Herbicide Formulations and Calculations: Active Ingredient or Acid Equivalent?

Most people who routinely use pesticides are familiar with the term active ingredient. The active ingredient is the component of a pesticide formulation responsible for its toxicity (phytotoxicity for herbicides) or ability to control the target pest. The active ingredient is always identified on the pesticide label, either by common name (atrazine, bentazon, for example) or chemical name (2,4-dichlorphenoxy acetic acid, diglycolamine salt of 3,6-dichlor-o-anisic acid, for example). The active ingredient statement may also include information about how the product is formulated and the amount of active ingredient contained in a gallon or pound of formulated product. For example, the Basagran label indicates the active ingredient (bentazon) is formulated as the sodium salt, and one gallon of Basagran contains four pounds of active ingredient.

Usually, when a herbicide trade name is followed by a number and letter designation (4L, 75DF, 7EC, etc), the number indicates how many pounds of active ingredient are in a gallon (for liquid formulations) or pound (for dry formulations) of the formulated product. The formulation designations for Basagran 4L, AAtrex 90DF, and Prowl 3.3EC indicate Basagran 4L contains 4 pounds of active ingredient (bentazon) per gallon of formulated product, AAtrex 90DF contains 0.90 pounds of active ingredient (atrazine) per pound of formulated product, and Prowl 3.3EC contains 3.3 pounds of active ingredient (pendimethalin) per gallon of formulated product, respectively.

Active Ingredient (AI)

Some herbicides (atrazine for example) have specific maximum per year application rates that cannot be exceeded. These maximum per year application rates are generally presented in terms of the total amount of active ingredient that can be applied per year. How would one calculate the pounds of active ingredient applied at a given product use rate? There are several calculations that can be used to determine the amount of active ingredient applied at a given product use rate. One of the easiest calculations is:

$$\text{pounds active ingredient applied per acre} = \frac{\text{gallons or lbs of product applied}}{\text{acre}} \, x \, \frac{\text{lbs active ingredient}}{\text{gallon or lbs of product}}$$

Using this equation, we can calculate the amount of active ingredient (bentazon) which is applied when we apply 2 pints (0.25 gallon) per acre of Basagran 4L:

$$\text{pounds of bentazon (active ingredient) applied per acre} =$$

$$\frac{0.25 \text{ gallon of product applied}}{\text{acre}} \, x \, \frac{4 \text{ lbs active ingredient}}{\text{gallon of product}} = 1 \text{ pound active ingredient per acre}$$

Acid Equivalent (AE)

Sometimes, however, the numbers preceding the formulation designation (L, EC, DF, etc.) do not indicate pounds active ingredient per gallon or pound, but rather the acid equivalent per gallon or pound. The term acid equivalent is one that many people are less familiar with. Acid equivalent may be defined as that portion of a formulation (as in the case of 2,4-D ester for example) that theoretically could be converted back to the corresponding or parent acid. Another definition of acid equivalent is the theoretical yield of parent acid from a pesticide active ingredient which has been formulated as a derivative (esters, salts, amines are examples of derivatives). For instance, the acid equivalent of the isooctyl ester of 2,4-D is 66% of the ester formulation, but 88% of the ethyl acetate ester formulation.

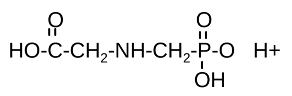
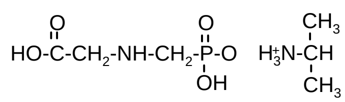
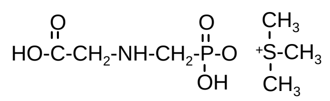
Why would a herbicide (one that has the acid as the parent molecule) be formulated as a derivative (ester, salt, amine, etc.) of the parent acid?

