



## **Reducing the Environmental Impact of the Green Industry with Green Chemistry**

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### **Overview of Green Chemistry**

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Chemistry has had such a beneficial impact on our society in terms of the advances in treating disease, improving the efficiency of food production, and synthesis of the myriad of products that we use in everyday life. Crop protection and growth enhancement chemicals have helped us in the last century to increase the world population from 1.6 to over 6 billion, with an increase in life expectancy of 60%.[1] This has come with a price; our collective human health and the environment are now threatened by the waste products produced. Our bodies are contaminated with a large number of synthetic chemicals deemed toxic, carcinogenic, or their effects are unknown. In the USGS national water quality assessment program, at least one pesticide was detected in more than 95% of stream samples collected at 115 sites.[2] Many of the chemicals used work their way up the food chain and circulate around the global environment. Chemicals like flame retardants used in furniture and electronics are commonly found in our marine mammal populations, and pesticides used in the tropics and in our own latitude are being found commonly in the arctic where they were not originally applied. We need to look hard at the implications of our actions and how they affect the global society and environment.

Even with government regulatory actions, there are chemical manufacturers that do not do full testing on their products and do not promote the production of inherently safer chemicals. With the green chemistry movement, the focus is now to overhaul the way chemicals are designed from the onset. This makes sense and has shown to be a means by which companies can increase their bottom line. Green chemistry principles work to make industry much more sustainable and reduce wastes of processes. This allows companies to use less feedstock and reduce the expense of disposal and/or treatment of the historical disproportionate amount of waste from traditional synthesis of chemicals. The goal of green chemistry is to create better, safer chemicals while choosing the safest, most efficient ways to synthesize and reduce waste. This practice of eliminating hazards from the onset of the design stage has benefits for our health and the environment. Pollution in almost all legal contexts is defined as chemical pollution. Green chemistry is a "fundamental" approach to environmental problems caused by pollution.[3]

The current chemical industry uses petroleum as the primary feedstock to create chemicals. This production is very energy intensive, inefficient, and toxic! One principle that drives green chemistry is the idea that

companies should prioritize the use of renewable materials as feedstocks. Generally, the use of these materials as feedstocks produces processes that are significantly less hazardous than with petroleum products. Pest management techniques have evolved over the past 50 years. Inorganic chemical pesticides were replaced by synthetic organic chemicals, and now biopesticides constitute a significant part of pest management technology.[4] Today chemists have the knowledge to determine the potential toxicity of the molecules they design and the reactants that they use. They can use this knowledge of synthesis to design molecules to avoid or reduce the toxic properties of chemicals in the past. The only way to prevent costs from rising is to avoid the use or generation of hazardous substances by designing chemistry through the use of green chemistry techniques.[3] They can design things in a way that they are very selective to certain modes of action and can prevent them from absorbing into the skin or so that they may safely break down in the environment. The idea of chemists taking a life cycle approach to these chemicals is very powerful and is essential to protect from furthering the ills of the chemical industry of the past. This green chemistry approach is the only way we will get close to processes and products that are safe in natural ecosystems and will ultimately produce products that safely degrade as a biological nutrient or will be safely recycled.

## Objectives

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When I first embarked on this topic, I was thinking really broadly about how the everyday chemicals we use in our society effect the environment. The focus for this unit will be with the chemicals that are used by professional land care managers and by Joe Public purchased at the Home Depot. I early on want to also discuss the concept that green industry's use of chemicals is very regulated and applicators must have a certification and must pass a rather in depth exam in order to apply these chemicals commercially. My students in 12<sup>th</sup> grade all take the exam to gain this pesticide/fertilization certification and not all pass, even with many hours of instruction and a desire to do well on it. I have even witnessed experienced landscape contractors not being able to pass this exam. Many think that the ills from landscape chemicals felt by the environment come from the professionally maintained golf courses and from farms. I sincerely believe that that is not the case with these chemicals. These applicators are well versed in the proper application of these chemicals and they are driven by economics. These chemicals are very expensive and they are not going to apply more than needed to their crops or to the turf and landscape areas than they need to. This cuts into their bottom line and can ultimately reduce profits to the point where it is more economical to abandon a crop rather than to apply another round of pesticide.

On the other hand you hear radio commercials about lawn chemicals and see the numerous pallets of turf chemicals and pesticides lined up at the big home improvement stores. Anyone can buy enough of these chemicals to eradicate any sort of pest and to eutrophy and contaminate the surface waters and aquifers in their watershed. The problem with access to all these chemicals is that, just like our students and maybe yourself, when all else fails the applicator follows the directions. Many just get out their rotary spreader and just run back and forth across their lawn until they can see a large coverage of pellet all over their lawn. They haven't done a soil test; they haven't calculated the amount they will need; they just use up the bag they bought since they figure that if a little bit is good, more is going to be even better! In a study conducted on "amateur" applicators of pesticides, there are a few findings that prove this point. In the study, all participants were subjected to a high exposure of the chemical since it did not warn to use gloves during mixing and loading; the concentration of the solution they made was inaccurate in all but one instance and the

concentration was between 55 and 177% of that recommended.[5] This is why I feel that it is essential to teach my students what the different classes of chemicals are, for them to understand what the toxicological impact of different chemicals will be when they handle them, and also what effect they may have on the environment if handled incorrectly and applied at the improper rate.

This unit is designed to help ensure that my students have a sound understanding of the different chemicals they may come in contact with working in the green industry in whichever capacity they choose to pursue. Through my high school landscaping curriculum and also the DE State Pesticide Certification students engage in during their senior year, the actual chemistry of these pesticide materials is not explored at all. Students are told to read the label and follow the instructions on them, but they do not explore the chemical compounds they are applying to the landscape. My students take chemistry in 11<sup>th</sup> grade, but, in talking with the chemistry teacher at our high school, there is no mention of any of these compounds in the class. Being an environmental scientist, I know of the impacts of organic compounds and their persistence in the environment and feel the knowledge through this unit will have great benefits to my students.

This unit will be used with my 12<sup>th</sup> grade students enrolled in my Environmental Landscape Technology (ELT) program. The timing of this unit will be in January / February right before the Delaware State Pesticide Applicator exam is given in late February. The training for the pesticide certification takes approximately six weeks and this unit will encompass two weeks within this block of time. If you teach horticulture related curriculum, this unit will be very helpful to you as a springboard to work towards getting your students their certification as well.

