IMPROVING EFFICACY OF METRIBUZIN AND RIMSULFURON IN POTATO PRODUCTION

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Improving Efficacy of Metribuzin

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ABSTRACT

Rimsulfuron and metribuzin are postemergence herbicides used to control broadleaf weeds in potato and are applied with adjuvants to improve efficacy. Postemergence weed control often coincides with fungicide treatments. Therefore, studies were conducted to determine the effect of adjuvants or fungicides (chlorothalonil or mancozeb) plus metribuzin and rimsulfuron on weed control, potato safety and yield.

Common sunflower and common lambsquarters visual control was ≥ 91% when metribuzin (420 and 210 g ha^{-1}) plus rimsulfuron (26 and 14 g ha^{-1}) combinations were applied with or without fungicides. Past the four leaf stage, metribuzin (340 g ha^{-1}) and rimsulfuron (21 g ha^{-1}) with adjuvants had no effect on hairy nightshade dry weight. Adjuvants and fungicides did not change yield.

These studies indicate that including fungicides with metribuzin and rimsulfuron reduce weed populations without negatively impacting yield. Additional research is needed to determine the effect of adjuvants with these herbicides on other weeds.

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INTRODUCTION

The only herbicides for postemergence control of hairy nightshade (*Solanum phsalifolium* Rusby.), common lambsquarters (*Chenopodium album* L.), and common sunflower (*Helianthus annuus* L.) in potato (*Solanum tuberosum* L.) production are metribuzin and rimsulfuron. If uncontrolled these weeds can reduce potato yields by harboring insects and pathogens and increasing competition for sunlight, nutrients and water (Boydston and Vaughan 2002; Callihan and Bellinder 1993). In order to limit yield loss and reduce costs, an effective weed control program in potato production should be used which includes the used of herbicides, such as metribuzin and rimsulfuron.

Activator adjuvants improve herbicide efficacy by increasing herbicide absorption, increasing wetting, decreasing antagonism, or providing rainfastness while utility adjuvants widen the range of conditions under which herbicide formulations can be useful (McWhorter 1982). Previous studies have reported on controlling hairy nightshade and common lambsquarters with activator adjuvants: nonionic surfactants, crop oil concentrates and methylated seed oils when combined with metribuzin and rimsulfuron; however, there is little information in the literature describing the effects of utility adjuvants including buffering agents, drift retardants, water conditioning agents and spreaders/stickers on control of these weeds (Hutchinson et al. 2004; Tonks and Eberlein 2001). This study will compare the effects of these adjuvants on control of hairy nightshade, common lambsquarters, common sunflower and potato crop safety. The effects of adjuvants with metribuzin and rimsulfuron on wild proso millet control will also be tested.

Fungicides are combined with herbicides to improve production efficiency and reduce costs associated with pesticide applications (Lancaster et al. 2005). Chlorothalonil and mancozeb are used in potato production to control the fungal pathogens *Alternaria solani* and *Phytophthora infestans*, which cause early and late blight respectively. Though effective at controlling these pathogens, little data exists to determine if chlorothalonil and mancozeb improve herbicide efficacy or result in increased injury to potato when combined with metribuzin and rimsulfuron.

The objectives of this research were to 1) determine the effect of different adjuvants on weed control and potato crop safety when combined with metribuzin and rimsulfuron and 2) determine if chlorothalonil and mancozeb interact with rimsulfuron and metribuzin to alter weed control and potato yields.

CHAPTER 1. LITERATURE REVIEW

The Potato

Description. The potato is dicotyledon perennial of the Solanaceae family along with eggplant (*Solanum melongena* L.), tomato (*S. lycopersicum* L.), tobacco (*Nicotiana tabacum* L.) and many other plants (Knapp 2002). The potato plant consists of one or more stems that grow from either true seed or from tubers (De Jong et al. 2011; Sieczka and Thornton 1993). Leaves are oval, broad with a dark green color. Though there are over 160 species in the genus *Solanum*, a single species, *Solanum tuberosum* L., is the most commonly consumed because of its ability to produce acceptable yields under short-day conditions (Riffat et al. 2012). Hils and Pieterse (2009) have identified over 45,000 cultivars of *Solanum tuberosum* L., which have been selected for useful characteristics including pest resistance, storage quality, shape, color, yield and dormancy.

Cultivars. Potato cultivars are typically classed into four categories based on skin color: white, red, russet (brown and netted) and specialty. These cultivars will enter either the fresh or processing markets. Common potato cultivars produced in the United States consist of all skin types (Table 1). ‘Shepody,’ ‘Rhine Red’ and ‘Alaska Red’ are examples of early maturing white- and red-skinned cultivars (Friesen and Wall 1984). ‘Russet Burbank’ and ‘Umatilla Russet’ are popular russet cultivars in North Dakota and Minnesota.

Table 1. Potato cultivars commonly grown in the United States with skin and flesh colors and market use.

Cultivar	Skin color	Flesh Color	Market use
Russet Burbank	Russet	White	Fresh, Processing
Russet Norkotah	Russet	White	Fresh
Dakota Pearl	White	White	Chipping
Yukon Gold	Yellow	Yellow	Specialty
Red Norland	Red	White	Fresh
Red Pontiac	Red	White	Fresh

Russet Burbank is the most commonly grown potato cultivar in the United States and Canada. Russet Burbank plants have white flowers and large spreading vines that grow indeterminately (Stark and Love 2003). A late maturing cultivar, Russet Burbank has a peak maturity of 140 days from planting and is well adapted to growing conditions in the western United States and Canada as well as Minnesota and North Dakota (De Jong et al. 2011). The tubers are long, with shallow eyes, russet-skin and white flesh.

High yields and good processing and storage qualities are responsible for the popularity of Russet Burbank. On average, a plant produces 1.4-1.8 kg of tubers per plant. Russet Burbank has excellent fry quality as a result of high specific gravity and survives in storage for periods of six months or more (De Jong et al. 2011; Prange et al. 1998; Schippers 1976). Russet Burbank potatoes are susceptible to hollow heart and sugar ends and often become malformed if exposed to infrequent irrigation or high heat (Stark and Love 2003).

Umatilla Russet shares many morphological characteristics with Russet Burbank; however, this cultivar differs in a number of ways. Unlike Russet Burbank which has white flowers and thin spreading vines, Umatilla Russet has purple flowers and large upright vines (De Jong et al. 2011). Tubers resemble Russet Burbank with medium russet skin and few visible defects (Stark and Love 2003). Umatilla Russet is also popular because it has consistent specific gravity and is resistant to both internal and external tuber defects including Verticillium wilt, net necrosis and tuber decay caused by *Phytophthora infestans* (Mosley et al. 2000). Umatilla Russet may exhibit secondary growth; pointed tubers caused by stress and is more susceptible to shatter bruise and dry rot infection than Russet Burbank (Stark and Love 2003). This cultivar also yields higher than Russet Burbank. In a three-year study Mosley (et al. 2000) demonstrated that Umatilla Russet yields were more than 8 Mg ha^{-1} higher than Russet Burbank when averaged across 13 locations in seven states.

Potato Production in North Dakota and Minnesota. There were approximately 122,000 acres of potatoes planted in 2014 in North Dakota and Minnesota. Total acres planted in North Dakota in 2012 was 88,000, but decreased to 79,000 by 2014 (USDA 2013; USDA 2015). Acreage planted in Minnesota has decreased from 49,000 in 2012 to 43,000 in 2014 with yields remaining constant at 20 Mg a^{-1} (USDA 2015). Potato production in North Dakota is concentrated in the eastern half of the state. Potatoes are predominantly produced from Towner County on the Canadian border to Dickey County in the south and from Kidder County in the west to the Red River in the east. In Minnesota, potatoes are produced from the Red River Valley in the west to Big Lake, Minnesota in the east.

Weeds

Weeds are a serious problem in North Dakota and Minnesota potato production because many species interfere with potato growth and reduce yield quantity and quality (Boydston and Vaughan 2002; Callihan and Bellinder 1993). Hairy nightshade, eastern black nightshade, common lambsquarters, common sunflower and proso millet are some of the weed species found in the Upper Midwest (Robinson, personal communication).

Nightshade Species. Hairy nightshade (*Solanum physalifolium* Rusby.), eastern black nightshade (*Solanum ptychanthum* Dunal.), black nightshade (*Solanum nigrum* L.) and cutleaf nightshade (*Solanum triflorum* Nutt.) are annual broadleaf weed species belonging to the same family as potato, Solanaceae. Like these other nightshade species, hairy nightshade is found in waste places and cultivated fields (Burril et al. 2000). Though sharing similar morphological characteristics with eastern black nightshade, black nightshade and cutleaf nightshade, hairy nightshade is distinguished from these plants by fine, small hairs on the stems (Blackshaw 1991). The color of berries is another distinguishable characteristic of hairy nightshade, though black nightshade and eastern black nightshade berries closely resemble one another with the exception that eastern black nightshade sepals bend backwards more than black nightshade (Miller and Parker 2006). Eastern black nightshade berries turn black at ripening, and cutleaf nightshade berries are green with cream-colored stripes, hairy nightshade berries are always green and lack stripes (Bryson et al. 2010; Burril et al. 2000). Hairy nightshade cotyledons are green on both the abaxial and adaxial surfaces and spoon-shaped. Hairy nightshade is a prolific seed producer; one plant can produce upwards of 45,000 seeds (Blackshaw 1991). This weed is particularly difficult to control because it is in the same family as potato and there are few herbicides that selectively control for this weed in potato production.

Several growth characteristics enable hairy nightshade to dominate potato fields and compete well with other weeds. For example, seedling emergence is highly dependent on moisture and the lack of shade from crops (Ogg and Dawson 1984). For this reason, hairy nightshade was more problematic from late March through early May when less shade is present (Ogg and Dawson 1984). This may give hairy nightshade an advantage if it emerges earlier than the potato crop. Tan and Weaver (1997) suggested that the low water requirements of hairy nightshade allowed it to be more drought tolerant than eastern black nightshade, but caused it to not compete well with potato. Given the ability of hairy nightshade to emerge throughout the growing season it becomes dominant once the potato begins to senesce (Greenland and Howatt 2005). If early season control efforts are ignored, hairy nightshade can quickly dominate a potato crop and hinder harvest operations.

Hairy nightshade seeds become dormant after a period of cold stratification at 4 ºC, while germination often occurs when temperatures exceed 20 ºC (Roberts and Boddrell 1983; Taab and Andersson 2009). Hairy nightshade germinates at temperatures ranging from 19 to 39 ˚C with optimum germination from 27 to 30 ˚C. Optimum pH for germination of hairy nightshade is between 6 and 8. Typical amount of time required for hairy nightshade germination is six weeks in the field and flowering can occur over several months (Masiunas and Perez 1990).

Russet Burbank is more competitive with hairy nightshade than Russet Norkotah. Hutchinson et al. (2011) demonstrated that one hairy nightshade plant m^{-1} row^{-1}, does not affect Russet Burbank yield, but 2, 3 and 100 plants m^{-1} row^{-1} negatively affected yield. Yield of Russet Norkotah decreased at the 1, 2, 3 and 100 plants m^{-1} row^{-1} level.

Hairy nightshade has been found to respond differently to metribuzin and rimsulfuron treatments. For instance, Hutchinson et al. (2004) reported that rimsulfuron, at 26 g ha^{-1} controls 88% of hairy nightshade plants at the one- to two- leaf stage. Metribuzin, however, does not control hairy nightshade, but may improve control when combined with rimsulfuron (Eberlein et al. 1991). For example, a study by Eberlein et al. (1994) found 98% control of hairy nightshade plants at the two- to four-leaf stage occurred when rimsulfuron at 27 g ha^{-1} plus metribuzin at 280 g ha^{-1} was applied compared to 94% control with rimsulfuron alone at 27 g ha^{-1}.

Wild Proso Millet. Wild proso millet (*Panicum miliaceum* L.) is an annual species belonging to the Paniceae tribe of the Poacae family (Bestel et al. 2013). It is found in agricultural fields, disturbed sites, and waste places. The seeds, averaging about 6 mm, are either olive brown or black and spread by harvesting equipment (Burril et al. 2000; Wax and Fawcett 1999). Wild proso millet is difficult to control because seeds are capable of persisting in soil for up to four years and survive better in sandy, dry soils (Anderson and Greb 1987; Colosi and Schaal, 1997). Seeds also have no seed dormancy and can germinate within days of shattering if conditions are suitable (James et al. 2011). Though there is no seed dormancy, the hardened lemma of wild proso millet inhibits imbibition, which delays germination until the lemma softens (Khan et al. 1996). Germination of wild proso millet was positively correlated with soil disturbance and may germinate throughout the growing season (Shenk et al. 1990). These growth and morphological characteristics make wild proso millet a serious competitor in most row crops.

Wild proso millet is a difficult weed to control preemergence because it is highly tolerant to herbicide phytotoxicity during the germinating stages (Harvey et al. 1987). Metribuzin applied postemergence at the cotyledon- to four-leaf stage at 67 g ha^{-1} can reduce wild proso millet biomass by 50% (Wilson et al. 2002). Many sulfonylurea herbicides, including rimsulfuron and nicosulfuron, have proven to be effective at controlling wild proso millet (Mekki and Leroux 1994). Mekki and Leroux et al. (1994) demonstrated that rimsulfuron rates as low as 6 g ha^{-1} controlled ≥ 85% of wild proso millet at the two- to four-leaf stage.

Common Lambsquarters. Common lambsquarters (*Chenopodium album* L.) is annual broadleaf weed species belonging to the family Chenopodiaceae along with such weeds as kochia (*Kochia scoparia* L.) and Russian thistle (*Salsola iberica*). Common lambsquarters is found in disturbed areas, cultivated areas and garden landscapes. This weed is often mistaken for netseed lambsquarters (C. *berlandieri* Moq.), but has distinguishable black mature seeds, whereas netseed lambsquarters seeds are generally brown (Burril et al. 2000). Netseed lambsquaters is less commonly found in agricultural fields. Temperature fluctuations from 20 to 30 ºC are needed for common lambsquarters to germinate (Martinez-Ghersa et al. 1997). Seedlings emerge throughout the growing season, but peak in emergence from the middle to the end of spring and are identifiable by two long, linear-shaped cotyledons (Bryson et al. 2010). Hairless green or light-green stems grow to heights of 2 m. Stems are often grooved and have red stripes. The leaves are deltoid in shape and have an alternate arrangement. The inflorescence consists of small, inconspicuous green flowers without petals that are clustered at branch ends on small spikes in leaf axils (Hartinger et al. 2002). Common lambsquarters grows best in well-drained soils that have undergone disturbance through tillage (Mulugeta and Stoltenberg 1997). Since common lambsquarters grows well in these types of soils, it is common in most agricultural fields.

This weed can be problematic in potato if relying only on rimsulfuron for postemergence control. Tonks and Eberlein (2001) reported that postemergence applications of rimsulfuron at rates of 9, 18, 26 and 35 g ha^{-1} with a nonionic surfactant at 0.25 % (v/v) resulted in 42, 55, 63 and 69% control respectively, of common lambsquarters at the two- to four-leaf stage. Post emergence applications are seldom effective because the leaves of common lambsquarters have a mealy coating which inhibits herbicide penetration through the leaf cuticle. Because rimsulfuron provides limited control of common lambsquarters, tank mixing with metribuzin and adding effective adjuvants is necessary to improve control.