Herbicidal activity refers to the ability of a particular herbicide to effectively bind to a target site within the plant and exert some type of lethal effect (i.e., you apply the herbicide to the plant and the plant eventually dies). A herbicide molecule may sometimes be altered to impart some property other than herbicidal activity. Such alterations are possible with herbicide molecules that are acids (for example, molecules that have a carboxyl group as part of their structure). The acidic carboxyl hydrogen is replaced by the desired ions to form a salt or reacted with an alcohol to form an ester. Why would this be done? One example might be that due to the chemical characteristics of a particular herbicide molecule, the parent acid may not be readily absorbed into a plant because it's not able to effectively penetrate the waxy cuticle covering the leaf. Somehow altering the parent acid may increase the ability of the herbicide to penetrate through the leaf much more effectively. For some postemergence herbicides, formulating the parent acid as an ester or salt is frequently done to facilitate absorption through the leaf. Other formulations or derivatives of the parent acid may increase the water solubility of the herbicide. 2,4-D (2,4-dichlorphenoxy acetic acid) is commonly formulated as an ester or amine. The ester formulation increases the lipid solubility of the herbicide, which allows it to more easily penetrate the waxy cuticle of the plant leaf. The amine formulation greatly increases the water solubility of the herbicide, which may be desirable if the product needs to be moved into the soil solution for root uptake (brush control, for example).

If a herbicide is formulated as a derivative of the parent acid, it is important to remember the parent acid is the herbicidally active portion of the formulation. The parent acid is what binds to the herbicide target site within the plant and causes plant death. The salt or ester portion of the formulated product may allow for greater absorption into the plant, but plays no role in binding to the herbicide target site. For example, when an ester herbicide penetrates the cuticle, enzymes convert the ester back to the parent acid, so following absorption the ester part of the formulation plays no role in herbicidal activity. Modification of the parent acid (formulation as a salt, ester, or amine) may increase the amount of active ingredient in a formulation since the amount of active ingredient listed on a product label includes both the weight of the parent acid as well as the weight of the salt or ester. Modification does not always, however, increase the amount of acid (herbicidally active portion) in the formulation. The acid equivalent represents the original acid portion of the molecule and is used for "apples to apples" comparisons of different formulations containing the same acid. Another example will hopefully alleviate some of your increasing confusion.

Example: Glyphosate

The parent acid glyphosate can be formulated as various salts. Let's assume we have two salt formulations of glyphosate: the first has one ammonia molecule and three carbon atoms forming the salt, the second has one sulfate and three carbon atoms forming the salt. The parent acid is the same in these two formulations; the only difference is the type of salt. These can be visualized in the following diagrams.

		
Glyphosate parent acid	Isopropylamine salt of glyphosate	Trimesium salt of glyphosate

The structure on the left is the parent acid of glyphosate. The second diagram is the parent acid formulated with the isopropylamine salt, and the third diagram is the parent acid formulated with the trimesium salt. These salts have a variety of important functions such as improving the handling and stability of the product. However, the salts have no effect on herbicidal activity, only the ***parent acid (the one depicted in the left diagram) acts at the target site within the plant***. The added atoms of the salts add weight to the formulation and may increase the amount of active ingredient of a formulation, but they **do not** increase the amount of parent acid in the formulation. If these two formulations were commercially available, and someone wanted to know equivalent rates, the calculation to use would be based on the acid equivalent of the formulations, not the active ingredient of the formulations.

Now, let's assume that both glyphosate salt formulations (isopropylamine and trimesium) are commercially available, and each contains five pounds of ***active ingredient*** per gallon. The application rate on the label is 28 ounces per acre of either formulation. Since the application rates and the pounds of ***active ingredient*** per gallon are identical for each formulation, the amount of ***active ingredient*** applied would be the same for each formulation. If you doubt this, plug in the appropriate numbers for each formulation in the formula given previously for calculating the amount of ***active ingredient*** applied. Even though the amount of ***active ingredient*** applied is the same for each formulation, the amount of ***acid*** applied is NOT the same. Remember, it is the ***parent acid*** that binds to the target site to control the weed; the salt portion of the formulation is not involved in binding to the target site.

How would we calculate the amount of acid applied?

The first step is to determine the amount of acid equivalent contained in a gallon of formulated product. Some labels indicate both the amount of active ingredient and acid equivalent contained in the formulation, while others list only one or the other. If the pounds acid equivalent is specified on the product label, all one needs do to determine the pounds acid equivalent applied per acre is substitute pounds acid equivalent for pounds active ingredient in the equation presented previously for calculating the pounds active ingredient applied. For this example, however, let's assume neither label of these glyphosate formulations indicates the amount of acid equivalent.