In Delaware our units are driven by what is called "Enduring Understandings". This is what you want the students to remember from your class 30 years from now. I was pondering what my enduring understanding would be and I kept coming up with a page of things that I want them to know! My enduring understanding for this unit is that students will be able to select pesticides based on effectiveness, toxicity to non-target species, site characteristics, as well as their solubility and persistence. If I can help students learn how to properly select pesticides in this way, I will have empowered them with the skills to make very informed decisions on pesticide use and reduce their impact on the environment.

I was honored with the distinction of being chosen as one of DuPont's National Agriscience Ambassadors for the National FFA organization. Through this appointment, I work with other teachers from around the country in order to put more age appropriate mathematics and science into the agriscience curriculum used. My hope with this unit is that other agriscience instructors can implement it with their students who are pursuing a pathway in horticulture, plant science, or landscaping. This will help those students have a better grasp on the power of the chemicals they apply and the precautions they should take for themselves and for the watersheds they apply them to.

## **Background Information**

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Pesticide literally means "pest killer". The specific type of pesticide is revealed in its name; i.e. herbicides kill plants (herbs), insecticides kill insects, fungicides kill fungi, rodenticides kill rodents and so forth. Pesticides work on pests in a variety of ways and each has a specific route of entry for the pest and certain possible routes of exposure for the applicator. The advantages of using pesticides in the landscape are that they are

usually quick acting, easy to use, and relatively cheap. Disadvantages include their possible toxicity to humans and non-target species, potential negative environmental effects, pesticide resistance due to overuse, and the unknown cumulative effects of their use over time.

There is a shift in the way pesticides are being made and used. Pesticide use in the U.S. has dropped significantly from a high of 1.46 billion pounds in the 1970s, compared to approximately 1.23 billion pounds today.[6] This is due to the advances in pesticides. Pesticides are now more selective and are applied at lower rates, while having lower inherent toxicity and a lower impact on human health and the environment. For example, tree farm herbicides use was approximately 2.1 pounds of active ingredient per acre before 2001, today it takes only about 0.25 fluid oz of active pesticide ingredient to fight the same weeds in that acre.

When the major water pollution control laws were enacted around 1970, a great concern was DDT and other very persistent insecticides that polluted water and sediments. In rural areas, the greater problem is from herbicides that, because they are applied directly to the land, have an inherent tendency to get into runoff and into water sources. These older more potentially toxic pesticides are being phased out under numerous changes to pesticide regulated legislation. The Food Quality Protection Act has allowed the EPA to fast track reduced risk synthetic pesticides and biopesticides helping these products get to market much sooner. This act has helped transition pesticide use in the U.S. to safer pesticide use. These new pesticides reduce risks to non-target organisms and reduce the contamination of valuable environmental resources.

Integrated pest management (IPM) has also become common practice in agriculture as well as landscape management. This relies on the life cycles of pests and controls pests economically by withholding use of pesticides until their damage reaches a certain threshold. Pesticides are really the last line of defense in a green chemistry approach to managing pests of the landscape. You should teach your students the practice of IPM. There are many great websites about IPM; you should do more research on this if you are not familiar with this idea. I have a limited amount of space for this unit, so I will not be elaborating much more on this topic. One place to get you started is an online book on IPM at the University of Minnesota website.[7] IPM is a way to control pests that uses both chemical and non-chemical methods. The steps taken through this approach really are designed to minimize the risk to humans and non-target organisms. The first step is preventing an outbreak which is accomplished by keeping the plants in the landscape as healthy as possible through the proper selection of plants for site conditions and proper nutrition, and by using good cultural practices to reduce the conditions that cause disease. Secondly, you must monitor the landscape for pests, noting areas that have any sort of disease or pest that is affecting them and then assessing the extent of infestation. Identification of the pest is critical to the effectiveness of treatment; you have to go over the common pests with the students and the signs of infestation to allow them to make good decisions for the last step. The last step is to plan the control strategy for the pest in question. There are many biological control methods you can use such as the use of predator insects, parasites, pathogens, and they are developing more and more biopesticides to control a myriad of pests and diseases. Chemical intervention is the last line of defense once the pests have reached the tolerable threshold. Many times at this point you can treat the smaller affected areas with a very selective or narrow spectrum pesticide. Using a broad spectrum pesticide, which kills lots of different organisms, is not an ideal situation. This will harm many non-target organisms such as pollinators, fish and other aquatic organisms.

All pesticides contain active ingredients that control pests by interfering with their natural body functions. The chemical structure of the active ingredient determines what chemical class it belongs to. This information can be found on the Material Safety Data Sheet (MSDS) for the product you are applying. I believe this is knowledge that the applicator should be aware of, and it is important in protecting not only the environment

but also the pesticide applicator. Understanding the properties and modes of actions of the common chemicals used in the landscape will help my students use the pesticides most effectively and minimize adverse environmental and health effects.

## Exploring the Classes of Pesticides

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This section of the unit will cover five days of class time and will be a great mix of reading, hands-on lab experiences and research. I am fortunate in that I have my students for 2.5 hours each day so breaking that period up into three or four transitions is the norm and allows students to have ample time to explore topics both through lecture and hands-on. During this portion of the unit we will be reading and discussing an article about Atrazine (a herbicide used with corn) everyday as a warm up activity. This goes right along with the topic and is a great way to incorporate literacy into my classroom. I was able to find some great articles to use in this way with the students. [8] My district has a big push for literacy in all classrooms; in academic areas, as well as in all of our vocational classrooms, students are reading at least three times a week using different reading strategies. I have found the pyramid reading strategy to work best with my students.[9] Using it has helped them gain a better understanding of the topic when they read and it helps them put the new knowledge in their own words. The bulk of the period will be spent engaged in discussing a class of pesticides and the last portion of the class will deal with the students engaging in a lab activity on thinning of eggshells included at the end of my unit, adapted from an access excellence lesson published online.[10] This lab is based on making up particular concentrations of chemicals and then titrating solutions, this is the basis for most of the analytical work that is done in soil and water chemistry and a concept that my students need to relate to if they wish to pursue a career in the environmental sciences. Analytical techniques are important for my students and this lab on eggshell thinning is a great way to access their lab skills and give them a "sense of wonder" so to speak.

The first day of this section we will go over reading the pesticide label and also design an Excel sheet that they will record all the pertinent information about the pesticides we discuss throughout this section. The remaining four days we will also explore a class of synthetic organic pesticides and look at their mode of action, persistence in the environment, exposure issues for applicators of the chemical, examples of chemicals used in the industry, and an example of how green chemistry has improved the class of chemicals. This will be done each day using a PowerPoint presentation developed using the information contained within each of the next sections of this unit, as well as labels and MSDS sheets for each of the chemicals mentioned in each group. If you would like to acquire my PowerPoint presentations on these topics feel free to e-mail me at [justin.benzncvt.k12.de.us](mailto:justin.benzncvt.k12.de.us).