Common Sunflower. Common sunflower (*Helianthus annuus* L.) is an annual broadleaf weed species belonging to the Asteraceae family. Common sunflower is prevalent in the Great Plains region of the United States and is one of the few pervasive weeds to have a North American origin (Harter 2004). It is often found in cultivated fields, pastures and disturbed sites of prairies. The seeds, or achenes, range from 0.32 to 1.5 cm long and are glabrous with small hairs. Seeds can remain in the seedbank for 3 to 5 years (Burnside et al. 1981; Clay et al. 2014; Snow et al. 1998). Common sunflower has an erect growth pattern, with large seeds heads borne on thick, hairy stems which makes this weed competitive for light, especially if it emerges earlier than a crop and grows above the crop canopy. Geier (et al. 1996) found that yields of soybean (*Glycine max*) decrease by 96% with five common sunflower plants m^{-2} following a 390 µmol m^{-2} s^{-1} decrease in photosynthesis.

Insects and Diseases

Weeds also act as alternate hosts for defoliating insects, disease-carrying insects and nematodes (Boydston et al. 2008). Weeds may be infected with viruses, thus creating a place where insects transmit diseases to potato plants (Alvarez and Srinivsan 2008). Two destructive potato insect pests, the Colorado potato beetle (*Leptinotarsadecem lineata*) and the green peach aphid (*Myzus persicae*), are commonly found on nightshade plants. The Colorado potato beetle is the most common and destructive, and if left uncontrolled may reduce potato yields by 64% in just weeks, and 100% if total defoliation occurs (Hare 1980). Hairy nightshade is problematic because it begins its life cycle earlier than other nightshade species and may harbor large concentrations of the beetle before potatoes emerge. Boydston et al. (2008) reported that both pupae and adults were significantly heavier and fecundity rates were higher for those raised on hairy nightshade than those raised on eastern black nightshade. Controlling nightshade weeds in potato fields is important for high quality potato production.

Considering all pests of potato, green peach aphid, is the second most important because of its ability to transmit potato leaf roll virus and potato virus Y (Radcliffe et al. 1991; Ragsdale et al. 2001). Walgenbach (1997) found that the aphid concentration is directly correlated with yield loss potential. Potato leaf roll virus lower yields by as much as 80% by reducing the number and/or size of tubers, and may cause net necrosis of daughter tubers (Noy et al. 2002; Rietveld et al. 1993). Potato virus Y also causes losses in a potato crop, with some estimates being as high as 90%, though losses of 10% are more common (Noy et al. 2002). The presence of potato virus Y or potato leaf roll virus in a seed crop increases the risk of that crop losing its certification. If this downgrading occurs, growers may be forced to sell their crop as commercial seed, resulting in a financial loss (Solomon-Blackburn and Barker 2001). These losses are the result of decreased tuber size and overall number of harvested tubers (Zimnoch-Guzowska et al. 2013).

Herbicides

There are a number of herbicides registered for use in potato to control broadleaf weeds. Herbicides available to potato producers for preemerence broadleaf weed control include protoporphyrinogen oxidase inhibitors, mitosis inhibitors, photosynthesis inhibitors, and acetolactate synthase inhibitors (Navarre and Pavek 2014). For example, flumioxazin is a protoporphyrinogen oxidase inhibitor and when applied preemergence at 105 g ha^{-1} controls ≥ 90% of both common lambsquarters (Taylor-Lovell et al. 2002) and hairy nightshade (Wilson et al. 2002). Postemergence broadleaf weed control in potato is limited to the use of two herbicides (rimsulfuron and metribuzin) because some herbicides, including flumioxazin, may injure potatoes if applied postemergence (Anonymous 2014).

Rimsulfuron. The registration of rimsulfuron, 1-(4,6-dimethoxypyrimidin-2-yl)-3-(ethylsulfonyl-2-pyridylsulfonyl) urea in 1996 provided a preemergence and postemergence herbicide for control of annual and perennial grasses and broadleaf weeds (Guttieri and Eberlein 1997). Rimsulfuron controls weeds through the inhibition of the plant enzyme acetolactate synthase, which blocks synthesis of isoleucine, leucine and valine which are branched-chained amino acids that are essential for cell division and plant growth (LaRossa and Schloss 1984). Symptoms occur in the meristematic tissues of treated plants, and include growth inhibition followed by yellow and brown coloring and/or red veining (Blair and Martin 1988). This chlorosis will most often occur at the growing point and after a period of stunting the plant dies.

Rimsulfuron is effective on many annual broadleaf weeds when applied to weeds in the two- to five-leaf stage, or when the weeds are no more than 2.5 cm tall (Mekki and Leroux 1994). However, it only suppresses hairy nightshade and does not control common lambsquarters (Zollinger et al. 2014). Besides broadleaf weeds, rimsulfuron also provides excellent control of annual grasses (Reinke et al. 1991). Experiments by Mekki and Leroux (1994) have shown that annual grasses are best controlled by rimsulfuron when applied before the three leaf stage.

Though rimsulfuron is an effective herbicide in most potato production systems, this herbicide may cause injury to potato. Preeemergence applications of rimsulfuron are unlikely to damage potato plants; however, if rimsulfuron is applied postemergence at temperatures exceeding 29 ºC and combined with oil based adjuvants damage potato plants may occur (Anonymous 2009). Boydston (2007) found that injury to Umatilla Russet was 39% when rimsulfuron was applied at 26 g ha^{-1} and combined with a methylated seed oil at 1% (v/v).

Metribuzin. Metribuzin, 4-amino-6-tert-butyl-3-methylthio-1,2,4-triazin-5(4H)-one, is a triazine photosystem II inhibiting herbicide, which causes interveinal chlorosis at leaf margins (Bouchard et al. 1982). Metribuzin is a xylem mobile herbicide. This means that the herbicide is absorbed by the roots and leaves and then translocated from the roots into leaf tissue through the xylem. As a triazinone herbicide, metribuzin inhibits electron transport in the chloroplast by binding to the D1 protein of the photosystem II complex (Hess 2000).

Many grasses and broadleaf weeds are controlled by metribuzin. Though metribuzin effectively controls common lambsquarters and redroot pigweed when applied alone, this herbicide is more commonly included in tank mixtures with rimsulfuron when applied postemergence. However, studies have shown that sole applications of metribuzin at 240 g ha^{-1} reduce redroot pigweed dry weight by 90% (Kahramanoglu and Uygur 2012). Previous research has also shown that metribuzin can cause > 90% necrosis of common sunflower plants (Al-Khatib et al. 2000). Combining metribuzin and rimsulfuron is important because certain biotypes of common lambsquarters are known to exhibit triazine resistance (Machado et al. 1978).

Metribuzin can damage potato plants if rates are too high, if applied at the wrong time, or if used on sensitive cultivars. Injury to Russet Burbank from metribuzin is less common than in many cultivars; however, metribuzin damage is possible if Russet Burbank plants experienced three consecutive days of cloud cover prior to herbicide application (Anonymous 2004; Renner and Powell 1998). Metribuzin may also cause injury to tomato if applied under cloud cover or low light conditions (Stephenson and Phatak 1973). The increase in damage is a result of decreased growth and herbicide metabolism (Gawronski et al. 1985). Many white- and red-skinned cultivars are susceptible to metribuzin. A study conducted on the cultivars Irish Cobbler, Kenebec, Netted Gem and Sebago showed that early postemergence applications caused less damage than late postemergence applications when applied at 500 g ha^{-1}, 700 g ha^{-1} and 1,000 g ha^{-1} (Ivany 1979).

Russet cultivars are typically not affected by postemergence treatments of metribuzin. Using a nutrient solution that included metribuzin with ^{14}C, Gawronksi et al. (1985) determined that Russet Burbank accumulated 13 and 39% metribuzin in petioles and stems respectively. Conversely, 'Chipbelle' only accumulated 6 and 13% metribuzin in petioles and stems respectively. Eight days after treatment, Russet Burbank accumulated 30% of metribuzin in leaf blades while Chipbelle accumulated 68% in leaf blades. Chipbelle was more susceptible to phytotoxicity because photosystem II inhibiting herbicides acted directly on the chloroplasts in the leaves. This was a result of the cultivar Chipbelle lacking the amount of enzymes required for metribuzin metabolism.

Fungicides

Combining fungicides and herbicides is a procedure commonly used in integrated pest management in order to reduce the number and rate of applications of pesticides. This in turn allows growers to benefit economically by saving fuel, reducing the amount of labor involved in crop production and reducing potential damage to both the crop and equipment (Lancaster et al. 2005). One study conducted in the Philippines demonstrated that farmers could reduce herbicide applications by 65% and fungicide applications by 25% when these pesticides were applied together (Cuyno et al. 2001). Chlorothalonil and mancozeb are multi-site protectant-only fungicides. This means that fungicide particles remain on leaf surface and do not penetrate through leaf cuticle (Gullino et al. 2010). This forms a protective barrier which inhibits pathogen development by restricting the fungi from entering plant tissue (Ulrich and Sierotzki 2008). Two fungicides, chlorothalonil and mancozeb, are widely used in potato production yet no research has demonstrated the effect of these fungicides in combination with rimsulfuron and metribuzin.

Chlorothalonil. Chlorothalonil (2,4,5,6-tetrachloro-1,3-benzenedicarbonitrile) or (tetrachloroisopthalonitrile) is a broad spectrum non systemic fungicide used to control anthracnose (*Colletotrichum graminicola*), early blight (*Alternaria solani*), septoria leaf spot (*Septoria* sp.), botrytis blight (*Botrytis cinerea*), downey mildew (Peronospora antirrhini) rust (*Puccinia malvacearum*), and late blight (*Phytophthora infestans*) (Long and Siegel 1975; Robinson and Soltani 2006). Chlorothalonil binds to sulfydryl groups of amino acids, proteins and peptides which bind glutathione in the fungal cells. The binding of glutathione inhibits respiratory enzyme pathways and prevents fungal infection (Long and Siegel 1975).

Research has examined the effect of chlorothalonil combined with rimsulfuron and metribuzin for weed control in tomato. Robinson and Soltani (2006) demonstrated that postemergence applications of 1,600 g ha^{-1} chlorothalonil mixed with 15 g ha^{-1} rimsulfuron and 150 g ha^{-1} metribuzin resulted in ≥ 89% reduction of common lambsquarters at the two- to four-leaf stage. Redroot pigweed was also reduced by ≥ 89%. When no chlorothalonil was included in the tank mixture the redroot pigweed population was reduced by 98% and the population of common lambsquarters by 91%. Thus, the inclusion of chlorothalonil with metribuzin and rimsulfuron may reduce pesticide application costs, but did not improve weed control compared to treatments lacking chlorothalonil.

Mancozeb. Mancozeb ([1,2-Ethaznediyibis(carbamodithio) (2-)] manganese [[1,2-ethanediylbis[carbamodithioate]] (2-) zinc) is a non-systemic, broad-spectrum fungicide commonly used in potato production. Mancozeb is also commonly used in the production of other crops, including onion (*Allium cupa* L.), mustard (*Brassica juncea* L.), cucumber (*Cucumis sativus* L.), apple (*Malus* spp.), strawberry (*Fragaria* x *ananassa* Duchesne.), lettuce (*Latuca sativa* L.), and solanaceous crops including tomato (Gullino 2010). Mancozeb belongs to the dithiocarbamate family of fungicides, but more specifically to a group of compounds known as ethylene bisdithiocarbamates (Grabski and Gisi 1987; Gullino 2010). Ethylene bisidithiocarbamates fungicides break down and release ethylene bisisothiocyanate sulfide which is then converted to ethylene bisisothiocyanate when exposed to ultra violet light. These anions are toxic and interfere with enzymes containing thiol groups (Ludwig and Thorn 1960). When enzymatic function is interrupted, biochemical processes in the mitochondria and cytoplasm in the fungal cell become inhibited and spore germination decreases (Ludwig and Thorn 1960; Szkolnik 1981).

Adjuvants

An adjuvant is defined as “any substance in a pesticide formulation that modifies herbicidal activity or application characteristics” (WSSA 1994). Adjuvants are either chemically and/or biologically active compounds which improve herbicide efficacy by increasing spray droplet retention, herbicide deposition, and absorption (Penner 2000; Tu and Randall 2003). Most postemergence herbicides require the inclusion of an adjuvant in tank mixtures to be effective. An understanding of adjuvant types, and how these adjuvants interact with different herbicides and plants, is important for improving weed control.

Adjuvants are separated into two categories: activator adjuvants and utility adjuvants (Tables 2 and 3). Activator adjuvants enhance herbicide performance by directly interacting with herbicide molecules and utility adjuvants interact with the solution but do not directly interact with the herbicide (McMullan 2000). Utility adjuvants broaden the range of conditions of use for an herbicide or herbicide formulation (McWhorter 1982). Examples of activator adjuvants include surfactants, methylated seed oils, crop oil concentrates, translocation agents, humectants, spreaders, stickers, spreader-stickers, wetting agents and penetrants (Hazen 2000;

Tu and Randall 2003). Examples of utility agents include antifoaming agents, drift control agents, water conditioning agents, acidifying agents, alkalinity agents, buffering agents, deposition agents, compatibility agents, and colorants (McMullen 2000).

Table 2. Activator adjuvants, active ingredients and source.

Adjuvant type	Examples active ingredients	Source
Surfactants		
Cationic	Alkyl betaine, cetyl trimethyl ammonium bromide and others	Hazen 2000;Van Valkenburg et al. 1982
Anionic	Sulfonates, phosphonates, carboxylates	Green and Beetsman 2007
Nonionic	Nonylphenol, fatty alcohols, alkyl phenols, vegetable oils, fatty amines, sugar esters, glycosides, alkylbenzenes and organosiloxanes	Miller and Westra 1996.
Methylated seed oils	Fatty acids from seed oils esterified with methyl alcohol	Miller and Westra 1996
Crop oil concentrates	Paraffinic oils, sorbitan ester ethoxylates, alkylphenolethoxylates polyethylene glycol esters	Hazen 2000 Manthey et al. 1989
Spreader-stickers	Alklylarylpolyglycol ether Poly(2-p-menthene)	McWhorter 1982

Table 3. Utility adjuvants, active ingredients and source.

Adjuvant type	Examples active ingredients	Source
Buffering agents		
Alkalinity agents	Carbonic acid, dipotassium salts	Anonymous 2013a
Acidifying agents	Malic, maleic, lumaric, suliamic acids	Jones 1946
Antifoaming agents	Silocones, dimethopolysiloxane, oils, perfluoroalkylphosphonic and phosphinic acids, perfluouroaliphatic polymers, malic or tartaric acid derivatives	Monaco et al. 2002 Foy and Green 2002 Aven and Schmidt 2002 Meier et al. 2002
Drift control agents	Swellable polymers, hydroxylethyl cellulose, polysaccharide gums	Monaco et al. 2002
Water conditioning agents	Ammonium sulfate	Anonymous 2013b
Deposition agents	Ammonium salts and gums	Gryzik and Reiss 2002
Compatibility agents	Alkylphenoxypoly(ethyleneoxy) ethyl phosphate	McWhorter 1982

Adjuvants in tank mixtures improve herbicide efficacy. Adjuvants reduce problems associated with application that may render the herbicide ineffective such as drift and foaming. Adjuvants are required in postemergence applications of rimsulfuron whether applied alone or in combination with other herbicides. For example, Green and Green (1993) demonstrated that rimsulfuron applied at 2 g ha^{-1} and combined with a surfactant controlled 93% of giant foxtail, but only controlled 23% of giant foxtail when a surfactant was not included in the tank mixture.

