Supplement: Information on characteristics of some bareground chemistries

Information on the characteristics and behavior of some bareground herbicides should be useful to rights of way vegetation managers. The following tables (Tables 1a-g) present information on characteristics of some older and newer products. Only one product name is listed but the active ingredient may be included in multiple products and mixtures. The Mechanism of Action (MOA) Group(s) should be included on newer labels and is important information to manage and reduce the risk of selecting for resistant weed populations.

Summary of Herbicide Mechanism of Action (MOA) according to the Weed Science Society of America (WSSA) (Shaner, 2014)

MOA Group 2 Acetolactate Synthase (ALS) Inhibitors
These herbicides inhibit acetolactate synthase (ALS), a key enzyme in the biosynthesis of branched-chain amino acids isoleucine, leucine, and valine. Plant death results from events occurring in response to ALS inhibition and low branched-chain amino acid production, but the actual sequence of phytotoxic processes is unclear.

MOA Group 3 Inhibitors of microtubule assembly
These herbicides bind to tubulin, the major microtubule protein. The herbicide-tubulin complex inhibits polymerization of microtubules at the assembly end of the protein-based microtubule but has no effect on depolymerization of the tubule on the other end, leading to a loss of microtubule structure and function. As a result, the spindle apparatus is absent, thus preventing the alignment and separation of chromosomes during mitosis. In addition, the cell plate can be formed. Microtubules also function in cell wall formation. Herbicide-induced microtubule loss may cause the observed swelling of root tips as cells in this region neither divide nor elongate.

MOA Group 4 Synthetic Auxins
These herbicides act similar to that of endogenous auxin (IAA), although the true mechanism is not well understood. The specific cellular or molecular binding site relevant to the action of IAA and the auxin-mimicking herbicides has not been identified. Nevertheless, the primary action of these compounds appears to affect cell wall plasticity and nucleic acid metabolism. These compounds are thought to acidify the cell wall by stimulating the activity of a membrane-bound ATPase proton pump. The reduction in apoplastic pH induces cell elongation by increasing the activity of enzymes responsible for cell wall loosening. Low concentrations of auxin-mimicking herbicides also stimulate RNA polymerase, resulting in subsequent increases in RNA, DNA, and protein synthesis. Abnormal increases in these processes presumably lead to uncontrolled cell division and growth, which results in vascular tissue destruction. In contrast, high concentrations of these herbicides inhibit cell division and growth, usually in meristematic regions that accumulate photosynthate assimilates and herbicides from the phloem. Auxin-mimicking herbicides stimulate ethylene evolution which may in some cases produce the characteristic epinastic symptoms associated with exposure to these herbicides.

MOA Group 5 Inhibitors of photosynthesis at photosystem II site A
MOA Group 6 Inhibitors of photosynthesis at photosystem II site B
MOA Group 7 Inhibitors of photosynthesis at photosystem II site A; different binding behavior from group 5
All the herbicides that fall under these three classifications kill plants by inhibiting photosystem II. However, there often is not cross resistance from one class to another, hence the three classifications. These herbicides inhibit photosynthesis by binding to the Q_B-binding niche on the D1 protein of the photosystem II complex in chloroplast thylakoid membranes. Herbicide binding at this protein location blocks electron transport from Q_A to Q_B and stops CO_2 fixation and production of ATP and $NADPH_2$, which are needed for plant growth. However, plant death occurs by other processes in most cases. Inability to reoxidize Q_A promotes the formation of triplet state chlorophyll, which interacts with ground state oxygen to form singlet oxygen. Both triple chlorophyll and singlet oxygen can extract hydrogen from unsaturated lipids, producing a lipid radical and initiating a chain reaction of lipid peroxidation. Lipids and proteins are attacked and oxidized, resulting in loss of chlorophyll and carotenoids and in leaky membranes which allow cells and cell organelles to dry and disintegrate rapidly.

MOA Group 14 Inhibitors of protoporphyrinogen oxidase (Protox, PPO)
These herbicides appear to inhibit protoporphyrinogen oxidase (PPG oxidase or Protox), an enzyme of chlorophyll and heme synthesis catalyzing the oxidation of protoporphyrinogen IX (PPGIX) to protoporphyrin IX (PPIX). Protox inhibition leads to accumulation of PPIX, the first light-absorbing chlorophyll precursor. PPGIX accumulation apparently is transitory, as it overflows its normal environment in the thylakoid membrane and oxidizes to PPIX. PPIX formed outside its native environment probably is separated from Mg chetalase and other pathway enzymes that normally prevent accumulation of PPIX. Light absorption by PPIX apparently produces triplet state PPIX which interacts with ground state oxygen to form singlet oxygen. Both triplet PPIX and singlet oxygen can abstract hydrogen from unsaturated lipids, producing a lipid radical and initiating a chain reaction of lipid peroxidation. Lipids and proteins are attacked and oxidized, resulting in loss of chlorophyll and carotenoids and in leaking membranes which allows cells and cell organelles to dry and disintegrate rapidly.

MOA Group 29 Inhibitors of Cellulose biosynthesis
These herbicides inhibit cell wall biosynthesis (cellulose) in susceptible weeds.