## Pesticide Labels

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Pesticides are developed, manufactured and sold with the premise that they are to be used for a certain purpose. Applicators must read, understand, and follow the instructions that are found on the product label. The label is designed to provide information on achieving the maximum product benefit while minimizing risks

to human health and the environment. The label is a binding contract which requires the person using the product to do so, exactly as directed according to the law. The information contained on the label is a result of quite a bit of scientific investigation and details how to use the product so that you stay within regulations when applying the product.[11] The EPA may classify a pesticide as "restricted-use" if it poses a special threat to human health or environmental quality. Restricted use pesticides may be purchased and applied only by a "certified applicator," trained and licensed under EPA guidelines.[12]

Students need to become familiar with the pesticide label contents in order to select the most appropriate pesticide products and receive maximum effectiveness when using them. When you have students fold out the labels from a container of pesticide it looks rather intimidating to them. It is not all that complicated; there are really only four main parts: safety information, environmental information, product information, and use information. The best way to go over the chemicals is to have them actually use a pesticide label and fill out some sort of product profile worksheet. I have one I developed at the end of my unit under lessons which you can recreate for your students.

The safety information is the section that must be prominent on the front of the container, especially the signal word. The signal word indicates the product's potential toxicity to humans. There are three signal words, in decreasing order of toxicity, Danger (highly toxic, a few drops to one tsp will kill an average person), Warning (moderately toxic, one tsp to one oz is lethal), and Caution (slightly toxic, lethal dose is over one oz). This signal word is assigned after testing all exposure routes of the chemical, ingestion, inhalation, and the dermal absorption; the route of exposure that shows the highest toxicity potential determines the signal word assigned to the product's label.

Hazards to humans and domestic animals are also included in the safety information section indicating specific hazards, routes of exposure, and precautions to take in order to avoid injury. There is also a personal protective equipment (PPE) and clothing statement that aids the applicator in reducing their exposure to the chemical. The minimum PPE requirements for all pesticides are a long-sleeved shirt, long pants, and waterproof footwear. Specific instructions are included when there is a need for chemical resistant gloves, aprons, goggles, and boots, etc. There is also a statement of practical treatment, i.e. first aid, which provides information to help if the applicator is exposed to the product. This also informs physicians and emergency responders of the appropriate medical procedures to help someone who has been poisoned by the product.

The environmental hazard section of the label is one that I feel is not really a priority for most applicators. This section should be a big determinant in where and when certain pesticides are applied, not just due to cost and the pesticide's effectiveness in killing the pest. The potential for the chemical to harm nontarget organisms is determined by a series of tests which evaluate a pesticide's toxicity to wildlife such as mammals, fish, birds, aquatic invertebrates, and pollinating insects. Statements on the potential environmental impact are also included in this section. The label will tell you how to reduce the impact on the environment if it has been shown to contaminate water, etc.

The product information section tells what the brand name is of the chemical, it also tells by whom and where the pesticide was produced, the EPA registration number, and the establishment number of the production facility it was synthesized in. The ingredient information is also included which identifies the name and percentage of the pesticide product that affects the target pest. Some of these are very complex, and, therefore, there is also a list of EPA approved common names. I was able to find a few great websites that you could use with the students to find out more about these chemicals.[13] This will help them better understand the complexity of the chemicals that they are using.

The use information section is critical to applying the chemical in a safe manner. This is usually the bulk of the label and provides guidance on the pests that can be controlled with the product, site that is registered to be used on, compatibility of the pesticide with other pesticides, mixing and dilution rates, application rates, equipment that maximizes the effectiveness of the pesticide, timing and frequency of applications, and general information you need to follow in order to have effective results with the product. There is always a re-entry or restricted entry statement to let you know how long you must wait before you may enter the area treated without personal protective equipment.

## Herbicides

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Herbicides are applied more than any other chemicals to the landscape. Herbicides come in an enormous variety of chemical compounds. Weeds are known to cause enormous losses due to their interference in agroecosystems. Because of environmental and human health concerns, worldwide efforts are being made to reduce the reliance on synthetic herbicides to reduce weeds.[4] One of the most widely synthetically produced type of herbicide contains the triazine structure, which has a 6-membered ring in which C atoms alternate with N atoms ("triazine" denotes 3 nitrogen atoms). To understand this structure use this informative website on triazine herbicides.[14] Two of these triazine herbicides that are widely used in the industry are atrazine and simazine. These chemicals have been used as herbicides since they are effective at inhibiting the photosynthetic electron transport processes in annual grasses and broadleaf weeds. There are some ill effects of these herbicides since they are relatively mobile in soils and they degrade rather slowly. Also, the manner in which they are applied ensures that they are susceptible to being washed off with rainfall with the high potential to become water contaminants. These triazine herbicides are widely spread contaminants and are commonly found in drinking water supplies. Municipalities with high concentrations are required to use activated carbon filtration to remove these herbicides from municipal drinking water. Triazines also threaten our environment since they bioaccumulate in microorganisms, macroinvertebrates, worms, snails and fish.[14]

Green chemistry has helped develop more sustainable herbicides. In 1996, Monsanto received the Presidential Green Chemistry Challenge award for the manufacturing of glyphosate herbicides. Glyphosate is an isopropylamine salt and the active ingredient in Round-up herbicide. Round-up also contains water and a surfactant system which adheres the product to the leaves of the plant so the active ingredient can penetrate. Glyphosate kills weeds by interfering with the synthesis of some kinds of amino acids essential to plant proteins. Glyphosate moves throughout the plant deteriorating the plant tissue from the leaves to the root system. Glyphosate also binds tightly to most soils and is not available for uptake to other nearby plants. There is no risk to humans or animals since it disrupts an enzyme, EPSP synthase, that is not present in humans or animals.

Commonly used herbicides to use for review of the labels and MSDS sheets, to fill in the product profile worksheet at the end of the unit and to discuss with the students include Atrazine 90DF (Atrazine), Envoy Plus (Clethodium), Confront (Triclopyr), Lontrel (Clopyralid), Quicksilver (Carfentrazone-ethyl), and Round-up (Glyphosate). Students should contrast and compare the different herbicides and determine the use limitations of each of the chemicals. Their Excel sheet should be filled out for each of these chemicals with their half-life in the environment, water solubility, partition coefficient ( $K_{oc}$ ), and calculated Groundwater Ubiquity Score (GUS).