Surfactants. The term surfactant is derived from "surface active agent." A substance is considered a surface active agent if it concentrates on the surface of a liquid in which it is dissolved (Van Valkenburg et al. 1980). Surfactants dissolve at the surface of the liquid because their molecules consist of both polar and nonpolar segments (Monaco et al. 2002). There are four types of surfactants: anionic, cationic, amphoteric and nonionic (Hazen 2000). Anionic surfactants are those in which the active portion of the surfactant molecule containing the lipophilic segment has an exclusively negative charge in aqueous solution (ASTM 1995). Examples of anionic surfactants include sulfonates, phosphonates and carboxylates (Green and Beetsman 2007). Cationic surfactants are those in which the active portion of the surfactant molecule containing the lipophilic segment has an exclusively positive charge in aqueous solution (ASTM 1995). Examples of cationic surfactants include weakly basic amine surfactants with $pKa < 11.5$ (Green and Beetsman 2007). Amphoteric surfactants can be either anionic or cationic in aqueous solution depending on solution pH (ATSM 1995). Amphoteric surfactants are rarely used in agriculture because little published research exists describing the use and efficacy of this type of adjuvant (Hazen 2000; Tu and Randall 2003). Nonionic surfactants are the most commonly used adjuvant type because they universally "fit" with most herbicide types (Penner 2000; Valkenburg et al. 1980). These surfactants do not have cationic or anionic polar ends but are instead comprised of hydrophilic and lipophilic portions (ATSM 1995). These surfactants also do not ionize in solution (Hazen 2000). Linear or nonylphenyl alcohols are the principal components of nonionic surfactants (Foy 1989; Miller and Westra 1996).

The dual nature of surfactants means that the polar segments of surfactants can interact with water, while the nonpolar segments interact with lipophilic herbicides and waxy leaf cuticles (Green and Foy 2004; Monaco et al. 2002). The polar (hydrophilic) segment in most nonionic surfactants is comprised of ethylene oxide (Valkenburg et al. 1980). Polarity increases with the number of ethylene oxide units (Coret et al. 1993; Coret et al. 1995). Fatty alcohols, alkyl phenols, vegetable oils, fatty amines, sugar esters, glycosides, alkylbenzenes and organosiloxanes are commonly found in nonpolar (lipophilic) segments of nonionic surfactants. A hydrophilic-lipophilic balance is used to determine the proportion of hydrophilic portions to lipophilic portions in a surfactant and gives a clear indication of how surfactants will behave with herbicides. The hydrophilic-lipophilic balance of nonionic surfactants is calculated as the percentage of the molecule that is hydrophilic divided by 5 yielding a number between 0 and 20 (Griffin 1949; Griffin 1954). This calculation is useful for understanding how surfactants will interact with lipophilic herbicides and plant surfaces as well as aqueous solutions.

Hydrophilic-lipophilic balance is usually based on the water solubility of the herbicide. Surfactants with low hydrophilic-lipophilic balance are more suitable to insoluble herbicides, while surfactants with high hydrophilic-lipophilic balance (≥12) are more suitable to water soluble herbicides (Green and Foy 2004; Stock et al. 1993). Most surfactants are soluble at low concentrations in aqueous solution, but less soluble or insoluble as a result of increased concentrations (Monaco 2002). At a certain concentration, the hydrophobic center regions of surfactant molecules begin to associate with one another to form cylindrical or spherical aggregates called micelles. The point at which micelles form is called the critical micelle formation (Dominquez et al. 1997). Micelles are important because they emulsify herbicides in solution and aid in penetration of herbicide particles through the leaf surface (Green and Foy 2004). Besides reducing surface tension, Penner et al. (2000) has proposed seven other modes of action of surfactants including solubilization of leaf cuticle, prolonged drying time of spray droplets on leaf surfaces under dry weather conditions, increased retention of spray droplet on leaf surfaces under adverse environmental conditions, protection from antagonistic salts in spray solution, increased rainfastness, increased contact area of water droplets, and enhanced movement of water droplet on the surface of the plant to allow for greater absorption.

Methylated Seed Oils and Crop Oil Concentrates. Methylated seed oils are oils that have been extracted from seeds, and then chemically methylated (ASTM 1995). Methylated seed oil adjuvants are highly effective, and enhance herbicide efficacy more than nonionic surfactants. This is because methylated seed oils are more aggressive in dissolving leaf wax and cuticle, which results in more herbicide absorption (Gauvrit and Cabanne 2006). The increased effectiveness of methylated seed oils is often offset by the increased risk of crop injury.

Crop oil concentrates are similar to methylated seed oils but are paraffinic in nature and are not derived from vegetable oils, though both adjuvant types aid in penetration (Manthey et al. 1989). Most adjuvants designed to penetrate leaf surfaces require emulsifiers or emulsion stabilizers in order to increase surface activity in an aqueous spray solution (Stock and Briggs 2000). Some adjuvants of this type combine aspect of both methylated seed oils and crop oil concentrates and also have surfactant qualities.

Spreaders, Stickers and Spreader/Stickers. Adjuvants that spread water droplets over a larger area of a leaf surface are called spreaders. Spreading is achieved by lowering the contact angle of a spray droplet on a substrate surface or by reducing surface and internal surface tension of a spray droplet (Hartley and Bryce 1980; Hazen 2000). Most spreaders are nonionic surfactants. This is because most spreader adjuvants contain nonylphenolic compounds (Van Valkenburg 1982). It is important to note that the efficacy of spreader adjuvants will decrease if surfactant concentration has not reached the proper critical micelle formation or velocity of spray droplets is too high (Friloux and Berger 1996; Hazen 2000). Stickers are viscous materials that combine with pesticide particles and adhere to plant surfaces (Hazen 2000). Vegetable gels, emulsifiable resins, emulsifiable mineral oils, vegetable oils waxes and water soluble polymers are used as stickers. Stickers are often combined with spreaders to form spreader-stickers. These types of adjuvants serve the same function as spreaders, but include other ingredients that aid in herbicide retention on leaf surfaces under wet conditions. Thus, spreader-sticker adjuvants are particularly useful when employed against plant species that have leaf surfaces that are difficult to wet (Gaskin et al. 2000). In this way, spreader stickers promote rainfastness. Spreaders, stickers and spreader stickers are often fatty acids, polymerized fatty acids or polymer latex (Van Valkenburg 1982). Though useful for ensuring retention of herbicides on leaf surfaces, latex materials may inhibit herbicide absorption.

Buffering agents (Alkalinity Agents). A buffering agent is defined as "a compound or mixture that, when contained in solution, causes the solution to resist a change in pH, with a characteristic limited range of pH over which it is effective" (ASTM 1995). Buffering agents are similar to, but different from acidifying agents which are compounds added to a spray mixture to lower pH. Lowering pH can increase biological activity of an herbicide. If the herbicide is a weak acid herbicide, and solubility is not limiting, lower pH changes weak acids into a neutral form which more readily penetrate cuticles (Molin and Hirase 2004). In most cases, buffering agents reduce pH; however, some buffering agents raise pH and are considered alkalinity agents (Anonymous 2013a). Changing pH range is dependent on the herbicide in solution.

Buffering agents maintain a certain pH range, either below or above 7, for a number of reasons. One function of alkalinity agents is to raise pH above 7 in order to make sulfonylurea herbicides more soluble in spray solution. Rimsulfuron is a weak acid herbicide. This aids in penetration through the waxy leaf cuticle. This occurs, because when pH in a spray mixture is raised above the pKa of a weak acid herbicide, the herbicide becomes an anion and is easily dissolved (Green and Beestman 2007). Adjusting the pH of the spray mixture may also increase herbicide efficacy by adjusting the pH to reflect the pKa value (McMullan 2000). This inhibits interactions between the herbicide/adjuvant compounds and antagonistic ions in the spray mixture. Buffering agents have been shown to increase herbicide efficacy when included with reduced rates of herbicide. One study demonstrated that the inclusion of alkalinity agents reduced precipitate formation which improved weed control in sugarbeet (*Beta vulgaris* L.) (Van Valkenburg 1982). Liu (2002) demonstrated that the absorption of weak acid herbicides, applied at low rates, increases when pH is raised. The inclusion of buffering agents is more common with fungicides and insecticides than with herbicides (Foy 1989).

Antifoaming Agents. Antifoaming agents are defined as “materials that eliminate or suppress foam in a spray tank” (ASTM 1995; Foy and Green 2004). Antifoaming agents are either applied alone with herbicides or in combination nonionic surfactants as in the case of Preference® (Anonymous 2013b). Though kerosene and diesel fuel can be added to tank mixtures to reduce foaming, most antifoaming agents are polymers with silicon backbones. The silicone compound is comprised of a hydrophobic portion suspended in silicone oil (Green and Beetsman 2007). Not all antifoaming agents contain silicone-based active ingredients. Other antifoaming agents include dimethopolysiloxane and oils (Anonymous 2013b; Foy and Green 2004).

Water Conditioning Agents. Water conditioning agents are compounds that minimize or prevent ions in the spray solution from reacting with herbicides that may form salt precipitates that weeds cannot absorb (Green and Foy 2004). Antagonistic ions include iron, zinc, calcium, magnesium, sodium, and potassium. Ammonium sulfate is a compound included in many water conditioning agents to overcome hard-water effects caused by these cations and enhance photoxicity of weak acid herbicides (McMullan 2000; Pratt et al. 2003; Ramsdale et al. 2003; Thelen et al. 1995). Because ammonium is a cation, it can compete with antagonistic ions in spray solution for binding sites on herbicide molecules. The newly formed ions, which consist of both ammonium and herbicide molecules, are easily taken up by plants. Sulfate, an anion, binds with the cations in solution to form salts which precipate.

Drift Retardants. Droplet size is an important factor in herbicide efficacy. Spray nozzles produce droplet sizes ranging from 10 to 1,000 µm (Bouse et al. 1990). Small droplets may be retained more readily on the leaf surface, but if the droplets are too small, around 150 µm, they may never reach the intended leaf surface because small particles take longer to fall and become more likely to drift away from the intended location or evaporate (Stock and Briggs 2000; Yates et al. 1985). Polymers are added which coarsen the solution by decreasing shear viscosity and increasing initial extensional viscosity (McMullan 2000; Stock and Briggs 2000). This has the effect of increasing average spray droplet size and possibly reducing the content of the smaller droplets which are more likely to drift than larger droplets (Bouse et al. 1988; Celen 2010). When initial viscosity is decreased and extensional viscosity is increased, larger droplets form which are less likely to drift.

Deposition Aids. Many weed species have leaf surfaces with heavy cuticular waxes that act as barriers against deposition and retention of herbicide spray particles (Xu et al. 2010). In order to overcome these barriers, deposition aids are added to spray mixtures. A deposition aid is defined as “a material that improves the ability of pesticide sprays to deposit on targeted surfaces” (ATSM 1995). Deposition aids are helpful in reducing the amount of herbicide applied, and also reducing drift (McMullan 2000). Reducing drift and increasing retention is not only economically beneficial, but minimizes the potential for environmental damage.

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CHAPTER 2. EFFICACY OF ADJUVANTS WITH RIMSULFURON AND METRIBUZIN ON HAIRY NIGHTSHADE CONTROL

Abstract

Rimsulfuron and metribuzin are the only postemergence herbicides labeled for control of broadleaf weeds in potato. Adjuvants may improve the efficacy of metribuzin and rimsulfuron. The objective of this study was to determine the effects of adjuvants combined with rimsulfuron plus metribuzin for hairy nightshade control. In 2015, two field trials were established to evaluate control of four- to six- leaf hairy nightshade using 21 g ai ha^{-1} rimsulfuron plus 340 g ai ha^{-1} metribuzin in combination with various adjuvants. Estimated visual control and plant height was measured at 28 days after treatment. Plants were subsequently harvested and plant dry weight and berry number per plant were measured after drying for 10 days. All treatments, except Climb, were effective at reducing hairy nightshade plant height when compared to the non-treated control. However, visual control was only 4 to 30% for both runs and most plants survived treatments. The lack of control of hairy nightshade was likely the result of late application timing and reduced rimsulfuron rate used confirming previous research which indicates that ideal hairy nightshade control is attainable before, but not after the four leaf stage (Hutchinson et al. 2004). Metribuzin plus rimsulfuron plus adjuvant applications should be made when hairy nightshade plants are smaller and more susceptible to herbicides.

Nomenclature: Metribuzin, 4-amino-6-6-(1,1-dimethylethyl)-3-(methylthio)1,2,4-triazin-5(4H)-one; Rimsulfuron, N-((4,6-dimethoxypyrimidin-2-yl)aminocarbonyl)-3-(ethylsulfonyl)-2-pyridinesulfonamide; Hairy nightshade, *Solanum physalifolium* Rusby; Potato, *Solanum tuberosum* L.

Key words: Plant height, dry weight, leaf stage

Introduction

Hairy nightshade (*Solanum physalifolium* Rusby.) is a troublesome weed species in potato production because it is an alternative host for many potato diseases and insects (Eberlein et al. 1992; Perez and Matsiunas 1990; Weaver et al. 1987). Green peach aphid (*Myzus persicae* Sulzer), Colorado potato beetle (*Leptinotarsa decemlineata* Say), (Alvarez and Srinivasan 2008; Alvarez and Hutchinson 2005; Horton and Capinera 1990; Xu and Long 1997) potato leaf roll virus (Alvarez and Srinivasan 2008) and mosaic viruses (Cervantes and Alvarez 2011) have been found on or in hairy nightshade plants. Additionally, Spongospora subterranean, a pathogenic protozoan of potato which causes the external defect powdery scab, is known to use hairy nightshade plants as alternative hosts during its life cycle (Braselton 2001; Corliss 1994; Nitzan et al. 2009; Walsh et al. 1996). The existence of these pests has made hairy nightshade a problematic weed species in potato production.

Several characteristics of hairy nightshade make it a difficult weed to control. Hairy nightshade germinates at temperatures ranging from 19 to 39 ºC, in soils with pH ranging from 4 to 9 and under both high- and low-light conditions (Zhou et al. 2005). Hairy nightshade has high reproductive potential with one hairy nightshade plant capable of producing over 45,000 seeds and is highly competitive with potato and other solanaceous crops for light, nutrients and water (Blackshaw 1991). Hutchinson et al. (2011) reported that as few as two hairy nightshade plants per m^{-2} row^{-1} can reduce U.S. No. 1 ‘Russet Burbank’ yields by 10% and ‘Russet Norkotah’ yields by 26%. Weaver et al. (1987) reported that competition from hairy nightshade at 1 and 2 plants m^{-2} row^{-1} was enough to reduce tomato (*Solanum lycopersicum* L.) yields by 32 and 66% respectively.

Hairy nightshade is more competitive with tomato than other nightshade species, including eastern black nightshade (*Solanum ptychanthum* Dunal.) because hairy nightshade germinates earlier and grows faster than eastern black nightshade. Greenland and Howatt (2005) found tomato yields infested with hairy nightshade were lower than tomato yields dominated by eastern black nightshade because hairy nightshade emerged 21 days earlier and were 30 cm taller on average by mid-July compared to eastern black nightshade. However, hairy nightshade is highly dependent on moisture for germination with peak germination occurring between April and June when precipitation is highest (Ogg and Dawson 1984).