The parameters extracted from the Herbicide Handbook (Shaner, 2014) for the tables include:

Water solubility: This is usually presented at 20 to 25 C and at known pH's as solubility can be quite different at different pH's (see Table 1f and penoxsulam). In general, as solubility increases, the compound's binding to soil particles and organic matter decreases which increases the likelihood of it moving deeper into the soil profile (leaching) or away from the site of application.

pKa: Some compounds have ionizable groups where they are neutral when protonated (with a hydrogen molecule) or with a negative charge when without a hydrogen. The proportion of molecules that are protonated or not depends on the pH of the environment. If the pH is at the

pKa then 50% of the groups are protonated and 50% are not. At a pH more basic than the pKa more than 50% of the groups are not protonated (negative charge). They are then less likely to bind to negatively charged clay and OM particles which would affect retention and movement in the soil.

Kow: This is the octanol-water coefficient, which represents a measure of the tendency of a compound to move from the aqueous phase into lipids (cell membranes). Octanol is non-polar and hydrophobic while water is polar and hydrophilic. Substances with high logKow values tend to adsorb more readily to organic matter in soils or sediments because of their low affinity for water.

Sorption: Koc measures the mobility of a substance in soil. A very high value means it is strongly adsorbed onto soil and organic matter and does not move throughout the soil. A very low value means it is highly mobile in soil.

Degradation: Some herbicides may degrade with light (photo degrade) and many are broken down by soil microbes.

Persistence: The longevity of a herbicide molecule is normally expressed in terms of half-life (t1/2) which is when half of the original amount remains. This is also a measure of the length of residual control.

Mobility: Summary of laboratory and field studies on mobility in the soil and the environment.

Literature Cited

Shaner, D.L. (2014) Herbicide Handbook. 10th Edition, Weed Science Society of America, Lawrence, 513 p.

Table 1a: Summary of Properties of Some Bareground Chemistries

Product	Active Ingredient	MOA Group	Water Solubility	pKa	K_{ow}	Behavior in Soil
Hyvar	bromacil	5	815 mg/L (25 C)	9.1 (weak base)	NA	**Sorption:** Low to moderate adsorption to soil. Average K_{oc} is 32 mL/g
						Degradation: Microbial degradation apparently contributes to bromacil degradation.
						Persistence: Average field half-life is 60 days. When used at higher rates, phytotoxic residues persist for more than 1 yr.
						Mobility: Moderately mobile
Karmex	diuron	7	42 mg/L (25 C)	None (non-ionizable)	589	**Sorption:** Adsorbs to OM and clay. Average K_{oc} is 480 mL/g
						Degradation: Not strongly photodegraded but losses can be significant if diuron remains on the soil surface for several days or weeks. Microbial degradation if the primary means of diuron dissipation from soil.
						Persistence: Average field half life is 90 days. Phytotoxic residues dissipate within a season when applied at lower selective rates. At higher selective rates, residues may persist for more than 1 year.
						Mobility: Moderadely leachable; leaching not a problem except on soils low in OM and clay.

Table 1b: Summary of Properties of Some Bareground Chemistries

Product	Active Ingredient	MOA Group	Water Solubility	pKa	K_{ow}	Behavior in Soil
Oust XP	sulfometuron	2	10 mg/L pH 5 (25 C) 300 mg/L pH 7 (25 C)	5.2 (weak acid)	NA	**Sorption:** Average K_{oc} is 78 mL/g at pH 7
						Degradation: Microbial breakdown occurs slowly. Non-microbial hydrolysis is moderately rapid at pH 6 but extremely slow at pH 8. Thus, degradation occurs most rapidly at lower soil pH values where rates are dominated by hydrolysis, whereas degradation rates are slowest at high pH and are dominated by microbial action.
						Persistence: Typical field half-life is 20-28 days at pH 6-7. Persistence is increased by cool temperatures, low soil moisture, and higher pH.
						Mobility: Generally greater at higher soil pH and lower OM content.
Polaris A/C Complete	imazapyr	2	11,272 mg/L pH 7 (25 C)	1.9, 3.6, 11.0 (weak acid)	1.3	**Sorption:** Generally weakly bound to soil, but adsorption increases as OM and clay increase.
						Degradation: micobial degradation is principal means of dissipation in soil.
						Persistence: Field half-life ranges from 25-142 days. Weed control efficacy persists from 3 mo to 2 yr, depending on application rate.
						Mobility: generally remains within top 50 cm of soil in field dissipation studies. In forest dissipation studies, it did not run off into streams and no evidence of lateral movement was observed.