## Organochlorine and Organophosphate Insecticides

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The insecticides that have caused the greatest water pollution problems, and that still do in developing countries, are the organochlorine insecticides. The crazy thing is that, if it is banned in the U.S., companies just sell it cheap to third world countries! There were many of these, best exemplified by DDT and chlordane. DDT was sprayed widely in the environment and helpful in killing mosquitoes that carried malaria. Highly persistent chlordane was the most effective insecticide against termites and was buried around buildings to prevent termite infestation.[6]

Organochlorine insecticides were dominant from the 1940s until the 1960s. They were not particularly toxic to humans and other animals. However, DDT and related compounds have even more detrimental characteristics because of their tendency to undergo bioaccumulation in fish and other organisms, concentrating in fat tissue. As these organisms are eaten by other organisms in higher trophic levels, the organochlorine compounds become concentrated in fat tissue, a process called biomagnification. This made the organochlorine insecticide go out of favor. This is best illustrated in the unit by the egg-shell-thinning lab experience students are engaging in at the latter portion of each class period that is related to thinning of egg shells of bald eagles caused by DDT. Today there are still remnants of these chemicals. I am not sure if you have heard of nurdles or not; they are small resin pellets that have not been made into plastic products yet. They are said to be 10 percent of the plastic trash in the ocean. These nurdles are attracting DDT and dioxins so that the nurdles actually have a concentration a million times higher than the surrounding water. This is really a bad thing since they are the size of fish eggs and they are ingested by organisms in the ocean.[15]

Organophosphate insecticides, organic derivatives of phosphoric acid,  $H_3PO_4$ , came into common use when organochlorine compounds were found to bioaccumulate. These had a big advantage in being biodegradable with no tendency to undergo bioaccumulation. Since then, organophosphates have been used extensively due to their effectiveness on a large variety of pests and because pests do not seem to develop a resistance to the chemicals in this class. Organophosphates are extremely toxic, particularly in the concentrated forms that they are sold in commercially.

These chemicals are more persistent than other classes that are currently used in the landscape. Organophosphates do eventually break down chemically under the influence of environmental factors such as sunlight, air, rainfall, and soil moisture, or biologically through plants, animals and microorganisms like bacteria and fungi.

Organophosphates can be absorbed directly through the skin or through the lining of the stomach or respiratory tract following ingestion or inhalation. They affect the nervous system by attaching to the enzyme acetylcholinesterase. When functioning normally, nerves transmit messages through the production of a chemical called acetylcholine (ACh). After a message is sent, the enzyme acetylcholinesterase breaks down the ACh to end stimulation of the nerve and return it to its normal state. Organophosphates inhibit the enzyme, causing the accumulation of ACh and over stimulating the nerves. This causes the insect to lose control of their nervous system, resulting in paralysis and respiratory failure.

The human nervous system also relies on acetylcholinesterase, and, therefore, is also susceptible to organophosphates. Just as in insects, if humans inhale, ingest, or absorb enough organophosphate pesticides through the skin, they are at risk of experiencing adverse health effects. An acute poisoning causes symptoms such as stomach cramps, sweating, muscle contraction, twitching, or just overall weakness. Chronic poisoning,



from long term exposure, could result in general feelings of illness, loss of appetite, anaemia, or liver, kidney or nerve damage.

Two examples that are commonly used are methyl parathion and Malathion. Parathion, once the most widely used organophosphate pesticide, is very effective since it affects the nervous system by attaching to the enzyme acetylcholinesterase like the military poison "nerve gases" and a significant number of fatal poisonings occurred due to parathion exposure. Parathion is now banned. Malathion remains on the market and is only about 1/100 as toxic to mammals. This is due to the differences in structure of the two molecules; Malathion can be cleaved with addition of water by enzymes possessed by humans and other mammals, but not insects.[6]

Green chemistry has advanced this class of chemicals with the development of spinetoram from Dow AgroSciences. This is made from naturally occurring fermentation products spinosyns J and L that are modified with a low impact synthesis in which catalysts and most reagents and solvents are recycled. Spinetoram is having a big benefit for human health since it replaces the existing organophosphate insecticides azinphos-methyl and phosmet which are used on pome fruits, stone fruits, and tree nuts. The mammalian acute toxicity of spinetoram is more than 1,000 times lower than azinphos-methyl and 44 times lower than phosmet. There is also a lower impact to the environment since its toxicity to non-target species is low and its persistence in the environment is much less. Spinetoram is effective at use rates 10-34 times lower than the organophosphate pesticides it replaces. It is projected by Dow AgroSciences that in the first 5 years of its use it will eliminate about 1.8 million pounds of organic pesticides used in the fruit industry.[16]

Commonly used organophosphate insecticides to use for review of the labels and MSDS sheets, to fill in the product profile worksheet at the end of the unit and to discuss with the students include Acephate Pro 75 (Acephate), Malathion (Malathion), and Supracide 2E (Methidathion). Students should contrast and compare the different insecticides and determine the use limitations of each of the chemicals. Their Excel sheet should be filled out for each of these chemicals with their half-life in the environment, water solubility, partition coefficient ( $K_{oc}$ ), and calculated GUS.

## Carbamate Insecticides

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Carbamates are considered slightly less toxic than organophosphates since they are rapidly metabolized by the body and excreted. Carbamates are compounds based upon carbamic acid with various hydrocarbon groups substituted for H on the molecule. They also do not persist in the environment for as long as organophosphates, usually breaking down in a couple of days to a week. Carbamates generally have a low vapor pressure and low water solubility, meaning they are slow to evaporate and will not dissolve readily in water.

Carbamates act mainly as contact and oral poisons as they are absorbed readily through the skin, stomach lining or respiratory tract. They have a similar mode of action as organophosphates which are to inhibit the functioning of acetylcholinesterase, resulting in nervous system failure. Carbamates are considered to be reversible inhibitors, which mean recovery from over exposure is typically faster than with organophosphates. They do not remain in the body like other pesticides can, minimizing the poisoning risk.

Carbamates are considered moderately toxic. Acute poisoning happens within minutes of exposure and will last only a few hours as the body metabolizes the chemical. Symptoms include stomach cramps and sweating; if exposure continues, symptoms will mimic organophosphate poisoning with slurring of speech, twitching and jerky movements, and possibly dizziness and blurred vision. Chronic poisoning is not common since the body is able to metabolize and excrete carbamates.

The most widely used carbamate insecticide is Sevin (Carbaryl) which is used to kill insects on lawns or gardens and, because of its low toxicity to mammals, can even be sprinkled on pets! There are concerns through about its broad spectrum application for chewing insects. It also kills beneficial insects such as predator insects and the pollinators.