Metribuzin and rimsulfuron are the only herbicide options for postemergence broadleaf weed control in potato used in the United States (Alvarez and Hutchinson 2005; Eberlein 1994). Metribuzin, a triazinone herbicide, inhibits electron transport in the chloroplast by binding to the D1 protein of the photosystem II complex (Hess 2000). Rimsulfuron, a sulfonylurea herbicide, inhibits the plant enzyme acetolactate synthase (ALS) and thereby blocks the synthesis of the branched-chain amino acids isoleucine, leucine and valine (Hawkes et al. 1989; LaRossa and Schloss 1984). Hutchinson et al. (2004) reported that rimsulfuron, at 26 g ha^{-1} controlled 88% of hairy nightshade at the one- to two- leaf stage; however, when combined with metribuzin at 140 or 280 g ha^{-1}, control increased to $\geq$ 96%. Metribuzin alone did not control hairy nightshade at 140 or 280 g ha^{-1} even when hairy nightshade was in the one- to two-leaf stage (Eberlein et al. 1992; Eberlein et al. 1997; Tonks and Eberlein 2001). Furthermore, little research has been done demonstrating rescue treatments of tank mixing rimsulfuron and metribuzin on hairy nightshade control when plants have escaped previous control efforts and grown to heights greater than 3 cm.

Other solanaceous weed species have proved difficult to control with postemergence applications of metribuzin and rimsulfuron. At the three-leaf stage, only 31 to 68% of Jimsonweed (*Datura stramonium* L.) was controlled by postemerence applications of 35 g ha^{-1} rimsulfuron; however, control of jimsonweed increased to 91% when 280 g ha^{-1} metribuzin was included with 35 g ha^{-1} rimsulfuron (Ackley et al. 1997; Ackley et al. 1998). Less than 30% of cutleaf nightshade (*S. triflorum* Nutt.) at the four-leaf stage was controlled by postemergence applications of rimsulfuron at rates ranging from 9 to 35 g ha^{-1} (Eberlein et al. 1994). Eastern black nightshade is another nightshade species not controlled by postemergence applications of rimsulfuron. Greenland and Howatt (2005) demonstrated that rimsulfuron controlled 7 to 23% of eastern black nightshade even at rates greater than 35 g ha^{-1} and when weeds were at the two- to four-leaf stage.

Many studies have analyzed the effect of rimsulfuron and metribuzin on solanaceous crop tolerance. Robinson and Soltani (2006) demonstrated that 15 g ha^{-1} rimsulfuron plus 150 g ha^{-1} metribuzin applied postemergence caused only 0 to 6% injury to the tomato cultivar Heinz, which was not statistically different than the non-treated controls. Other cultivars, however, were susceptible to rimsulfuron. The use of 23 g ha^{-1} rimsulfuron over 6- to 8-leaf bell pepper (*Capsicum frutescens* L.) resulted in 60% injury to Camelot, 53% to Jupiter, and 53% injury to Memphis (Ackley et al. 1998). Ackley (1997) found that metribuzin at 280 g ha^{-1} applied to six- to eight-leaf ‘Agriset’ tomato plants caused 2% injury which was less than rimsulfuron applied at 26 g ha^{-1} which caused 11% injury. Not all cultivars of tomato are resistant to metribuzin. Fortino and Splittstoesser (1974) showed that 98% of 13 cm tall Campbell 1327 seedlings died 9 days after emergence following preemergence applications of metribuzin at 300 g ha^{-1}.

Similar to tomato, there are potato cultivars that are sensitive to metribuzin. Although metribuzin is labeled for weed control in potato, most red- and white-skinned cultivars are susceptible to postemergence treatments of metribuzin where use is limited to preemergence only. The cultivars Shepody and Caribe are reported to be susceptible to foliar applications of metribuzin when applied at 500 g ha^{-1} at 15 cm or less because both cultivars registered a level 5 tolerance on a scale of 0 (no tolerance) to 9 (complete tolerance) (Friesen and Wall 1984). Ivany (2002) has shown that preemergence applications of metribuzin at 500 g ha^{-1} caused no injury to Sebago. However, Sebago at 15 cm tall suffered 18% injury following postemergence applications of metribuzin at 500 g ha^{-1}. Injury symptoms of plants treated postemergence included chlorotic lesions on the margins of leaves stunting and resulted in yields that were 14% lower on average than plants treated with preemergence applications.

Russet cultivars are typically not affected by postemergence treatments of metribuzin. Using a nutrient solution that included metribuzin with ^{14}C Gawronksi et al. (1985) determined that Russet Burbank accumulated 13 and 39% metribuzin in petioles and stems respectively. Conversely, Chipbelle only accumulated 6 and 13% metribuzin in petioles and stems respectively, while Russet Burbank accumulated 68% metribuzin in leaves compared to 30% in Chipbelle 8 days after treatment. The cultivar Chipbelle was more susceptible to phytotoxicity because the photosystem II inhibiting herbicides acted directly on the chloroplasts in the leaves. This occurred because the cultivar Chipbelle lacked sufficient enzymes required for metribuzin metabolism (Gawronski et al. 1985).

An adjuvant is used to improve efficacy of weed control when postemergence herbicides are applied. Adjuvants are additives included in herbicide mixtures to improve herbicide efficacy in a number of ways. These include, but are not limited to, reducing the surface tension and contact angle of herbicides, increasing herbicide penetration through leaf surfaces, reducing drift and increasing the dispersion or solubility of herbicides (Foy and Smith 1965; Kocher and Kocur 1993; Linder 1973; Singh et al. 1984). The use of adjuvants to control hairy nightshade is important because the presence of fine hairs, called trichomes, on the surfaces of hairy nightshade leaves are capable of inhibiting droplets from making contact with leaf surfaces (Sanyal 2006).

Adjuvants commonly included with metribuzin plus rimsulfuron tank mixtures are nonionic surfactants, methylated seed oils and crop oil concentrates (Green and Green 1993; Hutchinson et al. 2004; Tonks and Eberlein 2001). Hutchinson et al. (2004) determined that metribuzin at 280 g ha^{-1} plus rimsulfuron at 26 g ha^{-1} controlled 98% of the hairy nightshade when combined with a methylated seed oil at 1% (v/v); control was 97% when these herbicides were combined with a crop oil concentrate at 1% (v/v), but decreased to 93% with a nonionic surfactant at 0.25% (v/v). An adjuvant is required in postemergence applications of rimsulfuron whether applied alone or in combination with other herbicides. For example, Green and Green (1993) demonstrated that rimsulfuron applied at 2 g ha^{-1} and combined with a surfactant controlled 93% of giant foxtail (*Setaria faberi* Herrm.), but only controlled 23% of giant foxtail when a surfactant was not included in the tank mixture. Other adjuvants, less commonly used with rimsulfuron and metribuzin, include buffering agents, spreader/stickers, drift retardants, water conditioning agents and antifoaming agents.

Adjuvant choice must take into account the herbicide to be mixed, weed species and environmental conditions. For example, the mealy coating of common lambsquarters (*Chenopodium album* L.) may necessitate the use of a methylated seed oil or crop oil concentrate which is effective at dissolving epicuticular wax. High surfactant oils have a similar function as methylated seed oils, but include a higher amount of surfactant. Methylated seed oil and crop oil concentrate adjuvants may increase crop injury, especially if applications are made when temperatures exceed 29 ºC (Anonymous 2009). Boydston (2007) found that injury to Umatilla Russet was 39% when rimsulfuron was applied at 26 g ha^{-1} and combined with a methylated seed oil at 1% (v/v). In addition, the inclusion of methylated seed oil and crop oil concentrate to herbicide treatments caused 7% foliar injury to potato plants compared to 1% injury from nonionic surfactant mixed with metribuzin and rimsulfuron (Hutchinson et al. 2004).

Often it is necessary to find weed control methods for weeds that have escaped previous efforts at control. In many cases, hand hoeing is employed to control these weeds, but this method is expensive and time consuming (Schweizer 1981). Tillage may be used, but also may increase the risk of injury to a crop. The use of herbicides is an alternative to these cultural control methods. However, there is little information in the literature describing the effect of late postemergence applications of rimsulfuron and metribuzin as rescue treatments with different adjuvants to control hairy nightshade. Therefore, the objective of this study was to determine the efficacy of various adjuvants with metribuzin plus rimsulfuron on hairy nightshade control when plants are at the four leaf stage or greater.

Materials and Methods

Two field trials were established in 2015 at the North Dakota State University research farm near Prosper, ND (47.001749, -97.1227773) on a Kindred-Bearden silty clay loam soil consisting of 25% sand, 47% silt and 28% clay and a pH of 7.3. Corn (*Zea mays* L.) was the previous crop. Field preparation consisted of a single pass with a harrow on June 3, 2015 and was followed by rototilling on June 9, 2015. Environmental conditions at the time of spraying are described in Table 4.

Table 4. Environmental conditions at experimental location for adjuvant study near Prosper, ND in 2015.

	Experimental run 1	Experimental run 2
Soil moisture	Damp	Dry
Residue (corn) cover	10%	25%
Wind speed	2.3 kph	9.7 kph
Wind direction	South	East
Dew presence	5%	0%
Cloud cover	15%	5%
Air temperature	27.2 ºC	25.6
Humidity	55%	51%
Soil temperature	22.8 ºC	28.3 ºC

The experimental design was a randomized complete block with 20 treatments and four replicates in plots that measured 3.7 by 7.6 m. All treatments included rimsulfuron (21 g ha^{-1}) plus metribuzin (340 g ha^{-1}), except the non-treated check. There were 17 different adjuvants tested in combination with rimsulfuron (21 g ha^{-1}) plus metribuzin (340 g ha^{-1}) (Adama Agricultural Solutions, 3120 Highwoods Blvd #100, Raleigh, North Carolina, United States, 27604) plus 21 g ha^{-1} rimsulfuron (Adama Agricultural Solutions, 3120 Highwoods Blvd #100, Raleigh, North Carolina, United States, 27604) (Table 5). Herbicide rates were chosen to simulate a postemergence herbicide treatment at 60% of maximum label-use rate for potato to help separate differences between adjuvants.

Table 5. List of rates, types and manufacturers of adjuvants included at Propser, ND in 2015. All treatments, except the non-treated, included rimsulfuron (21 g ha^{-1}) plus metribuzin (340 g ha^{-1}).

	Treatment	Rate	Adjuvant Type	Manufacturer
1	Non-treated	-	-	-
2	No adjuvant	-	-	-
3	R-11	0.5 %v/v	NIS[a] (spreader/activator)	Wilbur-Ellis www.wilburellis.com
4	R-11	1 % v/v	NIS (spreader/activator)	Wilbur-Ellis
5	Dyne-Amic	420 g ha^{-1}	MSO[b] and organosilicone surfactant	Helena Chemical Company www.helenachemical.com
6	Prefer90	0.5 % v/v	NIS	West Central Inc. www.westcentralinc.com
7	Class Act NG	2.5 % v/v	NIS and water conditioning agent	Winfield Solutions www.winfield.com
8	NIS-EA	0.25% v/v	NIS (spreader/activator)	Wilbur-Ellis
9	Preference	0.25% v/v	NIS and antifoaming agent	Winfield Solutions
10	Interlock[d]	279 g ha^{-1}	Deposition aid, penetrant, drift retardant	Winfield Solutions
11	Quad 7	1% v/v	NIS and buffering agent	Winfield Solutions
12	Climb	3.1 % v/v	Alkalinity agent	Wilbur-Ellis
13	Destiny HC	1,700 g ha^{-1}	HSMOC[c]	Winfield Solutions
14	AG14019	0.5% v/v	NIS and oil adjuvant	Winfield Solutions
15	AG14019	1 % v/v	NIS and oil adjuvant	Winfield Solutions
16	AG14020	0.5% v/v	NIS and buffering agent	Winfield Solutions
17	AG14020	1 % v/v	NIS and buffering agent	Winfield Solutions
18	AG14039	279 g ha^{-1}	HSMOC	Winfield Solutions
19	AG14039	447 g ha^{-1}	HSMOC	Winfield Solutions
20	Masterlock	447 g ha^{-1}	Spreader, sticker, canopy penetrant, drift retardant	Helena Chemical Company

[a] Nonionic surfactant
[b] Methylated seed oil
[c] High surfactant oil concentrate
[d] Interlock was applied with Preference at 0.25% v/v

A natural population of hairy nightshade was utilized and five plants were flagged in the first run on July 5, 2015 and the second run on July 6, 2015. Prior to flagging, plants were allowed to grow to heights of 5 to 8 cm before treatments were made in order to simulate a late postemergence treatment, or rescue treatment. Average density at time of treatment was 7.5 hairy nightshade plants m^{-2} with flagged plants averaging a height of 6.3 cm at the four- to six-leaf stage.

Treatments for the first experimental run were made on July 8, 2015 and the second experimental run on July 9, 2015. Environmental conditions at the time of herbicide application are shown in Table 4. Treatments were applied using a CO^2 pressurized backpack sprayer at 172 kPa and calibrated to deliver 140 L ha^{-1} with a 2.74 m boom and XR11002 flat fan nozzles spaced 0.45 m apart (TeeJet Spraying Systems Company, Wheaton, IL 60189). Carrier water came from Fargo, ND and had a pH of 8.2.

Visual estimates of weed control from 0 (no injury) to 100% (complete plant death) for each individual plant were made 28 days after treatment. Weed height of marked plants was measured from the base of the stem to the top of the stem at 28 days after treatment. At 28 days of treatment, the identified plants were cut at ground level, dried for 8 days at 32 °C, and weighed and followed by counting the number of berries per plant. Each weed was harvested and measured separately, thus resulting in a subsampling effect.

Data were subjected to analysis of variance (ANOVA) using the SAS GLM procedure (SAS Institute, Inc. Cary, NC 27513) with treatments considered fixed effects. Parameters were not pooled because homogeneity of variance did not exist for plant height, dry weight and berry number (Table 6). Fisher's least significant difference (LSD) test (0.05) was used to compare means.

Table 6. Tests for homogeneity of variance and analysis of variance and means squares for hairy nightshade parameters combined across two runs near Prosper, ND in 2015.

SOV	df	Visual efficacy	Height	Dry weight	Berry number
Location[a]	1	1	82***	298***	170**
Rep	3	5187	126***	180***	413***
Rep(location)	3	3293	15*	18*	247***
Trt	19	12749	88***	112***	122***
Rep*Trt	57	36606	6	12	55***
Error	308	134890	1809	3352	9719

[a] Type III mean square

*, **, *** Significant at 0.1, 0.05, and 0.01 probability levels, respectively.

Results and Discussion

No differences were found in visual efficacy or dry weight for either run (Tables 7 and 8). The mean visual rating showed that weed control was less than 21% for all treatments. Metribuzin and rimsulfuron alone caused 5 and 13% visual efficacy in runs one and two respectively. The level of visual control in this study was much lower than in a similar study conducted by Hutchinson et al. (2004) in which control of hairy nightshade was 93 to 98% when weeds were at the two- to four-leaf stage and herbicide rates were higher (metribuzin at 280 g ha^{-1} and rimsulfuron at 26 g ha^{-1}) compared to the present study. Results suggest that application timing and herbicide rate are important factors for hairy nightshade control. Another difference in our study that set it apart from previous work was that hairy nightshade lacked a crop to compete with, therefore causing a bushy growth compared to the erect growth typically caused by competition with a crop. This may explain why plants in control plots were taller on average, but weighed numerically less than plants treated by the other treatments. Hariy nightshade competed with other weeds in the non-treated checks, while the metribuzin and rimsulfuron controlled most weeds in the treated plots.

Table 7. Hairy nightshade parameters measurements 28 days after rimsulfuron (21 g ha^{-1}) plus metribuzin (340 g ha^{-1}) for first run with adjuvant treatments near Prosper, ND in 2015.