Table 1c: Summary of Properties of Some Bareground Chemistries

Product	Active Ingredient	MOA Group	Water Solubility	pKa	K_{ow}	Behavior in Soil
Plateau	imazapic	2	2200 mg/L (25 C)	2.0, 3.9, 11.1 (weak acid)	0.16 (pH 5) 0.01 (pH 7) 0.002 (pH 9)	**Sorption:** Weakly adsorbed in high pH soil, but adsorption increases with lower pH and increasing OM and clay content. **Degradation:** primarily degraded by microbes. Does not degrade appreciably under anaerobic conditions. **Persistence**: Average half-life is 120 days. **Mobility:** Field studies indicate that it remains in the top 30-45 cm of soil. Field studies do not indicate any potential for imazapic to move with surface water.
Pendulum Aquacap	pendimethalin	3	0.275 mg/L (25 C)	None (non-ionizable)	152,000	**Sorption:** Strongly absorbed by clay and OM. **Degradation:** Rapid degradation under anaerobic conditions. Aerobic biological degradation is slow. **Persistence**: Typical half-life in the field is 44 days, but varies with soil temperature and moisture. **Mobility:** Immobile, being strongly bound to OM and clay.

Table 1d: Summary of Properties of Some Bareground Chemistries

Product	Active Ingredient	MOA Group	Water Solubility	pKa	K_{ow}	Behavior in Soil
Proclipse	prodiamine	3	0.013 mg/L (25 C)	None (non-ionizable)	12,672 ± 2,270 (25 C)	**Sorption:** Strongly absorbed to soil. Average K_{oc} is 13,000 mL/g
						Degradation: Photodegradation is a potential concern. Half-life was 57 days for aerobic metabolism and 30 days for anaerobic metabolism.
						Persistence: Half-life averages approx. 120 days when incorporated at recommended rates. Half-life was 69 days for a sandy loam in Georgia on a turf site.
						Mobility: Not readily leached
Milestone	aminopyralid	4	212 g/L pH 5	2.56	log K_{ow} = -1.75 pH 5	**Sorption:** weakly adsorbed to soil.
			205 g/L pH 7		log K_{ow} = -2.87 pH 7	**Degradation:** Primarily aerobic microbial degradation
			203 g/L pH 9		log K_{ow} = -2.96 pH 9	**Persistence**: under field conditions had half-lives from 6-74 days with a median half-life of 32 days
						Mobility: Field experiments show very limited mobility in soil profile.

Table 1e: Summary of Properties of Some Bareground Chemistries

Product	Active Ingredient	MOA Group	Water Solubility	pKa	K_{ow}	Behavior in Soil
Method	aminocyclopyrachlor	4	4.2 g/L (25 C)	4.65	log K_{ow} = -1.12 pH 4 log K_{ow} = -2.48 pH 7	**Sorption:** K_{oc} ranged from 2.0 on sandly loam to 26 on clay loam (high potential for leaching) **Persistence**: slowly degrades by aerobic microbial metabolism with half-lives ranging from 114-433 days in different soils. **Mobility:** expected to be highly mobile in the environment
Payload	flumioxazin	14	1.79 mg/L (25 C)	none (non-ionizable)	log K_{ow} = 2.55 (20 C)	**Sorption:** NA **Degradation:** Primarily microbial, half-life in aerobic soil is 11.9 to 17.5 days **Persistence**: Not persistent in soil **Mobility:** Potential to leach in field agricultural soil is low

Table 1f: Summary of Properties of Some Bareground Chemistries

Product	Active Ingredient	MOA Group	Water Solubility	pKa	K_{ow}	Behavior in Soil
Cleantraxx	penoxsulam	2	5.7 mg/L (pH 5, 19 C) 410 mg/L (pH 7, 19 C) 1460 mg/L (pH 9, 19 C)	NA	log K_{ow} = -0.354	**Sorption:** weakly adsorbed to soil.
						Degradation: Primarily microbial
						Persistence: rapidly degraded with half-lives of 5 to 16 days under flooded field conditions (is used in rice)
						Mobility: Potential for mobility in soil is high based on K_{oc} values between 50 and 150 mL/g
	oxyfluorfen	14	0.1 mg/L (20 C)	none (non-ionizable)	log K_{ow} = 4.47 (25 C)	**Sorption:** Strongly absorbed to soil
						Degradation: Photodegredation: half-life on dry soil generally is 20-30 days. Microbial degradation rates are slow.
						Persistence: Moderate residual with an average field half-life of 30 days
						Mobility: Immobile in most soils, but slightly mobile on extremely sandy soils

Table 1g: Summary of Properties of Some Bareground Chemistries

Product	Active Ingredient	MOA Group	Water Solubility	pKa	K_{ow}	Behavior in Soil
Detail	saflufenacil	14	0.003 g/100 mL (pH 5) 0.21 g/100 mL (pH 7)	4.41	log K_{ow} = 2.57	**Sorption:** K_{oc} = 9 to 56 (6 soils)
						Degradation: found to degrade rapidly in the environment
						Persistence: terrestrial dissipation DT_{50} = 1-36 days (7 sites)
						Mobility: Mobile to very mobile, hydrophilic
Esplanade	indaziflam	29	2040 mg/L pH 7 (25 C) 18,300 mg/L pH 9 (25 C)	weak acid	2.0 (pH 2) 2.8 (pH 4, pH7, pH 9)	**Sorption:** K_{oc} >1000 (strongly adsorbed onto soil and organic matter and does not move throughout the soil)
						Degradation: dissipates in environment primarily through biotic degradation and leaching.
						Persistence: long residual with an average half-life >150 days
						Mobility: NA