Green chemistry has advanced this class of chemicals with a new synthesis of carbamates. Carbamates are used for herbicides, pesticides, and fungicides, as well as pharmaceuticals and the manufacturing of polymers, especially polyurethanes. The existing technology to produce them was based upon the use of very toxic reagents and intermediates. Many of these products used phosgene as the starting raw material and now through green chemistry alternative ways of producing these chemicals have been discovered. Recently an alternative approach was proposed for synthesis of carbamates that is based on the use of substituted carbonates or ureas as the reagents in the presence of solid basic catalysts (silica gel, the sodium form of zeolite ZSM-5, Li-MgO, Mg-Al hydrocalcite). There has also been an electrochemical method of synthesis of carbamates from CO<sub>2</sub>, oxygen, and amines.

Commonly used carbamate insecticides to use for review of the labels and MSDS sheets, to fill in the product profile worksheet at the end of the unit and to discuss with the students include Carzol (Formetanate hydrochloride), Furadan (Carbofuran), Sevin (Carbaryl), and Temik (Aldicarb). Students should contrast and compare the different insecticides and determine the use limitations of each of the chemicals. Their Excel sheet should be filled out for each of these chemicals with their half-life in the environment, water solubility, partition coefficient ( $K_{oc}$ ), and calculated GUS.

## Pyrethrin and Synthetic Pyrethroid Insecticides

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Pyrethrins are derived from a natural compound that is found in Chrysanthemum species, flowers such as daisies, called pyrethrum. The various natural pest-repellent pyrethrin compounds are extracted with the most common being pyrethrin I and pyrethrin II. Pyrethrins are most effective against flying insect pests.

Pyrethrins are thick, sticky, brown plant extracts. They are generally insoluble in water, but will dissolve in other chemicals such as alcohols, oil or organic solvents. Pyrethrins are usually mixed with synergists, chemicals that do not have any insecticidal properties but help them work. A common one is piperonyl butoxide which increases the toxicity of pyrethrin to pests.

Pyrethrins are not stable in light and air, and, therefore, are not persistent in the environment. Pyrethrins act on contact, quickly affecting the nervous system to "knockdown" the pest. A few minutes after application the pest cannot move or fly away. Pyrethrin I is highly lethal while Pyrethrin II is not. Pyrethrins are normally inhaled or ingested by the pest after contact and absorbed through the lining of the stomach or respiratory tract. They affect the nervous system by attaching to a protein found on the surface of nerves called the

sodium channel. This channel opens to stimulate the nerve and closes to end the signal when functioning normally. The Pyrethrins bind to the sodium channel and prevent it from closing, thus over stimulating the nerve and causing pests to lose control of their nervous system.

Pyrethrins are much more toxic to pests than mammals. Mammals are able to breakdown pyrethrins into less toxic chemicals which are readily excreted. If humans are exposed to large amounts of pyrethrins, they will show symptoms of sneezing, runny nose, sore throat and breathing difficulties. Ingestion will cause nausea and possibly vomiting.

Pyrethrins are already a green chemistry approach to pesticides since they are natural plant derived pesticides. They are suitable alternatives that can be used to reduce the risk of exposure to synthetic pesticide residues.

Synthetic pyrethroids are synthetic versions of naturally occurring pyrethrins. Pyrethroids exhibit greater stability in the environment, and, therefore, are more persistent. They are, however, designed to target specific host species. More than 100 pyrethroids have been synthesized with more insecticidal effectiveness than naturally occurring pyrethrins. One major drawback to the use of these chemicals is that insects become resistant to pyrethroids if they are overused.

Synthetic pyrethroids are insoluble in water, immobile in soil and have high absorption ability with particles such as wood. They are broken down by sunlight and microorganisms such as bacteria and, therefore, are generally not very persistent in the environment, although they are more persistent than pyrethrins.

Synthetic pyrethroids were designed to metabolize quickly in mammals and thus reduce the risk of poisoning, while still remaining toxic to insects. Synthetic pyrethroids have the same mode of action as pyrethrins, affecting the sodium channels in nerve cells and over stimulating the nervous system. Synthetic pyrethroids are less toxic to mammals than carbamates and organophosphates. Synthetic pyrethroids are not easily dissolved in water but do adhere strongly to substances. Therefore, there is a risk associated with food being consumed that has been exposed to them. Synthetic pyrethroids are quite toxic to fish and other aquatic organisms, so application near bodies of water should be done with care.

Exposure to synthetic pyrethroids can result in symptoms such as dizziness, headache, nausea, vomiting, and eye irritation. Extremely high exposure could lead to fatigue, muscular twitching and knock you unconscious. Chronic exposure includes brain and nervous system disorders and immune system failures.

Commonly used pyrethrin and synthetic pyrethroid insecticides to use for review of the labels and MSDS sheets, to fill in the product profile worksheet at the end of the unit and to discuss with the students include Astro (Permethrin), Cynoff (Cypermethrin), ExciteR (Pyrethrin), Talstar (Bifenthrin) and Warrior (Lambda-cyhalothrin). Students should contrast and compare the different insecticides and determine the use limitations of each of the chemicals. Their Excel sheet should be filled out for each of these chemicals with their half-life in the environment, water solubility, partition coefficient ( $K_{oc}$ ), and calculated GUS.

## Human Health and the Environment

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This section of the unit will focus on having students come to the realization of the dangers of pesticides to their health and gain an understanding of the mechanisms that drive the behavior of pesticides in the environment. Students will also now apply the pesticide knowledge gained in the first week of the unit to the decision making process when determining the type of product to apply to the landscape.

The first day of this portion of the unit will have the students reading a summary of scientists' opinions on what is known on endocrine disruption theory. This will follow with a PowerPoint and discussion on the endocrine system. Students will then be grouped and they will research the links between endocrine disrupting chemicals and health, the pesticides that are considered endocrine disrupting chemicals, how widespread these chemical pollutants are in the environment, and how long these chemicals persist in the environment. The next period will start out with the student groups reporting on their findings and leading into a discussion on the need to protect the environment from these chemicals. During a subsequent period, I will go over the mechanisms that drive how pesticides move through the environment. We will also discuss and engage in how to derive the essential information on pesticides in order to calculate their potential for contamination. Students will then be put into student groups and given the scenarios with which they will determine all relevant information on the chemicals and determine the greenest synthetic approach to alleviate the pest in question, supporting their choice with sound, detailed evidence on each of the chemical options.