	Adjuvant	Rate	Visual efficacy[a]	Height	Dry weight	Berries[b]
		g a ha^{-1}	%	cm	g	number
1	Untreated	-	0	48	2.1	9.3
2	No adjuvant	-	5	25	3.3	0.9
3	R-11	630	11	26	5.9	1.1
4	R-11	1,260	9	25	7.4	2
5	Climb	2,020	2	38	4.4	20.6
6	Dyne-Amic	420	21	25	4.2	5.4
7	Prefer 90	630	19	23	4.5	2
8	Class Act NG	1,770	20	20	3.4	0.6
9	NIS-EA	340	15	23	4.5	0
10	Destiny HC	1,800	8	24	4.9	6.4
11	Preference	310	5	24	6.1	2.9
12	Interlock[c]	310	25	22	2.7	2
13	AG14039	279	9	24	2.8	1.4
14	Masterlock	450	28	22	7.3	2.2
15	AG14039	447	16	23	6.7	0.7
16	AG14019	70	19	20	2.9	0.2
17	AG14019	140	19	21	4.6	1.6
18	AG14020	70	16	22	4.7	1.2
19	AG14020	140	5	27	6.6	4.9
20	Quad 7	140	5	28	4.6	2.3
		LSD (0.05)	NS	5.2	NS	6.3

[a] Hairy nightshade estimated visual control from 0 to 100% with 0 meaning no control and 100 mean complete control.

[b] Hairy nightshade berry number following drying.

[c] Interlock was applied with Preference at 310 g ha^{-1}.

Table 8. Hairy nightshade parameters measurements 28 days after rimsulfuron (21 g ha^{-1}) plus metribuzin (340 g ha^{-1}) for second run with adjuvant treatments near Prosper, ND in 2015.

	Adjuvant	Rate	Visual efficacy[a]	Height	Dry weight	Berries[b]
		g a ha^{-1}	%	cm	g	number
1	Untreated	-	0	39	1.2	7.6
2	No adjuvant	-	13	23	3.1	0.6
3	R-11	630	10	23	3.5	2.2
4	R-11	1,260	20	22	4.7	2.4
5	Climb	2,020	4	37	4.1	14
6	Dyne-Amic	420	8	28	2.7	2.2
7	Prefer 90	630	12	21	2.2	0.7
8	Class Act NG	1,770	12	21	2.5	0.4
9	NIS-EA	340	29	19	2.5	0.7
10	Destiny HC	1,800	8	22	3.9	2.9
11	Preference	310	30	17	2.3	1.2
12	Interlock[c]	310	12	20	3.2	0.2
13	AG14039	279	18	21	2.2	0.2
14	Masterlock	450	10	22	1.6	1.4
15	AG14039	447	5	24	3.3	2.3
16	AG14019	70	28	16	3.4	0.6
17	AG14019	140	15	19	3.4	0.3
18	AG14020	70	11	20	2.8	1.2
19	AG14020	140	7	26	1.7	0.7
20	Quad 7	140	29	18	2.5	0.6
		LSD(0.05)	NS	5.4	NS	4.2

[a] Hairy nightshade estimated visual control from 0 to 100% with 0 meaning no control and 100 mean complete control.

[b] Hairy nightshade berry number following drying.

[c] Interlock was applied with Preference at 310 g ha^{-1}.

Reducing herbicide rates may lead to reduced weed control efficacy. This may occur when herbicides are not applied at the critical period of weed control or when the weed populations are at densities and heights that do not cause reductions in crop yields (DeFelice et al. 1989; Hagwood et al. 1980; Steckel et al. 1990; Hall et al. 1992; Van Acker et al. 1993). Tonks and Eberlein (2001) determined that decreasing rimsulfuron rate from 35 g ha^{-1} to 9 g ha^{-1} resulted in 92 and 69% control of hairy nightshade at the two- to four- leaf stage, respectively. Furthermore, the low rate of visual control is in agreement with a survey of studies conducted by

Zhang et al. (2000) which states that combining reduced herbicide rates and adjuvants had little to no effect on weed control.

Dyne-Amic, a methylated seed oil plus organosilicone surfactant, and Destiny HC, a high surfactant oil concentrate, were predicted to provide the greatest effiacy. Previous research indicates that methylated seed oil adjuvants provided better control of hairy nightshade in combination with metribuzin and rimsulfuron than nonionic surfactant because this type of adjuvant is more effective in dissolving epicuticular wax and therefore increasing herbicide penetration (Hutchinson et al. 2004; Manthey et al. 1989). Similar results were expected with the high surfactant oil concentrate treatment, but this did not occur in our study.

Adjuvants may have no effect on herbicide efficacy if one of a number of conditions predominate: stress or weeds are past a growth stage in which herbicides effectively control the weeds (Kudsk and Streibig 1993). The most likely explanation for our results is that the adjuvants had no effect on weed control because the weed sizes at treatment were too large. This was further demonstrated by the herbicide treatment (with no adjuvant) that had 11% visual effiacy. Previous research combining rimsulfuron, metribuzin and adjuvants for hairy nightshade control found that treatments were effective when hairy nightshade was at the cotyledon- to two-leaf stage, or the two- to four-leaf stage (Eberlein et al. 1994; Hutchinson et al. 2004). Furthermore, Mekki and Leroux (1994) demonstrated that sulfonylurea herbicides most effectively control broadleaf weeds when applied early postemergence, usually around the two- to five-leaf stage, or when the plants are no more than 2.5 cm tall. Bellinder et al. (2003) reportated that hairy nightshade control decreased as plants grew past the four leaf stage when treated with bentazon, a PSII inhibitor. The hairy nightshade in our study were between the four- and six-leaf stage, averaging 6.3 cm tall, and most likely were too large for effective control with metribuzin and rimsulfuron. It was observed that many four-leaf hairy nightshade plants suffered more necrosis than six-leaf plants, though a distinction was not made in the data (Figure 1).

Differences in treatment were found in plant height and berry number for both runs (Tables 7 and 8). As expected, the non-treated control had the tallest hairy nightshade plants when compared with the other treatments. The non-treated check and Climb treatment had the most berries compared to the other treatments. The treatment with Climb resulted in plants that were at least 35% taller than the other adjuvant treatments at 28 days after treatment.

There are a number of explanations for Climb's inability to control hairy nightshade as well as the other adjuvant treatments. Climb is an alkalinity agent which raises the pH of a spray solution to 10.6 in order to make sulfonylurea herbicides more soluble (Anonymous 2013). Increasing the pH of a solution makes weak acid herbicides more ionic and soluble, but less likely to pass trichomes and penetrate cuticular waxes (Stirling 1994). Sulfonylurea herbicides, including rimsulfuron, are weak acids that require the inclusion of surfactants to decrease surface tension or oil-based adjuvants to increase penetration through epicuticular waxes (Green and Hale 2005). The nonionic surfactant plus buffering agent Quad 7 is a "basic blend" adjuvant that increases the pH of a solution while simultaneously reducing surface tension (Nalewaja et al. 1997). Climb, on the other hand, only raises solution pH and does not improve herbicide efficacy by reducing surface tension, increasing penetration of the spray droplet through the leaf cuticle or increasing wetting or spreading. If the pH of a solution is raised, but no adjuvant is included in the mixture, it becomes difficult for the negatively charged herbicide particles to pass through the negatively charged surfaces of the plant (Stirling 1994).

Though Climb is registered for use with sulfonylurea herbicides, pH dependency is commonly associated with fungicides and insecticides, not herbicides (Foy 1989; McMullan 2000). Although alkaline buffers may be needed to solubilize herbicides that remain particulate in form while in solution, that was not the case in our study (Nalewaja et al. 1997). Additionally, pH buffers have the greatest effect on herbicide efficacy when used in extremely alkaline or acidic water (McWorter 1982). Carrier water used in this study had a pH of 8.2, which was likely not high enough to improve the efficacy of the herbicides.

Late postemergence herbicide treatments are often made to control weeds that have escaped previous efforts at control. This study demonstrated that late postemergence applications on four- to six-leaf hairy nightshade with 340 g ha^{-1} metribuzin plus 21 g ha^{-1} rimsulfuron with or without an adjuvant were not effective as resuce treatments on hairy nightshade. Hairy nightshade must be controlled when plants are smaller and more susceptible to herbicides. Future work needs to evaluate the effect of higher herbicide rates for large weed control postemergence in potato.

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CHAPTER 3. POTATO AND WEED RESPONSE TO METRIBUZIN, RIMSULFURON AND ADJUVANT COMBINATIONS

Abstract

Postemergence broadleaf weed control can be difficult in potato because of limited herbicide options. One method to enhance herbicide efficacy is the addition of adjuvants. The objectives of this study were to determine the effect of adjuvants on weed control, potato crop safety and yield. The presence of an adjuvant in tank mixtures did not improve visual estimates of control of wild proso millet in 2014, but improved common lambsquarters in 2015 when Dyne-Amic or Climb was included in tank mixtures. Destiny HC caused more injury (11%) than all other treatments except Dyne-Amic (6%). Treatments had no effect on graded yield indicating that the use of adjuvants can improve weed control and not affect yield, although crop injury may occur.

Nomenclature. Metribuzin, 4-amino-6-6-(1,1-dimethylethyl)-3-(methylthio)1,2,4-triazin-5(4H)-one; Rimsulfuron, N-((4,6-dimethoxypyrimidin-2-yl) aminocarbonyl)-3-(ethylsulfonyl)-2-pyridinesulfonamide; *Common lambsquarters*, Chenopodium album L. CHEAL; Wild proso millet, *Panicum miliaceum* L. # PANMI; Potato, *Solanum tuberosum* L.

*Key words***.** Visual estimate of weed control, yield, crop injury, Russet Burbank, Umatilla Russet

Introduction

Metribuzin and rimsulfuron are the only available herbicide options for postemergence broadleaf weed control in potato in the United States. One way to improve herbicide efficacy for hard-to-control weeds is by including additives (Alvarez and Hutchinson 2005; Kleppe and Harvey 1991; Rabaey and Harvey 1997; Renner and Powell 1998). Adjuvants are common additives used to improve herbicide efficacy. Metribuzin, a triazinone herbicide, inhibits electron transport in the chloroplast by binding to the D1 protein of the photosystem II (PSII) complex (Hess 2000). Rimsulfuron, a sulfonylurea herbicide, inhibits the plant enzyme acetolactate synthase, and thereby blocks the synthesis of the branched-chain amino acids isoleucine, leucine and valine (LaRossa and Schloss 1984). Not all broadleaf weeds react similarly to metribuzin or rimsulfuron.

Common lambsquarters (*Chenopodium album* L.) and hairy nightshade (*Solanum phsalifolium* Rusby.) are two broadleaf weed species that respond to metribuzin and rimsulfuron differently. Eberlein et al. (1994) demonstrated that postemergence applications of rimsulfuron at 18 g ha^{-1} controlled 25% of common lambsquarters at the two- to four-leaf stage, while Robinson et al. (1996) showed that preemergence applications of rimsulfuron at 35 g ha^{-1} controlled 93% of the common lambsquarters. Both preemergence and postemergence applications of metribuzin control common lambsquarters. The literature indicates that preemergence applications of metribuzin at 280 g ha^{-1} controlled 83 to 90% of the common lambsquarters while postemergence applications at this same rate improved control slightly from 97 to 98% when plants were at the two- to four-leaf stage (Ackley et al. 1996; Renner and Powell 1998). A study by Renner and Powell (1998) showed that when rimsulfuron is applied at rates of 35 g ha^{-1} in combination with metribuzin at 280 g ha^{-1}, common lambsquarters control reached levels of 100%. Hairy nightshade, on the other hand, is not controlled by postemergence applications of metribuzin, but is controlled by rimsulfuron applied postemergence. When applied at 280 g ha^{-1}, metribuzin only controls 32% of hairy nightshade and control increases to only 63% when metribuzin rate is increased to 420 g ha^{-1} (Eberlein et al. 1994). Hutchinson et al. (2004) reported that rimsulfuron, at 26 g ha^{-1} controls 88% of hairy nightshade at the one- to two-leaf stage; however, when combined with metribuzin at 140 or 280 g ha^{-1}, control increased to ≥ 96%.

The use of rimsulfuron may control of annual grasses (Ackley et al. 1996). Ackley (et al. 1997) demonstrated that large crabgrass (*Digitaria sanguinalis* L.) had an 89% visual control and an 87% reduction in height when rimsulfuron was applied at 35 g ha-1 and Damalas and Eleftherohorinos (2001) demonstrated that 9 g ha-1 of rimsulfuron controlled 91% of johnsongrass (*Sorghum halepense* (L.) Pers.) at the two- to four-leaf stage. Wild proso millet is an annual grass species commonly found in North Dakota crop production (Nalewaya et al. 1998). This weed is problematic because it is highly tolerant to sulfonylurea herbicide phytotoxicity during the early germinating growth stages; thus, it is seldom controlled by preemergence applications of nicosulfuron (Harvey et al. 1987). Mekki and Leroux (1994) demonstrated that postemergence applications of rimsulfuron, however, at rates as low as 6 g ha^{-1} were sufficient to control wild proso millet at the two- to four-leaf stage when combined with an adjuvant, specifically a nonionic surfactant, at 0.25 % (v/v).

Adjuvants are included in herbicide mixtures to improve herbicide efficacy in a number of ways. These include, but are not limited to reducing the surface tension and contact angle of herbicides, reducing drift and increasing the dispersion or solubility of herbicides (Foy and Smith 1965; Kocher and Kocur 1993; Linder 1973; Singh et al. 1984; Western et al. 1999). Adjuvants that have been included with metribuzin and rimsulfuron tank mixtures are nonionic surfactants, methylated seed oils, and crop oil concentrates (Hutchinson et al. 2004; Tonks and Eberlein 2001). Hutchinson et al. (2004) determined that metribuzin at 280 g ha^{-1} plus rimsulfuron at 26 g ha^{-1} controlled 98% and of hairy nightshade at the two- to four-leaf stage when combined with a methylated seed oil at 1% (v/v); control was 97% when these herbicides were combined with a crop oil concentrate at 1% (v/v), but decreased to 93% with a nonionic surfactant at 0.25% (v/v). An adjuvant is required in postemergence applications of rimsulfuron whether applied alone or in combination with other herbicides. For example, Green and Green (1993) demonstrated that rimsulfuron applied at 2 g ha^{-1} and combined with a surfactant controlled 93% of giant foxtail (*Setaria faberi* Herrm.), but only controlled 23% of giant foxtail when a surfactant was not included in the tank mixture. Other adjuvants, less commonly used with rimsulfuron and metribuzin, include buffering agents, spreader/stickers, drift retardants, water conditioning agents and antifoaming agents (Annonymous 2002; Anonymous 2009).

Adjuvant choice must take into account weed species, environmental conditions at the time of application and susceptibility of potato cultivars. For example, the mealy coating of common lambsquarters (*Chenopodium album* L.) may necessitate the use of a methylated seed oil, crop oil concentrate or high surfactant oil concentrate because these adjuvants are effective at dissolving epicuticular wax. High surfactant oils have a similar function as methylated seed oils, but include surfactants. Hutchinson et al. (2004) reported that the addition of a methylated seed oil at 1% (v/v) or crop oil concentrate at 1% (v/v) compared to a nonionic surfactant at 0.25% (v/v) when mixed with metribuzin and rimsulfuron improved control of common lambsquarters by up to 9% and hairy nightshade by up to 5%. However, the increase in weed control from methylated seed oil and crop oil concentrate adjuvants may be offset by increased crop injury, especially if applications were made when temperatures exceed 29 ºC (Anonymous 2009). Boydston (2007) found that injury to Umatilla Russet was 39% when rimsulfuron was applied at 26 g ha^{-1} and combined with a methylated seed oil at 1% (v/v). On the other hand, Hutchinson et al. (2004) demonstrated that a methylated seed oil at 1% (v/v) only caused 7% foliar injury to Russet Burbank.

