has a pronounced effect and hydrogen peroxide has a lesser effect (Muszkat et al., 1998). The photolytic process in bromacil is initiated by hydroxyl radicals generated by hydrogen peroxide photolysis (Muszkat et al., 1998). In a study carried out by Singh et al. (2003), the immediate photolytic products in the presence of titanium dioxide were 5-hydroxy-3-secbutyl-6-methyl uracil and diisopropyl urea.

PERSISTENCE AND DEGRADATION OF BROMACIL

Increasingly, herbicides are continually being applied onto the environment. Ideally a herbicide should control or eradicate the targeted species selectively, remain stationary at the site of application and degrade rapidly once its purpose is achieved, however, their persistence in the environment together with their low degradability rates have become a cause of concern especially the ecological risks they might possess (Dowd et al., 1998, Muszkat et al., 1998, Singh et al., 2003, Rosner et al., 1999, Girotti et al., 2008). The degree of bromacil persistence and mobility (Hornsby et al., 1995) is mainly dependent on soil properties and environmental conditions such as water availability.

Any herbicide's persistence in soils is often described by its half-life (also known as the DT_{50}). The half-life is the time it takes for half of the herbicide applied to the soil to be dissipated (Tu et al., 2001). Bromacil has a lengthy half-life. Its soil half-life ranges from 2 to 8 months depending upon the patterns of use and other environmental factors such as temperature and availability of water (Fishel, 2005; Meister, 1998). Bromacil activity, movement and persistence in the soil depend on the interaction of the bromacil molecule with the soil's colloids adsorption capacity (Paterson and Mackay, 1994). Soil organic carbon-water partitioning coefficient (Koc) is the the ratio of the mass of a chemical that is adsorbed in the soil per unit mass of organic carbon in the soil per the equilibrium chemical concentration in solution. Koc value of less than 100 indicates that a pesticide is very mobile in soils (Branham et al., 1995). Bromacil moves quite readily through the soil (EXTONET, 1993, Rosner et al., 1999); this is because bromacil adsorbs only slightly soil particles, with a Koc value of 32 g/ml (de Paz and Rubio, 2006; EXTONET, 1993; Gomez de Barreda Jr. et al., 1998). Bromacil is a good candidate for leaching and therefore, a groundwater contaminant (Gomez de Barreda Jr. et al., 1998).

Due to its ability to move readily through the soil and its solubility in water, concerns on the use of Bromacil arise as it is able to contaminate groundwater (EXTONET, 1993; Rosner et al., 1999, Singh et al., 2003). Relatively Bromacil behaves differently on different types of soils with different constituents. Thus Bromacil is more strongly adsorbed to by organic matter colloids rather than clay particles; as a result it is more persistent and less mobile in soils with high organic matter content (5% or more) (James and Lauren, 1995). Soils with moderate to high organic matter content may retain bromacil residues for 1 to 2 years, thus, a soil half-life of 3 to 7 months is more likely in soils with low organic matter content (less than 5%) (EXTOXNET, 1993). A soil with high organic matter content will also bind bromacil and prevent it from being available in soil solution, this obviously will affect it effectiveness on plant. In a study carried out by de Paz and Rubio (2006), involving eight of the most frequently applied herbicides in citrus orchards (glyphosate, diuron, diquat, bromacil, simazine, linuron, terbuthylazine, and terbumeton), a ranking according to the potential to leach was obtained. The leaching potential of the herbicides was as follows, from highest to potential to least; terbumeton > bromacil > simazine > terbuthylazine > diuronNlinuron > glyphosate > diquat. On relative terms, bromacil is one of the polluters of groundwater that should be given considerable attention (EXTONET 1993, Rosner et al., 1999; Singh et al., 2003). Other report by Sanders et al., (1996) showed that bromacil was degraded within 4 to 6 months when it was applied once compared to when it was applied twice in the same season; it was also reported that Bromacil persisted in the top 75 mm of soil for nearly a year (Alavi et al., 2008). Soil with no previous bromacil use had higher chemical residue levels in lower depths and slower degradation rates than soils with a 10 year history of asparagus management and associated bromacil use.

CONCLUSION

Bromacil falls under the uracil family; the general character of this family is that they have a methyl group located at the sixth position on the ring. Bromacil based herbicides are effectively used to control annual and perennial weeds. The family possesses a broad toxicity to many plant species, however, the specific compounds differ in their toxicity to plants, solubility in water and persistence in soil. The chemical is absorbed through the root system and translocated upwards via the xylem vessels to the leaves where it interferes with light harvesting complexes by blocking the photosystem II reaction. These compounds disrupt cell membranes and cause chloroplast swelling and cellular destruction. The early symptoms of bromacil kill activities in a plant is leaf chlorosis concentrated around the veins, this is often noticed at the lower leaves and gradually moves up the plant.

The current use of bromacil in agriculture is necessary so as to sustain high productivity, reduce cost, reduce drudgery and give high profit margins. There are various ways of applying bromacil; the most appropriate method is determined by the weed being treated, the herbicide being applied, the skills of the applicator and the application site. The application method determines the extent of contact with target plant and its movement within the soil. The conventional methods of application include aerial spraying and direct application to the soil. The performance of bromacil is influenced by soil characteristics, thus soils with low clay or organic matter content are highly leachable, therefore require lower application rates. The vegetation structure and composition are also very important factors to consider.

Bromacil is non-toxic to mammals, however, it is slightly toxic to fish and amphibians. The effect of Bromacil on microbial populations depends on herbicide concentration and microbial species present. Most environmental fate and impact concerns linked to the use of herbicides are related to offsite movements into aquatic ecosystems. Bromacil is mainly degraded by micro-organisms in the soil and in natural waters. The chemical is degraded mainly by light in the atmosphere through photo-oxidation. Bromacil provides for sustained weed control because of its persistence in the environment and its low degradability rates, however, this has become the cause of environmental concern especially the ecological risks. We therefore concluded that the use of bromacil in areas with important aquatic ecosystems should be carefully undertaken and monitored.

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