## Pesticides as Human Endocrine Disruptors

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With all the PowerPoint presentations and discussion about the different types of pesticides and the analysis of the MSDS and labels, students should realize that they are dealing with things that can potentially have some lasting effects on them if handled improperly. Many of the chemicals that are used in the landscaping industry disrupt cellular development in order to impair living things at ultra-low, environmentally relevant concentrations. Clear scientific evidence indicates that humans are not immune from the effects of these chemicals. Endocrine disruptors put the welfare of our children at stake and make these chemicals a top priority of green chemistry efforts.

Endocrine disrupting chemicals are substances that can cause adverse effects by interfering in some way with the body's hormones or chemical messengers. Hormones play a crucial role in normal cell differentiation in early life stages, so exposure to endocrine disrupting substances in the egg or womb can alter the normal process of development. Mature organisms can be affected, but the developing organisms are especially vulnerable. Exposure at this early stage may not be evident until later in life, causing effects such as learning disability, behavior and reproduction problems, and increased susceptibility to cancer and other diseases.[17]

The effects of the endocrine disruptor are dependent upon which hormone system is targeted. They can either bind to the hormone's receptor and mimic the hormone, or block the action of the hormone. They can also stimulate or inhibit the enzymes responsible for the synthesis or clearance of the hormone, and, thereby, give rise to an increased or decreased action of the hormone. Landscape chemicals are identified in all of the

categories! These chemicals include sex hormone disruptors, thyroid hormone disruptors and suppressors of the hormones released by the brain, and they have affects on steroid synthesis and metabolism.[17]

Wildlife is especially vulnerable to the endocrine disrupting effects of pesticides, because these chemicals are deliberately released into the environment. Effects linked to endocrine disruption have been found in invertebrates, reptiles, fish, birds, and mammals living in polluted areas. Humans are also exposed from residues on fruits and vegetables and from contaminated meat, fish, and dairy products due to the build up of persistent and bioaccumulating pesticides in the food chain.

To have students explore this concept, I will have them do a lesson on endocrine disruptors.[18] Through this two period lesson, they are introduced to the endocrine system and study what is known and not known about chemicals that disrupt this system in humans. This lesson introduces environmental surprises, scientific uncertainty, and social decision making in the context of the environmental change represented by endocrine disruptors.

## **Environmental Movement of Pesticides**

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My students actually work through two different agriscience pathways in my Environmental Landscape Technology class. They not only get a landscaping background, they also get an environmental science background. This makes for excellent opportunities to look at things in an interdisciplinary nature. This next section does just that; students will explore how to protect the environment from the chemicals used in the landscape industry. The goal is to have the students always asking themselves two key questions before applying a pesticide to treat the landscape. Where is the pesticide going to go in the environment after it leaves its container or application equipment? What effects can this pesticide have on non-target sites it may reach in the environment?

Proper application procedures are essential to reducing the environmental impact of pesticide use. Pesticides can move away from the application site by wind or air currents by a process called drift. Drift is a major problem and something that must be controlled when applying pesticides. Studies have shown that a significant percentage of pesticides may never reach the intended target due to drift. This can be a significant factor in contaminating the environment by contaminating sensitive plants, poisoning bees, posing health risks to humans and animals, and contaminating soil and water adjacent to the area being treated. Students need to know that they are legally responsible for the damages resulting from an off-target movement of pesticides. This can be avoided by paying close attention to spray droplet size and the wind direction and speed. I am fortunate to have quite a bit of equipment. We will look at a spray table that I have where we can swap out nozzles and look at the effects of different pressures and orifices on droplet size. You may want to delve into this if you can do something hands on. The premise is just common sense, the larger the droplet, the less likely to drift. To get a larger droplet, you typically use a larger orifice in the nozzle and lower the pressure. Other ways to do this are by viscosity and you can buy different adjuvants, additives intended to reduce drift; you just have to check their compatibility with the chemical you are using. Weather is a big determining factor when trying to minimize your impact when applying chemicals. The wind is affected by the temperature difference between the ground and the air above it. The best time to apply chemicals is when there is cooler air near the soil surface. The warm air on the ground is usually when the sun is higher in the sky and shining on the soil. So the conditions in which you have cooler air and less wind will be in the early

morning and in the evening and these are the best times to apply these chemicals to the site.[19] This is why I love this type of work, it is so interdisciplinary, and you must be a soil scientist, chemist, entomologist, and meteorologist all at once in order to be effective at pesticide application!

Once the pesticide is applied to the landscape, the potential for pesticide runoff is greater for some pesticides than others, and my students need to be aware of those that are most susceptible to runoff. Solubility and persistence are two important factors that contribute to the runoff potential. This information is on the MSDS available from the pesticide manufacturer. All certified applicators are required to have the MSDS for each of the chemicals they have on hand. Danger to aquatic organisms is a factor when choosing a pesticide, as well as the danger to animals and the applicator themselves. The effectiveness is obviously another consideration when choosing a chemical to use for an application; many pesticides are not particularly effective under certain weather conditions, so that must be understood as well before applying a chemical.[19] Applying pesticides at a time or in an amount that is not effective is a wasted application and, therefore, an environmental hazard! Students also need to understand that it is illegal to apply chemicals at a different rate than listed on the label, especially a more concentrated application. Proper application is important for optimal pest control and safety for my students and the environment.

In order to have the students fully understand how these chemicals may move in the environment, they need to understand the physical and chemical characteristics of pesticides and how that drives the movement they undergo in the environment. The characteristics that they need to explore are solubility, adsorption, and persistence. Solubility is the measure of the ability of a pesticide to dissolve in a solvent, usually water. Pesticides that are highly soluble in water are more likely to move with water into surface and groundwater supplies compared to those that are less soluble in water. This characteristic was looked at when the students worked through the lesson on pesticide labels and MSDS and derived the water solubility number that is now in their Excel sheet. This is due to the charge of the pesticide molecules and the constituents present in the underlying soils. Adsorption is the process by which a pesticide binds to soil particles. Solubility and adsorption are inversely related characteristics. Students have done quite a bit with soil science by this point in my class so they have explored physical properties of soils, chemical properties of soils and even cation exchange capacity. They should come with the knowledge that most soils have a net negative charge and so the pesticides that have molecules with positive charges will bind readily with the soil and are, therefore, less likely to move from the site of application. Another thing to discuss is that typically oil-soluble pesticides are more attracted to clay particles and organic matter than are the water-soluble pesticides. A partition coefficient ( $K_{oc}$ ) is the most useful way to quantify pesticide sorption. The  $K_{oc}$  value is the ratio of pesticide concentration in the adsorbed state (bound to soil) and the solution phase (dissolved in water). This means that the greater the concentration of pesticide in solution, the smaller the  $K_{oc}$  value. You can find  $K_{oc}$  values in tables that are determined by the chemical properties of the pesticide such as its solubility and melting point.[22]

Pesticide persistence is described as its half-life in the environment, the time that is required for half of the original quantity to break down. They are divided into three categories based on half-lives: non-persistent pesticides with a soil half-life of less than 30 days, moderately persistent pesticides with a soil half-life of 30-100 days, or persistent pesticides which have a soil half-life of more than 100 days. Organic chemicals will ultimately degrade into water, carbon dioxide, and minerals, but the intermediate degradation products of pesticides are of concern. Pesticides degrade by soil microbial activity of fungi and bacteria, chemical activity usually through hydrolysis with water, and/or photodegradation as the chemical reacts with sunlight.