Because of the many adjuvants choices and the varying responses of these adjuvants, there is a need to test the effects of metribuzin plus rimsulfuron in combination with adjuvants to determine their effectiveness on weed control and crop injury. There is also a need to determine if including adjuvants with metribuzin and rimsulfuron tank mixtures improves control of common lambsquaters and wild proso millet compared to treatments lacking adjuvants. Therefore, the objectives of this study were to determine the effect of adjuvants on weed control, potato crop safety and yield.

Materials and Methods

A field trial was conducted in a commercial potato field near Ottertail, MN (46.408270, -95.57692) in 2014 and in a commercial potato field near Park Rapids, MN (47.00179, -97.1228773) in 2015. The soil near Ottertail, MN was a Hubbard loamy sand described by 90% sand, 8% silt, and 2% clay, while the soil near Park Rapids, MN was a Verndale-Sandy loam with 64% sand, 30% silt, and 6% clay. Russet Burbank seed pieces weighing 85 to 142 grams were planted at 36 cm within-row spacing in rows that were spaced 91 cm apart in 2014, while Umatilla Russet seed pieces weighed 60 grams and were planted 90 cm apart at 31 cm within-row spaces in 2015. Potatoes were planted on May 5, 2014 with approximately 50% plant had emergence on June 5, 2014, while two weeks later there was 50% row closure. Potatoes were planted on April 27 in 2015. Buckwheat (*Fagopyrum esculentum* Moench.) was planted prior to potatoes in Ottertail, MN and corn (*Zea mays* L.) was planted prior to potatoes in Park Rapids, MN. All production practices were conducted according to University of Minnesota recommended commercial potato production practices, except no herbicides were applied in the research area.

Experiments were designed as a randomized complete block design with 11 treatments and four replicates. Plots measured 2.7 m by 9.1 m. Two non-treated controls (weedy and weed-free) were included with the 11 treatments. Weeds were removed from the weed-free control at the time of herbicide application. All treatments included 562 g ha^{-1} metribuzin and 26 g ha^{-1} rimsulfuron to simulate a postemergence herbicide treatment, except the non-treated control and hand weeded treatments. Adjuvants were mixed with the herbicides according to standard mixing practices (Table 9).

Table 9. List of rates, type and manufacturers of adjuvants included in this study. All treatments, except controls, included rimsulfuron (26 g ha^{-1}) plus metribuzin (520 g ha^{-1}) and were applied to Russet Burbank in 2014 at Ottertail, MN and Russet Umatilla in 2015 at Park Rapids, MN.

	Treatment	Rate	Adjuvant Type	Manufacturer
		g ha^{-1}		
1	Weedy control	-	-	-
2	Weed free control	-	-	-
3	No adjuvant	-	-	-
4	R-11®	0.5% v/v	NIS[a] (spreader/activator)	Wilbur-Ellis www.wilburellis.com
5	R-11	1 %v/v	NIS (spreader/activator)	Wilbur-Ellis
6	Climb®	3.1 %v/v	Alkalinity agent	Wilbur-Ellis
7	Dyne-Amic®	6% v/v	MSO[b] and organosilicone surfactant	Helena Chemical Company www.helenachemical.com
8	Prefer90®	0.5% v/v	NIS	West Central Inc. www.westcentralinc.com
9	Class Act NG®	2.5% v/v	NIS and water conditioning agent	Winfield Solutions LLC www.winfield.com
10	NIS-EA®	0.25% v/v	NIS (spreader/activator)	Wilbur-Ellis
11	Destiny® HC	1,700	HSMOC[c]	Winfield Solutions LLC www.winfield.com

[a] Nonionic surfactant

[b] Methylated seed oil

[c] High surfactant oil concentrate

Weed density for wild proso millet and common lambsquarters was low in 2014 and 2015. In 2014, wild proso millet plants averaged 11 m^{-2} and were at the two- to four-leaf stage at the time of herbicide plus adjuvant treatments. In 2015, common lambsquarters density was 9 plants m^{-2} and were also at the two- to four-leaf stage at the time of herbicide plus adjuvant treatments. Potato plants were between 30 to 38 cm tall at the time of treatment in both years.

All treatments were applied using a CO^2 pressurized backpack sprayer at 172 kPa and calibrated to deliver 140 L ha-1 with a 2.74 m boom and XR11002 nozzles spaced 0.45 m apart (TeeJet Spraying Systems Company, Wheaton, IL 60189).

Visual estimates of crop injury and weed control from 0 (no injury) to 100% (complete plant death) were made at 28 days after treatment (Wilcut and Swann 1990). Plots were harvested on September 23, 2014 and September 18, 2015 with a single row plot harvester. Two, 7.5 m rows were harvested, one row was weighed and the other weighed and graded. Tuber graded yield were determined according to USDA standards with U.S. No.1 tubers being those ≥ 113g with no defects (USDA 2011); U.S. No. 2 tubers were those ≥ 113g with moderate defects and total marketable yield as U.S. No. 1 and U.S. No. 2 tubers ≥ 113g.

Analysis of variance (ANOVA) was conducted using the SAS GLM procedure (SAS Institute, Inc. Cary, NC 27513) with location considered to be random effects and treatments set as a fixed effect. Fisher's least significant difference (LSD) test (0.05) was used to separate treatment means. Yield data were separated by year because homogeneity of variance did not exist for most yield parameters measured at ($p < 0.05$) (Table 10). Crop injury data was separated by year due to a lack of homogeneity of variance (Table 10).

Table 10. Analysis of variance and tests for homogeneity of variance for metribuzin (520 g ha^{-1}) plus rimsulfuron (26 g ha^{-1}) with different adjuvants on Russet Burbank marketable yield near Ottertail, MN in 2014 and Umatilla Russet marketable yield near Park Rapids, MN in 2015

SOV	df	<113g[b]	113-170g	170-287g	287-397g	>397g	Total	U.S. No. 1	U.S. No. 2	TMY	P > 170[c]	P > 283[d]	Crop injury 28 DAT
Location	1	12	59***	630***	2278***	92***	62	6513***	1	5991***	273	2586***	462***
Rep	1	0.1	0.2	2	1	0.3	0.1	2	0.1	2	16	3	7
Rep(Location)	1	4	6	3	1	0.1	25	15	0.1	17	1	1	4
Trt[a]	10	4	8	56	15	4	108	77	2	67	37	20	80
Location*Trt	10	6	7	18	20	5	66	49	2	42	46	24	27
Error	19	84	108	666	892	95	2196	1576	56	1569	2590	1149	911

[a] Type III mean square

[b] U.S. No. 1 tubers weigh ≥ 113 g without defects U.S. No. 2 tubers weigh ≥ 113 g with defects and malformations were included with U.S. No. 1 tuber yields.

[c] Percent of tubers greater than 170g.

[d] Percent of tubers greater than 283 g

*, **, *** Significant at 0.1,0.05, and 0.01 probability levels, respectively.

Results and Discussion

In 2014, there were differences in crop injury 28 days after treatment (Table 11). Metribuzin at 520 g ha^{-1} plus rimsulfuron at 26 g ha^{-1} without an adjuvant caused significant injury to potato plants (10%) when compared to the controls. Climb did not increase injury to potato plants compared to the non-treated controls. However, NIS-EA was the injurious with 20% injury. Russet Burbank potato injury symptoms included chlorotic and necrotic lesions on the margins of leaves and stunted growth.

Table 11. Effect of metribuzin (520 g ha^{-1}) plus rimsulfuron (26 g ha^{-1}) 28 days after treatment with different adjuvants on Russet Burbank injury and wild proso millet control in 2014 near Ottertail, MN and Umatilla Russet injury and common lambsquarters control in 2015 near Park Rapids, MN.

			2014		2015	
	Treatmentb	Rate	WPM[a]	Crop injury	CLQ[b]	Crop injury
		g ha^{-1}		%		
1	Weedy control[c]	-	0	0	0	0
2	Weed-free control	-	100	0	100	0
3	No adjuvant	-	95	10	78	1
4	R-11	630	96	14	85	1
5	R-11	1,260	90	13	85	5
6	Climb	2,020	91	6	99	2
7	Dyne-Amic	420	95	14	98	6
8	Prefer 90	630	90	14	93	3
9	Class Act NG	1,770	84	10	84	4
10	NIS-EA	340	96	20	81	2
11	Destiny HC	1,800	95	9	91	11
	LSD (0.05)		8.1	8.5	16.2	6.2

[a] Wild proso millet % visual control
[b] Common lambsquarters % visual control
[c] Both non-treated controls were included in the analysis

Crop injury had a significant effect in 2015. Destiny HC, a high surfactant oil concentrate, caused 11% visual injury, which was more than most treatments (Table 11). Umatilla Russet injury was similar to previous studies in which crop oil concentrates caused more injury to potato plants than nonionic surfactants when combined with metribuzin and rimsulfuron. Other adjuvant treatments averaged 1 to 6% crop injury. Huchinson et al. (2004) reported that injury to Russet Burbank was only 1% when a nonionic surfactant at 0.25% (v/v) was combined with rimsulfuron at 26 g ha^{-1} with metribuzin at 280 g ha^{-1}, though injury may increase to 7% when combined with a crop oil concentrate at 1% (v/v).

Treatment had a significant effect on wild proso millet control (Table 11). Visual estimate of proso millet control ranged from 84 to 96% for the treatments including herbicides. The lowest control for an adjuvant treatment was the nonionic surfactant plus water conditioning treatment, Class Act NG (84%), which had less control than herbicide alone. No other adjuvant inhibited or enhanced control of wild proso millet.

Ammonium sulfate, the water condition agent in Class Act NG, has been found to reduce hard water antagonism caused by ions such as calcium and sodium bicarbonate (McMullan 2000). Ammonium sulfate is an effective water conditioning agent for reducing antagonism caused by calcium in glyphosate solutions (Buhler and Burnside 1983; Nalewaja and Matysiak 1993) and has improved glyphosate efficacy in johnsongrass and yellow nutsedge (*Cyperus esulensus* L.) (Chandler et al. 1983; Costa and Appleby 1986). Less is known about the efficacy of ammonium sulfate in mixtures with rimsulfuron and metribuzin on control of annual grasses.

Wild proso millet control was not improved by the addition of the Dyne-Amic. Methylated seed oils may not improve control of annual grasses when compared to nonionic surfactants. For example, (Tonks and Eberlein 2001) demonstrated that rimsulfuron at 26 g ha^{-1} with a methylated seed oil at 1% (v/v) only improved control of volunteer oat (*Avena sativa* L.) 3% (from 94 to 97%) when compared to a nonionic surfactant at 0.25 % (v/v). However, the level of control with metribuzin and rimsulfuron alone was the same as Dyne-Amic, demonstrating that methylated seed oils may not improve wild proso millet control.

In 2015 there was a treatment effect for common lambsquarters control (Table 8). Visual estimates of control ranged from 78 to 99% for all the herbicide treatments. The only two adjuvants that improved weed control were Climb and Dyne-Amic when compared to the herbicide only treatment. The other adjuvants had a numerical advantage over the herbicide only treatment, but were not statistically different.

Methylated seed oils are especially useful against weeds, such as common lambsquarters, that have a mealy, waxy coating on the adaxial leaf surface. Control of common lambsquarters with the treatment including Dyne-Amic was 98% and more than NIS-EA at 81%. Although Tonks and Eberlein (2001) and Hutchinson et al. (2004) found that methylated seed oils with rimsulfuron plus metribuzin resulted in greater common lambsquarters control than nonionic surfactant treatments, our results did not show a clear advantage to methylated seed oils over other adjuvants tested.

There were no differences among treatments for any yield parameter measured for both locations at ($p < 0.05$) (Tables 12 and 13). These findings suggest that weed control and the influence of crop injury had no effect on yield. Previous research indicates that low densities of common lambsquarters (< 45 plants m^{-2}) do not reduce U.S. No. 1 or total marketable yields in Russet Burbank compared to weed-free and weedy controls following metribuzin applications at 430 g ha^{-1} (Gutierri and Eberlein 1997). Common lambsquarters densities (9 m^{-2}) in our study were below these thresholds, and therefore did not impact yield. Wild proso millet densities were also low and did not impact yield in 2014.

Table 12. Effect of metribuzin (520 g ha^{-1}) plus rimsulfuron (26 g ha^{-1}) with different adjuvants on Russet Burbank marketable yield near Ottertail, MN in 2014.

	Treatment		Yield										
		Rate	<113g[a]	113-170g	170-283g	283-397g	>397g	Total	U.S. No. 1	U.S.No. 2	TMY[b]	P>170[c]	P> 283[d]
		g ha^{-1}	Mg ha^{-1}										
1	Weedy control[e]	-	10	17	28	12	5	72	62	3	65	63	24
2	Weed-free control	-	11	17	27	11	5	71	60	2	62	61	23
3	No adjuvant	-	10	15	25	12	6	68	58	4	62	63	26
4	R-11	630	11	17	21	9	6	64	53	3	56	56	23
5	R-11	1,260	10	18	21	8	3	60	50	1	51	53	18
6	Climb	2,020	11	16	27	12	3	69	58	3	61	61	22
7	Dyne-Amic	420	12	18	29	10	5	74	62	3	65	59	20
8	Prefer 90	630	9	16	26	10	5	66	57	3	60	62	23
9	Class Act NG	1,770	12	18	24	12	4	70	58	2	60	57	23
10	NIS-EA	340	12	18	27	10	7	74	62	2	64	59	23
11	Destiny HC	1,800	10	15	23	10	3	61	51	3	54	59	21
	LSD (0.05)		NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS

[a] U.S. No. 1 tubers weigh ≥ 113 g without defects. U.S. No. 2 tubers weigh ≥ 113 g with defects and malformations. Total marketable yield includes U.S. No. 1 and U.S. No. 2 tubers.

[b] Total marketable yield was calculated as U.S. No. 1 and included U.S. No. 2 tubers

[c] % of tubers greater than 170 g,

[d] % of tubers greater than 283 g.

[e] Both non-treated controls were included in the analysis.

These results demonstrate that applying 520 g ha^{-1} metribuzin plus 26 g ha^{-1} rimsulfuron without an adjuvant was an effective method for controlling wild proso millet. However, common lambsquarters control was increased with the inclusion of Climb or Dyne-Amic, though and additional year of common lambsquarters control data is needed to confirm results observed in 2015. These results also demonstrate that when common lambsquarters densities are ≤ 9 m^{-2} and wild proso millet densities are ≤ 11 m^{-2} in an irriated potato system, there is no potato yield or grade advantage when herbicides are applied.

Table 13. Effect of metribuzin (520 g ha^{-1}) plus rimsulfuron (26 g ha^{-1}) with different adjuvants on Umatilla Russet marketable yield near Park Rapids, MN in 2015.

	Treatment		Yield										
		Rate	<113g[a]	113- 170g	170- 283g	283- 397g	>397g	Total	U.S. No. 1	U.S No. 2	TMY[b]	P> 170[c]	P> 283[d]
		g ha^{-1}						Mg ha^{-1}					
1	Weedy control[e]	-	9	14	13	20	1	57	48	2	50	60	37
2	Weed-free control	-	8	13	18	28	2	69	61	3	64	70	43
3	No adjuvant	-	10	15	19	28	2	69	64	5	69	71	43
4	R-11	630	8	13	17	26	2	74	58	3	61	61	38
5	R-11	1,260	8	12	18	26	2	66	58	3	61	70	42
6	Climb	2,020	11	16	21	31	1	80	69	2	71	66	40
7	Dyne-Amic	420	9	14	16	25	2	66	57	4	61	65	41
8	Prefer 90	630	12	14	17	25	1	67	57	5	62	64	39
9	Class Act NG	1,770	9	14	17	25	3	68	59	2	61	66	41
10	NIS-EA	340	10	15	19	27	3	74	64	2	66	66	41
11	Destiny HC	1,800	8	13	17	25	4	67	59	4	63	69	43
	LSD (0.05)		NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS

[a] U.S. No. 1 tubers weigh ≥ 113 g without defects. U.S. No. 2 tubers weigh ≥ 113 g with defects and malformations. Total marketable yield includes U.S. No. 1 and U.S. No. 2 tubers.