The formula that can be used to calculate the amount of acid equivalent contained in a gallon of formulated product is:

$$Acid\ Equivalent = \frac{molecular\ weight\ of\ the\ acid - 1}{molecular\ weight\ of\ the\ salt\ or\ ester}\ x100$$

So, we now need to provide some molecular weights (i.e., how much the molecule weighs) to complete these calculations. The molecular weight of the parent glyphosate acid is 169. The molecular weight of the isopropylamine salt is 59 (weight of the three carbons, ten hydrogens, and one nitrogen atom) + 169 (weight of the parent acid) = 228. The molecular weight of the trimesium salt formulation is 245.

The acid equivalent of the **isopropylamine salt** formulation is:

$$Acid\ Equivalent = \frac{169-1}{228} x100 = 74\%$$

So the amount of ***acid equivalent*** in one gallon of formulated product is:

$$74\%\ acid\ equivalent\ x \frac{5 lbs\ active\ ingredient}{gallon} = 3.70 lbs\ ae$$

The acid equivalent of the **trimesium salt** formulation is:

$$Acid\ Equivalent = \frac{169-1}{245} x100 = 69\%$$

So the amount of ***acid equivalent*** in one gallon of formulated product is:

$$69\% \, acid \; equivalent \; x \frac{5 \, lbs \, active \, ingredient}{gallon} = 3.45 \, lbs \, ae$$

Again, we applied 28 ounces (0.22 gallon) per acre of each formulation, and since they both contain five pounds active ingredient per gallon, the amount of ***active ingredient*** applied is equal. The amount of ***acid*** applied (that part of the formulation that actually controls the weed) for each formulation is NOT equal:

The amount of ***acid*** applied per acre with the **isopropylamine salt** formulation is:

$$pounds \, acid \; equivalent \; applied \; per \; acre = \frac{0.22 \, gallon \, of \; product \; applied}{acre} \, x \frac{3.70 \, lbs \, ae}{gallon \, of \; product} = 0.81 \, lbs \, ae \; per \; acre$$

The amount of ***acid*** applied per acre with the **trimesium salt** formulation is:

$$pounds \, acid \; equivalent \; applied \; per \; acre = \frac{0.22 \, gallon \, of \; product \; applied}{acre} \, x \frac{3.45 \, lbs \, ae}{gallon \, of \; product} = 0.76 \, lbs \, ae \; per \; acre$$

This example demonstrates that there was more ***acid*** applied with the isopropylamine salt formulation than with the trimesium salt formulation. In practical terms, more of the part of the formulation that actually controls the weeds was applied with the isopropylamine formulation. To compare the herbicidally active portion of two ester, salt, or amine formulations, product equivalents should be based on the ***acid equivalent*** of a salt, amine, or ester formulation.

This exercise was done not to add confusion but to illustrate that to calculate equivalent rates of salt or ester formulations, the ***acid equivalent*** calculation should be used. If there is only one formulation of a salt or ester product commercially available, it wouldn't really matter if one calculated active ingredient or acid equivalent. For example, Pursuit is formulated as the ammonium salt of imazethapyr, but currently only one manufacturer markets Pursuit. There are, however, several commercial formulations of 2,4-D and glyphosate. Currently over 20 different commercial formulations of glyphosate available today, and likely more will be available in the future. Not all of these formulations contain the same amount of ***acid equivalent*** so if you want to determine equivalent rates of two glyphosate-containing formulations with respect to how many molecules of glyphosate are applied, you must calculate these rates based on ***acid equivalent***. When calculations are based on the same acid equivalent the amount of formulated product applied may not always be equal. ***It is the acid portion of a salt formulation that binds at the target site.***

Will differences in the amount of acid equivalent applied between two formulations result in weed control differences? One might argue that if the difference in amount of acid applied is large enough differences in weed control might result, and might be noticed on weeds the herbicide is "marginal" against. However, it is difficult to make an all inclusive statement that weed control differences will always result if differing amounts of acid are applied, especially when the difference in amount of acid applied is small. Labeled application rates are established by herbicide manufacturers based on product testing. It does not seem very likely that a herbicide manufacturer would market a herbicide at an application rate that would consistently result in reduced weed control compared with a competitive formulation.

More Information

See Table 8 in the 2004 Illinois Agricultural Pest Management Handbook for information on glyphosate formulations.

Authors:

Dawn E. Nordby (dnordby@uiuc.edu)
Aaron G. Hager (hager@uiuc.edu)