To estimate a pesticide's potential to contaminate the environment, you need to look at the half-life and the

partition coefficient together. Pesticides with a small  $K_{oc}$  (less than 100) and a long half-life (more than 100 days) pose a considerable threat to groundwater resources through leaching. Pesticides with intermediate to large (500-1000)  $K_{oc}$  values and short half-lives are the safest in terms of groundwater protection. Non-volatile pesticides with large  $K_{oc}$  values (1000 or more) and long half-lives are likely to remain on or near the soil surface, increasing their chance of being carried to surface water bodies through sediment runoff. If a pesticide has a short half-life, the possibility of it polluting groundwater depends primarily on site characteristics, such as, permeability and the depth to the water table, and weather issues such as rain and irrigation timing after application. Without water to move them, pesticides with short half-lives remain in the root zone and they may be degraded rapidly. Ideally the best pesticide are ones with intermediate to large  $K_{oc}$  values and short half-lives since they are retained in the soil and then degrade rather rapidly. This pesticide movement rating can be calculated using the Groundwater Ubiquity Score (GUS). This can be calculated to rank pesticides for their potential to move toward groundwater. The formula is  $GUS = \log_{10}(\text{half-life in days}) \times [4 - \log_{10}(K_{oc})]$ . Extremely low potential to move toward groundwater values are less than 0.1, values 1.0-2.0 are low, 2.0-3.0 are moderate, 3.0-4.0 are high, and values greater than 4.0 have a very high potential to move toward groundwater.[20]

By correctly identifying the pests, knowing the site conditions, and using the persistence, solubility and sorption rates of the different choices of pesticides to be used, you can make very informed decisions on pesticide use. This is most important when you are working on a site that has soils with low organic material and with very permeable subsoils or high water tables. Here in the Delaware Coastal Plain, we have these conditions. Many of our soils are sandy in nature and there are many areas where the water table is not far from the surface. Most of our drinking water here in New Castle County is derived from groundwater, so it is critical to protect the aquifers we utilize for this resource. This is why I devised this unit to be an in-depth look at the deleterious effects of pesticide applications, and why I feel it is critical to empower students with the knowledge they need to make informed decisions on pesticide selection and application.

## Lessons

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### **Pesticide Label and MSDS Interpretation Lesson**

After the lecture on the classes of pesticides each day of the unit, pass out pesticide labels and MSDS sheets for the chemicals that are examples for the day's lesson. Have students work in groups and fill out the following worksheet for each of the chemicals explored. If you want to use this format, you can cut and paste the cells below into Word and expand the table to make enough space for them to write in the pertinent information on the chemicals you are working with. There are many places to find the MSDS and Labels for these chemicals online, but I found one company that must sell just about every agrochemical you can think of. It makes it a one stop shop for these and they are in PDF format so you can save them or print them out for your classes.[20]

What is the chemical name of the pesticide?

What are the active ingredients and the percentages of them in the container?

What is the PPE that should be worn while handling this pesticide?

What can this pesticide be applied to?

What is the level of toxicity of this pesticide?

What are the potential environmental hazards of this pesticide?

Any other important information that needs to be known from this label?

Understanding how the pesticides will move in the environment is another piece that is critical for students to make informed decisions on which pesticides to apply to the land so as to not contaminate our most valuable resource, our water supplies. Have students also keep a running Excel file on all the chemicals you discuss throughout this unit on a spreadsheet like the one below. Students will have an excellent resource by the time they are done with the unit and it should put your students on the right track to determining these values for the chemicals you will be exploring with them.[21]

Chemical Name (Product)	Partition Coefficient (soil $K_{oc}$ )	Soil Half-life (days)	Water Solubility (mg/l)	Movement Rating (GUS) $GUS = \log_{10}(\text{half-life}) \times [4 - \log_{10}(K_{oc})]$
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### Eggshell Thinning Lab

This lab will work well to use as an ongoing piece during the days in which you are talking about each class of pesticides. This lab was adapted from an access excellence lesson published online.[10] This lab also is a great way to have students work on their lab skills and it helps them to conceptualize the effects of pesticides on biological systems. There are a number of steps to this lab and advance preparation is needed to be sure all the materials are readily available. The first day do steps 1 and 2, the second day do steps 3 and 4, the third day do steps 5 and 6, and the final day do steps 7 and 8.

This activity will be done individually (ideal) or in pairs so each group will need:

Eggshells brought from home (3)

(Eggshells from nestbox monitoring would be an interesting variable...)

Mortar and pestle

Hot Plate

Four 125 ml Erlenmeyer flasks

Burette

Pipette

Phenolphthalein

Step 1: Preparing the eggshells

- Boil three eggshells and remove the membrane from the shells
- Grind the shells in a mortar and pestle into a fine powder
- Place in a drying oven overnight
- Weigh out 1.0 gram of shell material



## Step 2: preparing a standard acid

- Label the four 125 ml Erlenmeyer flasks
- On a zeroed balance, weigh four 0.61 g samples of KHP, potassium acid phthalate
- Design a data table to record the exact amount of KHP that was placed in each

Place samples in each of the flasks and dissolve the KHP in 25 ml of distilled H<sub>2</sub>O

Add three drops of phenolphthalein

## Step 3: Preparing the working base

(go over how to make a 0.1 M NaOH solution on the board and make up the solution as a demo and have students make subsequent solutions if needed due to number of students)

- Prepare 1 liter of a 0.1 M NaOH solution in a 1000 ml volumetric flask
- Cap this tightly. Keep the cap on all of the time!