[b] Total marketable yield was calculated as U.S. No. 1 and included U.S. No. 2 tubers

[c] % of tubers greater than 170 g,

[d] % of tubers greater than 283 g.

[e] Both non-treated controls were included in the analysis.

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CHAPTER 4. EFFICACY OF METRIBUZIN AND RIMSULFURON WITH FUNGICIDES ON WEED CONTROL AND POTATO CROP SAFETY

Abstract

Postemergence weed control may coincide with foliar fungicide treatments, allowing producers to tank mix these products to improve production efficiency by reducing costs associated with pesticide applications and damage to equipment and crops. It is unknown what effect tank-mixing fungicides with herbicides may have on weed control or crop injury. The objectives of this study were to determine the effect of combining fungicides with metribuzin and rimsulfuron on weed control, potato crop safety, and yield. In 2015, two field trials were established near Park Rapids, MN to evaluate the effect of rimsulfuron and metribuzin plus either chlorothalonil or mancozeb on common sunflower and common lambsquarters control and potato crop safety. There were no differences in common sunflower and common lambsquarters control at 14, 28 and 56 days after treatment for herbicide treatments, except in one instance where common lambsquarters control was 6% less when treated with Penncozeb at 2,129 g ha^{-1} than Bravo Weather Stick tank mixtures at 790 and 1,580 g ha^{-1}. Overall, the herbicide plus fungicide combinations resulted in ≥ 94% common lambsquarters and ≥ 98% common sunflower control. There were also no yield differences between any of the treatments tested. This study demonstrates that incorporating chlorothalonil and mancozeb with metribuzin and rimsulfuron is a pest control option that does not reduce crop yield or negatively affect weed control, though the effect on fungi populations still need to be determined.

Nomenclature. Chlorothalonil (2,4,5,6-tetrachloro-1,3-benzenedicarbonitrile); Mancozeb ([1,2-Ethaznediybis(carbamodithio) (2-)] manganese [[1,2-ethanediylbis[carbamodithioate]] (2-) zinc); Metribuzin, 4-amino-6-6-(1,1-dimethylethyl)-3-(methylthio)1,2,4-triazin-5(4H)-one;

Rimsulfuron, N-((4,6-dimethoxypyrimidin-2-yl) aminocarbonyl)-3-(ethylsulfonyl)-2-pyridinesulfonamide; *Common lambsquarters*, Chenopodium album L., CHEAL; Common sunflower, *Helianthus annuus* L. HELAN; Potato, *Solanum tuberosum* L.

Introduction

Metribuzin and rimsulfuron are the only available herbicide options for postemergence broadleaf weed control in potato currently used in the United States. Metribuzin, a triazinone herbicide, inhibits electron transport in the chloroplast by binding to the D1 protein of the photosystem II complex (Hess 2000). Rimsulfuron, a sulfonylurea herbicide, inhibits the plant enzyme acetolactate synthase and thereby blocks the synthesis of the branched-chain amino acids isoleucine, leucine and valine (LaRossa and Schloss 1984).

Both preemergence and postemergence applications of metribuzin control common lambsquarters. For example, Eberlein et al. (1994) demonstrated that postemergence applications of rimsulfuron at 18 g ha^{-1} only controlled 25% of common lambsquarters at the two- to four-leaf stage while Robinson et al. (1996) showed that preemergence applications of rimsulfuron at 35 g ha^{-1} controlled 93% of common lambsquarters. The literature indicates that preemergence applications of metribuzin at 280 g ha^{-1} control 83 to 90% of common lambsquarters while postemergence applications at this same rate improved control slightly from 97 to 98% when plants were at the two- to four-leaf stage (Ackley et al. 1996; Renner and Powell 1998). A study by Renner and Powell (1998) showed that when rimsulfuron is applied at rates of 35 g ha^{-1} in combination with metribuzin at 280 g ha^{-1}, common lambsquarters control reached levels of 100%.

Control of common sunflower (*Helianthus annus* L. Helian) with rimsulfuron is highly dependent on weed density (Al-Khatib et al. 2000). Control of common sunflower may decrease if plant density exceeds 30 plants m^{-2} because the herbicide is not able to effectively cover all the plants (Al-Khatib et al. 2000). This was evident in a study by Al-Khatib et al. (2000) in which control of common sunflower by rimsulfuron at 47 g ha^{-1} was 48% at densities > 38 plants m^{-2}, but increased to 93% at 24 plants m^{-2}.

Herbicides and fungicides are often combined in the same mixtures to reduce costs associated with making applications of these pesticides separately (Jordan et al. 2003; Lancaster et al. 2005; Robinson et al. 2013). Combining herbicides and fungicides reduces damage to equipment and crops as well (Lancaster et al. 2003). Chlorothalonil and mancozeb are two fungicides commonly used in potato to control late blight (*Phytophthora infestans*) and early blight (*Alternaria solani*) in potato (Long and Siegel 1975; Robinson and Soltani 2006). Chlorothalonil and mancozeb are multi-site protectant-only fungicides, which allows particles to remain on the leaf surface and not penetrate through the leaf cuticle (Gullino et al. 2010). This forms a protective barrier which inhibits pathogen development and restricts fungi from entering plant tissue (Ulrich and Sierotzki 2008).

Researchers examining the effects of rimsulfuron plus metribuzin in combination with chlorothalonil or mancozeb in tomato have produced conflicting results. For instance, Stephenson et al. (1980) demonstrated that 250 g ha^{-1} of metribuzin plus 1,260 g ha^{-1} of chlorothalonil reduces tomato biomass by 27%, while mancozeb at 2,700 g ha-1 with metribuzin at 250 g ha^{-1} only reduces tomato biomass by 18% when weighed 30 days following treatment applications. However, Robinson and Soltani (2006) demonstrated that chlorothalonil at 1,600 g ha^{-1} with metribuzin at 150 g ha^{-1} and rimsulfuron at 15 g ha^{-1} causes 0 to 6% injury to tomato, which was no different than metribuzin and rimsulfuron alone.

Because metribuzin and rimsulfuron are the only postemergence options for broadleaf weed control in potato and chlorothanil and mancozeb are common protectant fungicides, there is little knwn about tank mixing these pesticides on the effect on weed control. Furthermore, though most russet-skinned cultivars are tolerant of postemergence treatments of metribuzin and rimsulfuron, there is still a need to determine if other additives, including these fungicides, increase injury to the cultivar 'Umatilla Russet'. Therefore, the objectives of this research were to determine the interaction of metribuzin plus rimsulfuron plus fungicide combinations (chlorothanil or mancozeb) on weed control and determine the effect of metribuzin plus rimsulfuron plus fungicide combinations on potato crop safety and graded yield.

Materials and Methods

Two field trials were established in 2015 on a commercial potato field near Park Rapids, MN (47.001749, -97.1228773) on a Verndale-Sandy loam with 64% sand, 30% silt, and 6% clay. The organic matter was 1.7% and soil pH 5.8. The experiment was a randomized complete block design with 12 treatments and four replicates in plots that measured 2.7 m by 9.1 m. Two non-treated controls (weedy and weed-free) were included in the 12 treatments (Table 14). Weeds were removed from the weed-free control at the time of the first herbicide application with hoes. Maize (*Zea mays* L.) was the previous crop. Umatilla seed pieces weighing an average of 60 g, were planted at 31 cm within-row spacing in rows spaced 91 cm apart. Irrigation and fertilization practices were conducted according to University of Minnesota recommended commercial potato production practices. Aerial applications of fungicide were applied by the grower in this field, but were not applied until after the treatments were made in this study.

Table 14. Treatment list for chapter 4 study located near Park Rapids, MN in 2015.

	Treatment[a]					
	Common name	Trade name	Rate	Herbicides	Rate	Fungicide manufacturer
			g ha^{-1}		g ha^{-1}	
1	Weedy control	-	-	-	-	
2	Weed-free control	-	-	-	-	
3	No fungicide	-	-	Metribuuzin + rimsulfuron	420 + 26	
4	No fungicide	-	-	Metribuuzin + rimsulfuron	210 + 13	
5	Chlorothalonil	Bravo Weather Stik	790	Metribuuzin + rimsulfuron	420 + 26	Syngenta Crop Protection, 11055 Wayzata Boulevard, Minnetonka, MN 55305; www.syngenta.com
6	Chlorothalonil	Bravo Weather Stik	1,580	Metribuuzin + rimsulfuron	210 + 13	
7	Chlorothalonil	Echo Zn	1,184	Metribuuzin + rimsulfuron	420 + 26	Sipcam Advan LLC, 2520 Meridian Pkwy # 525, Durham, NC 27713; www.sipcamadvan.com
8	Chlorothalonil	Echo Zn	2,369	Metribuuzin + rimsulfuron	210 + 13	
9	Mancozeb	Dithane	2,338	Metribuuzin + rimsulfuron	420 + 26	Dow AgroSciences LLC., 9330 Zionsville Road Indianapolis, IN 46268; www.dowagro.com
10	Mancozeb	Dithane	4,675	Metribuuzin + rimsulfuron	210 + 13	
11	Mancozeb	Penncozeb	1,064	Metribuuzin + rimsulfuron	420 + 26	UPI, 630 Freedom Business Center Suite 402,King of Prussia, PA 19406; http://www.cdms.net
12	Mancozeb	Penncozeb	2,129	Metribuuzin + rimsulfuron	210 + 13	

[a] Every treatment (except controls) included a nonionic surfactant applied at 0.25% v/v (NIS, R-11®, alkylphenolethoxylate, butyl alcohol, and dimethylpolysiloxane).

In both studies, treatments were made in the field when common lambsquarters reached the cotyledon to two-leaf stage, measuring on average 2.5 to 3 cm with a density of 9 plants m^{-2}. It was necessary to compare the effects of mancozeb and chlorothalonil formulations with metribuzin and rimsulfuron because these fungicides are commonly used in potato production. Wild sunflower plants measured 5.1 to 6.5 cm and had a density of 2 to 3 plants m^{-2}. Sunflower plants were at the two- to three- leaf stage at the time of application. Potato plants were 20 to 30 cm tall at the time of treatments. All treatments were applied using a CO_2 pressurized backpack sprayer at 172 kPa and calibrated to deliver 140 L ha^{-1} with a 2.74 m boom and XR11002 nozzles spaced 0.45 m apart (TeeJet Spraying Systems Company, Wheaton, IL 60189).

Visual estimates of weed control and crop injury from 0 (no injury) to 100% (complete plant death) were made at 14 and 28 days after treatment. Herbicide efficacy was also evaluated at 56 days after treatment. Visual estimates of weed control were based on reductions in population density and plant vigor and was taken 56 days after treatment to obtain an estimate of long term weed control (Brosnan 2012; Wilcut and Swann 1990). Weed control data was collected from the center two rows. Yield data was collected on one center row in plots. Following harvest with a single row digger, potatoes were graded for quality and quantity. Tuber graded yield were determined according to USDA standards with U.S. No.1 tubers at $\geq$ 113g with no defects (USDA 2011); U.S. No. 2 tubers were $\geq$ 113g with moderate defects and were included with U.S. No. 1 $\geq$ 113g for total marketable yield.

Data were subjected to analysis of variance (ANOVA) using the SAS GLM procedure (SAS Institute, Inc. Cary, NC 27513) with treatments considered fixed effects. A mean comparison was used using a Fisher's least significant difference (LSD) test (0.05). Due to homogeneity of variance all, parameters measured were pooled over both runs (Tables 15 and 16).

Table 15. Analysis of variance and homogeneity of variance for metribuzin and rimsulfuron applications with mancozeb and chlorothalonil near Park Rapids, MN in 2015.

SOV	df	<113g[b]	113-170g	170-287g	287-397g	>397g	Total	U.S. No. 1	U.S. No. 2	TMY	P > 170[c]	P > 283[d]
Location	1	0.04	0.4	24	122***	40*	528**	310*	18*	310*	106**	213**
Rep	3	23**	18**	78	66	16	623***	449	0.64	449***	101**	76
Rep(Location)[a]	3	11	17	16	12	0.6	60	19	1	19	33	47
Trt	11	8	10	32	28	17	214	143	9*	143*	67***	68
Location*Trt	11	7	19	44	15	16	211	183	6	183***	36	49
Error	57	344	679	1370	751	690	6373	4643	279	4643	1455	2743

[a] Type III mean square

[b] U.S. No. 1 tubers weigh ≥ 113 g without defects U.S. No. 2 tubers weigh ≥ 113 g with defects and malformations were included with U.S. No. 1 tuber yields.

[c] Percent of tubers greater than 170g.

[d] Percent of tubers greater than 283 g

*, **, *** Significant at 0.1,0.05, and 0.01 probability levels, respectively.

Table 16. Analysis of variance, mean squares and tests for homogeneity of variance for for weed control at 14, 28 and 56 days after treatment (DAT) for both locations near Park Rapids, MN in 2015.

SOV	df	Common sunflower			Common lambsquarters		
		14 DAT	28 DAT	56 DAT	14 DAT	28 DAT	56 DAT
Location[a]	1	267	1	1	551*	67	3
Rep	3	97	1	1	92	22	18
Rep(location)	3	125	1	1	301	65	127
Trt	11	5030***	6653***	6653***	4540***	6242***	4867***
Location*Trt	11	98	1	1	97	16	115
Error	66	7233	1	1	148	39	117

[a] Type III mean square

*, **, ***Significant at 0.1,0.05, and 0.01 probability levels, respectively

Results and Discussion

There were differences in visual injury at both 14 and 28 days after treatment (Table 17). Metribuzin and rimsulfuron alone caused significant injury compared to both the weedy and weed-free controls. Fungicides did not increase injury to potato compared to metribuzin and rimsulfuron alone. At 14 and 28 days after treatment, Echo Zn at 1,184 g ha^{-1} caused more injury than chlorothalonil plus spreader at 2,369 g ha^{-1}. Injury symptoms in this study included stunted growth, veinal chlorosis and necrotic lesion on the edges of leaves. Most injury was in the form of marginal leaf necrosis. Metribuzin plus rimsulfuron with chlorothalonil has caused necrosis in tomato cultivars. For example, metribuzin at 250 g ha^{-1} combined with chlorothalonil at 1,260 g ha^{-1} caused necrosis and stunted growth in 'Heinz 1706' tomato plants (Stephenson et al. 1980). Regardless, injury across both runs did not exceed 5% at 14 or 28 days after treatment. This is similar to a study by Hutchinson et al. (2004) in which metribuzin at 240 g ha^{-1} plus rimsulfuron at 26 g ha^{-1} caused only 1 to 7% injury to 'Russet Burbank' at 14 days after treatment even though a fungicide wasn't included in the tank mixture.

Table 17. Injury following herbicide plus fungicide applications 14 and 28 d after treatment (DAT) near Park Rapids, MN in

	Treatment[a]				Crop injury	
	Fungicide	Rate	Herbicide	Rate	14 DAT	28 DAT
		g ha^{-1}		g ha^{-1}	%	
1	None (weedy control)b	-	-	-	0	0
2	None (weed-free control)	-	-	-	0	0
3	No fungicide	-	Metribuzin + rimsulfuron	420 + 26	3	3
4	No fungicide	-	Metribuzin + rimsulfuron	210 + 13	4	3
5	Bravo Weather Stik	790	Metribuzin + rimsulfuron	420 + 26	4	3
6	Bravo Weather Stik	1,580	Metribuzin + rimsulfuron	210 + 13	2	2
7	Echo Zn	1,184	Metribuzin + rimsulfuron	420 + 26	5	5
8	Echo Zn	2,369	Metribuzin + rimsulfuron	210 + 13	1	1
9	Dithane	2,338	Metribuzin + rimsulfuron	420 + 26	3	3
10	Dithane	4,675	Metribuzin + rimsulfuron	210 + 13	2	2
11	Penncozeb 75 DF	1,064	Metribuzin + rimsulfuron	420 + 26	3	3
12	Penncozeb 75 DF	2,129	Metribuzin + rimsulfuron	210 + 13	3	2
	LSD (0.05)				2.7	2.7

[a] Every treatment (except non-treated controls) included a nonionic surfactant applied at 0.25% v/v (NIS, R-11®, alkylphenolethoxylate, butyl alcohol, and dimethylepolysiloxane).

[b] Both weedy and weed-free controls were included in the analysis.

There were no differences in estimated visual control of common lambsquarters or common sunflower at 14, 28 or 56 days after treatment (Table 18). This study demonstrates that fungicides neither inhibited nor improved common lambsquarters control when metribuzin and rimsulfuron.

Table 18. Weed control following herbicide plus fungicide applications 14, 28 and 56 days after treatment (DAT) near Park Rapids, MN in 2015.

	Treatment[a]				Common sunflower			Common lambsquarters		
	Fungicide	Rate	Herbicide	Rate	14 DAT	28 DAT	56 DAT	14 DAT	28 DAT	56 DAT
		g ha^{-1}		g ha^{-1}			%			
	Weedy control[b]	-	-	-	0	0	0	0	0	0
1	Weedy-control	-	-	-	100	100	100	100	100	100
2	No fungicide	-	Metribuzin + rimsulfuron	420 + 26	100	100	100	98	98	98
3	No fungicide	-	Metribuzin + rimsulfuron	210 + 13	99	100	100	93	98	97
4	Bravo Weather Stik	790	Metribuzin + rimsulfuron	420 + 26	99	99	98	96	96	99
5	Bravo Weather Stik	1,580	Metribuzin + rimsulfuron	210 + 13	99	100	100	93	95	100
6	Echo Zn	1,184	Metribuzin + rimsulfuron	420 + 26	99	100	100	91	91	98
7	Echo Zn	2,369	Metribuzin + rimsulfuron	210 + 13	100	100	100	94	99	97
8	Dithane	2,338	Metribuzin + rimsulfuron	420 + 26	100	100	100	94	91	97
9	Dithane	4,675	Metribuzin + rimsulfuron	210 + 13	98	100	100	96	100	97
10	Penncozeb 75 DF	1,064	Metribuzin + rimsulfuron	420 + 26	100	100	100	92	94	94
11	Penncozeb 75 DF	2,129	Metribuzin + rimsulfuron	210 + 13	100	100	100	94	96	97
12	LSD (0.05)				NS	NS	NS	NS	NS	NS

[a] Every treatment (except non-treated controls) included a nonionic surfactant applied at 0.25% v/v (NIS, R-11®, alkylphenolethoxylate, butyl alcohol, and dimethylepolysiloxane).

[b] Both weedy and weed-free controls were included in the analysis.

There were no differences in common sunflower control at any of the dates the weeds were measured (Table 12). Fungicides had no effect on season long control of common sunflower. Overall, control of common sunflower for all treatments was ≥ 98%. Control of common sunflower was high because the density of plants was only 2 to 3 m^{-2}. According to Al-Khatib et al. (2000) yield of common sunflower decreased when there were ≥ 30 plants m^{-2} as a result of better coverage through less competition.

There were no differences among treatments in any yield parameter measured (Table 19). Yields were similar for all treatments because crop injury levels were uniformly low at 14 and 28 days after treatment and weed control was high for all treatment combinations. Yield in nontreated plots was not statistically different than yield in treated plots. This supports findings by Robinson et al. (2006) which indicate that combining 150 g ha^{-1} metribuzin and 15 g ha^{-1} rimsulfuron with 1,260 g ha^{-1} chlorothalonil controls 89% of common lambsquarters and causes ≤ 6% visual injury, yet does not reduce yield when compared to control plots.

Table 19. Effect of herbicide and fungicide tank mixtures on Umatilla Russet yield in field trials located near Park Rapids, MN in 2015 averaged across two runs.

Treatment				Yield							
Fungicidea	Rate	Herbicides	Rate	<113g[b]	113-170g	170-283g	283-397g	U.S. No.1	U.S. No. 2	TMY	P170
	g ha^{-1}		g ha^{-1}	Mg ha^{-1}							
Weedy control c	-	-	-	9	15	29	16	65	4	65	69
Weed-free control	-	-	-	9	16	30	16	66	6	66	69
No fungicide	-	Metribuzin + rimsulfuron	420 + 26d	7	12	20	10	45	3	45	64
No fungicide	-	Metribuzin + rimsulfuron	210 + 13	10	16	25	12	56	4	56	63
Bravo Weather Stik	790	Metribuzin + rimsulfuron	420 + 26	10	16	25	12	57	7	57	63
Bravo Weather Stik	1,580	Metribuzin + rimsulfuron	210 + 13	11	16	27	10	57	3	57	62
Echo Zn	1,184	Metribuzin + rimsulfuron	420 + 26	10	16	26	13	58	3	58	65
Echo Zn	2,369	Metribuzin + rimsulfuron	210 + 13	11	17	24	10	54	3	54	60
Dithane	2,338	Metribuzin + rimsulfuron	420 + 26	10	15	26	12	58	3	58	65
Dithane	4,675	Metribuzin + rimsulfuron	210 + 13	11	16	28	14	62	6	62	64
Penncozeb 75 DF	1,064	Metribuzin + rimsulfuron	420 + 26	9	13	24	12	54	4	54	66
Penncozeb 75 DF	2,129	Metribuzin + rimsulfuron	210 + 13	10	14	24	12	53	3	53	63
LSD (0.05)				NS	NS	NS	NS	NS	NS	NS	NS

[a] Every treatment (except controls) included a nonionic surfactant applied at 0.25 % v/v (NIS, R-11®, alkylphenolethoxylate, butyl alcohol, and dimethylpolysiloxane).

[b] U.S. No. 1 tubers weigh ≥ 113 grams without defects. U.S. No. 2 tubers weigh ≥ 113 g with defects and malformations were included with U.S. No. 1 yields.

[d] Both weed and weed-free controls were included in the analysis.

[e] Lower rates of herbicide and fungicide were applied twice, two weeks apart, while full rates were applied once.

This study demonstrates that incorporating chlorothalonil and mancozeb with metribuzin and rimsulfuron is a pest control option that does not reduce crop yield or negatively affect weed control, though the effect on fungi populations still needs to be determined. Future research should focus on determining the effects of these herbicide plus fungicide combinations on different cultivars and against other weed species besides common lambsquarters and common sunflower. Future research should also address the use of fungicides with metribuzin and rimsulfuron for late postemergence weed control since fungicides are likely to be applied later in the season.

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CHAPTER 5. CONCLUSION

These studies illustrate the differing effects of additives with metribuzin and rimsulfuron. Adjuvants are not needed with metribuzin and rimsulfuron to reduce dry weight of hairy nightshade, though metribuzin (340 g ha^{-1}) plus rimsulfuron (26 g ha^{-1}) should not be applied to plants past the four leaf stage or in combination with Climb. On the other hand, Climb with metribuzin and rimsulfuron at 520 g ha^{-1} and 26 g ha^{-1} respectively, may improve control of common lambsquarters. With the exception of Class Act NG, adjuvants with metribuzin at 520 g ha^{-1} and rimsulfuron at 26 g ha^{-1} had no effect on control of wild proso millet. Still, further testing is needed to determine the impact of ammonium sulfate, the hard water-reducing agent in Class Act NG, on wild proso millet when combined with rimsulfuron and metribuzin. Chlorothalonil and mancozeb do not inhibit or increase control of common sunflower or common lambsquarters within 28 days of application.

Adjuvants do not impact marketable yield of potato, though future research should be conducted in potato fields to determine the effect of metribuzin and rimsulfuron when weed pressure is high. Combining chlorothalonil and mancozeb with metribuzin and rimsulfuron also has no effect on total marketable yield of potato, though this was likely the result of low weed pressure as well.

APPENDIX

Table A1. Analysis of variance and mean squares for hairy nightshade parameters for first run near Prosper, ND in 2015.

SOV	df	Visual efficacy	Height	Dry weight	Berry number
Rep	3	1461***	28***	240***	409***
Treatment[a]	19	705**	54***	22	190***
Rep x Treatment	57	625	6	16	72***
Error	120	369	5	15	4928

[a]Type III mean square

*, **, *** Significant at 0.1, 0.05, and 0.01 probability levels, respectively.

Table A2. F values and coefficients of variation for both runs near Prosper, ND in 2015.

	F Value		Coefficient of variation	
Parameter	Run 1	Run 2	Run 1	Run 2
Visual control	1.15	0.85	149.65	135.92
Height	3.35	4.34	24.94	32.25
Dry weight	1.32	0.62	79.27	85.11
Berry number	1.43	2.27	229.96	202.05

Table A3. Analysis of variance and tests for homogeneity of variance for metribuzin (520 g ha^{-1}) plus rimsulfuron (26 g ha^{-1}) with different adjuvants on Russet Burbank marketable yield near Ottertail, MN in 2014.

SOV	df	<113g[b]	113-170g	170-287g	287-397g	>397g	Total	U.S. No. 1	U.S No. 2	TMY	P > 170[c]	P > 283[d]
Rep	3	4	12	16	6	10	42	41	0.6	31	44	68
Trt[a]	10	3	7	30	7	7	101	75	2	82	45	21
Error	43	5	10	18	13	6	96	74	3	78	41	36
CV[e]		21	19	17	34	54	14	15	65	15	11	29

[a] Type III mean square

[b] U.S. No. 1 tubers weigh ≥ 113 g without defects U.S. No. 2 tubers weigh ≥ 113 g with defects and malformations were included with U.S. No. 1 tuber yields.

[c] Percent of tubers greater than 170g.

[d] Percent of tubers greater than 283 g

[e] Coefficient of variation

*, **, ***Significant at 0.1,0.05, and 0.01 probability levels, respectively.

Table A4. Analysis of variance and tests for homogeneity of variance for metribuzin (520 g ha^{-1}) plus rimsulfuron (26 g ha^{-1}) with different adjuvants on Umatilla Russet marketable yield near Park Rapids, MN in 2015.

SOV	df	<113g[b]	113-170g	170-287g	287-397g	>397g	Total	U.S. No. 1	U.S No. 2	TMY	P > 170[c]	P > 283[d]
Rep	3	0.7	8	12	24	6	107	57	1	49	18	10
Trt[a]	10	8	5	17	31	2	90	44	4	39	103	43
Error	43	5	5	21	38	4	72	36	3	44	121	45
CV[e]		25	16	26	24	83	12	18	52	18	17	17

[a] Type III mean square

[b] U.S. No. 1 tubers weigh ≥ 113 g without defects U.S. No. 2 tubers weigh ≥ 113 g with defects and malformations were included with U.S. No. 1 tuber yields.

[c] Percent of tubers greater than 170g.

[d] Percent of tubers greater than 283 g

[e] Coefficient of variation

*, **, ***Significant at 0.1,0.05, and 0.01 probability levels, respectively.

Table A5. F values and coefficients of variation for studies conducted near Ottertail, MN in 2014 and Park Rapids, MN in 2015.

	F Value		Coefficient of variation	
Parameter	Ottertail	Park Rapids	Ottertail	Park Rapids
< 113g	1.39	0.57	24.7	20.5
113-170g	1.72	0.65	15.9	18.5
170-283g	0.82	1.56	26.2	16.8
283-397g	0.83	0.79	23.6	32.4
>397g	0.46	1.1	83.3	51.4
Total	1.24	1.1	12.4	13.4
U.S. No. 1	1.19	0.97	17.9	14.6
U.S. No. 2	1.55	0.65	51.8	63.1
Total marketable yield	0.91	1.03	18.1	14.4
Percent greater than 170g	1.09	0.85	11.3	17.1
Percent greater than 283g	0.58	0.96	28.6	16.9

Table A6. Analysis of variance and means squares for wild proso millet control and crop injury in 2014 near Ottertail, MN and for common lambsquarters control and crop injury near Park Rapids, MN in 2015.

		2014		2015	
SOV	df	Wild proso millet control	Crop injury	Common lambsquarters control	Crop injury
Rep	3	98	8	91	11
Treatment[a]	10	56655***	146***	6500***	45***
error	30	31	34	124	20
CV[b]		7	64	53	17

[a] Type III mean square

[b] Coefficient of variation

*, **, ***Significant at 0.1,0.05, and 0.01 probability levels, respectively.

Table A7. Analysis of variance and means squares following metribuzin and rimsulfuron applications with mancozeb and chlorothalonil near Park Rapids, MN in 2015.

SOV	df	<113g[b]	113-170g	170-287g	287-397g	>397g	Total	U.S. No. 1	U.S. No. 2	TMY	P > 170[c]	P > 283[d]
Rep	3	44***	47**	134**	4**	25	1198***	798***	0.4	798***	72*	67
Trt[a]	11	7	15	54	2	18	357	248	10*	248	59*	47
Error	33	7	16	42	10	13	544	164	5	164	33	59
CV[e]		27	27	25	0.0002	23	21	23	61	23	9	28

[a] Type III mean square

[b] U.S. No. 1 tubers weigh ≥ 113 g without defects U.S. No. 2 tubers weigh ≥ 113 g with defects and malformations were included with U.S. No. 1 tuber yields.

[c] Percent of tubers greater than 170g.

[d] Percent of tubers greater than 283 g

[e] Coefficient of variation

*, **, *** Significant at 0.1,0.05, and 0.01 probability levels, respectively.

Table A8. Analysis of variance and mean squares for weed control at 14, 28 and 56 days after treatment (DAT) and crop injury at 14 and 28 DAT averaged across two locations near Park Rapids, MN in 2015.

SOV	df	Common lambsquarters control			Common sunflower control			Crop injury	
		14 DAT	28 DAT	56 DAT	14 DAT	28 DAT	56 DAT	14 DAT	28 DAT
Rep	3	29	22	112	97	18	18	17	8
Trt[a]	11	10739	11181	10683	10546	11550	11550	18**	16**
Error	78	46	38	105	111	13	13	9	7
CV		9	8	4	13	12	12	128	110

[a] Type III mean square

[b] Coefficient of variation

*, **, ***Significant at 0.1,0.05, and 0.01 probability levels, respectively

Table A9. F values and coefficients of variation for studies conducted near Park Rapids, MN in 2015.

	F Value		Coefficient of variation	
	Run 1	Run 2	Run 1	Run 2
< 113g	0.6	0.7	28.3	28.8
113-170g	0.7	0.6	29.6	26.2
170-283g	0.4	1.4	26.2	25.4
283-397g	1.1	1.5	31.1	34.6
>397g	2.1	0.6	41.8	54.9
Total	0.7	1.3	22.6	20.6
U.S. No. 1	0.7	1.5	23.7	21.1
U.S. No. 2	2.2	0.5	57.4	59.1
Total marketable yield	0.7	1.5	13.9	21.1
Percent greater than 170g	2.8	1.1	6.5	9.7
Percent greater than 283g	1.2	0.4	22.4	32.5