## Step 4: Titrating the base

- Prepare a burette for titration
- Fill burette up to the top mark with NaOH solution (don't forget the cap!)
- Titrate one KHP sample swiftly with the base solution to determine the end point
- Read and record the volume of NaOH that was required to neutralize the acid
- Titrate the other samples slowly with the base solution to determine the end points
- Calculate the exact concentration of your NaOH solution using each sample

Weight of KHP (g) X 1 mmol KHP/0.2042 g KHP = mmol of KHP

mmol KHP = mmol NaOH

mmol NaOH / ml NaOH = Molarity (M) of NaOH

## Step 5: Making an acid to react with eggshell

(go over how to make a 0.2 M HCl solution on the board and make up the solution as a demo and have students make subsequent solutions if need due to number of students measure out carefully! Remember acid into water!)

Prepare 500 ml of a 0.2 M HCl solution

## Step 6: Determining the concentration of the acid

- Pipette four 25 ml samples of the 0.2 M HCl solution into the 125 ml Erlenmeyers
- Add three drops of phenolphthalein
- Fill burette up to the top mark with NaOH solution and titrate acid samples
- Titrate the four samples for accuracy. Record the volume of each trial.
- Calculate the concentration of the HCl reaction acid

### Step 7: Determining the calcium carbonate content of shells

- Weigh and record 0.15 grams of shell into a clean and dry 125 ml Erlenmeyer
- Add 5 ml of ethanol to the flask
- Pipette 25 ml of the acid solution into the flask to dissolve the eggshell
- Dissolve the eggshell by gently swirling the flask to mix and washing down the sides with distilled H<sub>2</sub>O until the volume is approximately 50 ml
- Gently boil the solution for 5-10 minutes until all of the shell is dissolved, washing the sides with distilled H<sub>2</sub>O to ensure the volume is approximately 50 ml
- Once cool, add 4 drops of phenolphthalein to each flask

### Step 8: Calculating the percent calcium carbonate in shells

Devise a data and calculation table to arrive at the following items:

Exact weight of shell (mg)	Mmoles of HCl consumed in the reaction ( $\text{mmol}_{\text{total}} - \text{excess mmol} = \text{mmol reacted}$ )
Volume of HCl added to flask with shell	Mmol of CaCO <sub>3</sub> (there is 1 mmol of CaCO <sub>3</sub> that reacts for every 2 mmol of HCl)
Volume of NaOH added during titration of acid and shell	Molar Mass of CaCO <sub>3</sub>
Mmoles of HCl added to dissolve shell	Milligrams of CaCO <sub>3</sub> reacted (use mmol of CaCO <sub>3</sub> and molar mass of CaCO <sub>3</sub> )
Mmoles of NaOH to neutralize excess acid	Percent CaCO <sub>3</sub> in eggshell
Mmoles of HCl equivalent to mmoles of base (1 mmol base neutralizes 1 mmol acid)	

### Wrap Up

Lead a discussion with the students of how Ca moves through this biochemical system and how pesticide can prevent Ca from building eggshell.

### Landscape Pesticide Use Scenarios

This activity will be very beneficial for your students and will start them really looking critically at the impact of the chemicals that are applied to the landscape. This activity will utilize the worksheets they compiled on the various chemicals explored through the unit and the Excel sheet they constructed with the persistence and sorption data and potential impact on water resources. The idea with this activity is to mimic the decision making process that should happen on the job as a landscape professional.

#### Scenario #1 Broadleaf Weeds in Turfgrass

Mr. Griffith's lawn is a great place for you and your FFA agronomy team to study weeds since it contains just about every broadleaf weed imaginable. He has hired the company you work for to apply a round of selective herbicide in order to kill off the weeds from his tall fescue lawn. Living along a country club, his backyard has a mild slope that leads to the water hazard on hole number four. His children love to go to the water to observe the large population of crayfish and fish that live among the native wetland vegetation on the edges of the water. You go to the herbicide storage closet at work and pull out the products you could possibly use on the turf area. Your options are Atrazine 90DF (Atrazine), Envoy Plus (Clethodium), Confront (Triclopyr), Lontrel (Clopyralid), Quicksilver (Carfentrazone-ethyl), and Round-up (Glyphosate). Which herbicide will you use for the job and why is this herbicide the best choice compared to the other options?

## Scenario #2 Spider mite Infestation in Landscape Plantings

Mrs. Dobbs loves her Dwarf Alberta Spruce trees she has in her yard, especially when she puts lights on them around the holidays. She recently has noticed that they are starting to turn brown in patches and it looks like there are spider webs all over them. She tried spraying some methyl ethyl death she bought at the local hardware store but the trees are continuing to turn brown. She finally decided to call a professional and you and your crew were assigned to her job. Upon assessing the situation you determine that there is a very bad infestation of spider mites. You also notice that her soils are very sandy and since she lives in the coastal plain of Delaware the water table is rather close, under 20 feet, from the ground's surface. You go to the pesticide storage closet at work and pull out the products you could possibly use on the shrubs. Your options are Acephate Pro 75 (Acephate), Carzol (Formetanate hydrochloride), Supracide 2E (Methidathion), Talstar (Bifenthrin), Temik (Aldicarb), and Warrior (Lambda-cyhalothrin). Which pesticide will you use for the job and why is this pesticide the best choice compared to the other options?

## Scenario #3 Aphid Infestation in Landscape Plantings

Mrs. Reardon's landscape is full of large perennial flower beds which she loves to add to each year to increase the diversity of plants in them. This season she was at the big box store and saw this great deal on some Montauk Daisy plants. They were a bit wilting but she bought all that they had since they were such a great deal, and she cannot pass up a bargain! Over the Memorial Day weekend she planted numerous daisy plants in each of her perennial beds to add a splash of white accenting the other flowers in her garden. In the last month and a half, most of the flowers in her gardens have started to show wilting signs and she has noticed a large population of small green insects all around the different flowers as she cuts them to put in vases in her house and that they all are rather sticky. She calls the company you are working for and you are assigned to the job. You go to assess the extent and cause of the problem. You determine that the plants that she bought for such a bargain must have been infested with aphids and that by letting it go for so long they have exponentially increased in numbers and your only choice is to treat them with chemicals. You are also introduced to her three cats and two Jack Russell terriers that are always playing and hiding in the landscape beds. You go to the pesticide storage closet at work and pull out the products you could possibly use on the shrubs. Your options are Astro (Permethrin), Acephate Pro 75 (Acephate), Malathion (Malathion), Sevin (Carbaryl), Talstar (Bifenthrin), and Temik (Aldicarb). Which pesticide will you use for the job and why is this pesticide the best choice compared to the other options?

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