

Pesticides in Groundwater

SLIDE 1:

This is Steve Johnson, University of Maine Cooperative Extension, bringing you this information on how pesticides get into surface and groundwater. It is possible to receive a Maine Board of Pesticides Control recertification credit for this presentation. As this presentation is approximately a half hour, another presentation would also have to be viewed. Additionally, a test must be passed with a minimum of 80 percent correct answers on each presentation. While there is no charge for viewing this information, there is charge for taking each test, whether the tests are passed or not.

SLIDE 2:

Water quality issues is a growing concern for all people in the State of Maine, across the United States, as well as the entire world. Our lifestyle revolves around access to clean water. This is not a new lifestyle, as we as a population have always relied on water for drinking, cleaning, transportation, food, power, among other needs and wants. The recreational value of water resources can not be overlooked. As our population increases on a limited resource base, water becomes more and more critical. We owe it to all of future followers to have access to the same or better quality of water we enjoy daily. This may mean not being able to continue doing some of the practices we utilize today. All Maine residents are going to have to "buy" into water quality as an issue of concern. Urban dwellers are going to have to consider the costs of the landfills and the tremendous amount of recyclable items which fill the landfills every hour of every day. Sooner or later, the four to five gallons to flush a toilet will have to be given some hard thought by some. Agriculture will not be exempt from the issue of water quality either. In fact, agriculture and silviculture could become a visible and an easy target as a result of pesticide and fertilizer run off and leaching. Contrary to doomsayers, our water quality in Maine is good.

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There has been tremendous effort in this direction for years. Salmon in the Penobscot River near Bangor is a sign that water quality efforts have been underway for years. Those living in the rural areas are more in tune to this than the urban dwellers. Growers continually tell me that they soil quality is much better now than it was several or ten years ago. There is also more awareness of the pesticide dangers now than there was ten years ago. This awareness, which has come from being concerned, has led to improved practices in the agriculture communities across the State of Maine. It is exactly this awareness and concern and adopting practices over the past few years that keeps our growers proud. Each grower that adopts a practice to reduce erosion, reduce pesticide usage, drift, or

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contamination is an environmentalist. That concept is lost on many urban dwellers. Farm families eat what they produce and drink the water under their farm. Water quality is an issue with them too. There has been an improvement in the water quality recently. Today is being used as a reference point for water quality. There is fertilizer and pesticide contamination of water. There is likely less contamination now than there was a few years ago. That, unfortunately, doesn't diminish the fact that there is tremendous potential for further contamination. That is the key to the issue right now. Let's keep our quality water just that way.

SLIDE 4:

Even in the worst-case scenario, only a fraction of any pesticide applied to soils will be transported to surface or groundwater. Pesticides applied to the foliage eventually will end up on or in the soil before possibly ending up in a water body. That concept allows pesticide-water interactions to be mainly concerned with pesticide-soil interactions. If only a fraction of an applied pesticide reaches a water body, some break down of the pesticide has to be partitioned to the environment. Some of this environment is associated with the soil and some of it is associated with the atmosphere. Four critical factors which determine how much of a pesticide is lost to the environment and not available to contaminate water are: volatilization, adsorption, decomposition, and water transport.

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VOLATILIZATION

Volatilization occurs when pesticide surface residues change from a solid or liquid to a gas or vapor after an application of a pesticide has occurred. Once airborne, volatile pesticides can move long distances off site. Fumigant pesticides (used to treat soil before planting and to treat structures such as homes or storage bins) are especially volatile. But, not all pesticides are volatile.

Volatilization and subsequent drift of pesticides is the loss of pesticides in the vapor phase from the plant and/or soil surface. Volatilization is the principle way that pesticides spread across large areas. Highly volatile compounds, such as 2,4-D, are so volatile that their application is limited in some regions. It is not uncommon for 2,4-D volatilization to occur on a wheat field and affect actively growing grape plants miles away. Some volatilization occurs before actual deposition of the pesticide. This loss is fairly common under conditions of pesticide application on hot, dry days. The amount of volatilization that occurs is a function of pesticide's chemical nature and is a balance between volatilization and

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redeposition, as well as chemical processes at the soil-air interface. Volatile losses of a pesticide can run as high as 90 percent in extreme cases.

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Water content of soil, porosity, and the amount of organic material all play a role in pesticide volatilization. Wet soils have less volatilization loss than dry soils do. Volatilization is reduced on dry soils by increased adsorption of the compounds. Pesticide volatilization is reduced with increased bulk density (less porosity) because the density of adsorptive sites is increased in the soil. The amount of organic matter in the soil determines the amount of pesticide adsorbed in the soil. The more that's adsorbed, the less volatilization occurs. Increased clay fraction in the soil also reduces the amount of pesticide volatilization loss. However, clay does not have the same degree of adsorptive characteristics as organic matter. Environmental conditions -- temperature, wind speed, evaporation and precipitation -- all influence the volatilization of pesticides from the soil surface, as well. Increased temperature causes increased pesticide volatilization. Wind has a very important affect in pesticide loss by volatilization. The wind removes the volatilized pesticide immediately above the soil surface. Wind can also increase pesticide losses during application. This loss is called drift. Evaporation also increases the amount of pesticide loss in some cases. Pesticides such as aldicarb, which is not strongly absorbed by the soil organic matter, will have increased volatilization losses with increased evaporation. Pesticides such as paraquat, which is strongly absorbed by the soil, will have a noticeable increase in loss by volatilization. Rainfall can have an affect on volatilization of pesticides by moving the chemical around in the soil and on the soil surface. Usually, the volatilization is reduced as the pesticide leaches from the soil surface into the soil matrix. If excessive precipitation occurs, there is potential for runs off into surface waters. Management of the pesticide application has a direct affect on volatilization losses. The depth of pesticide incorporation, the amount of pesticide applied and the formulation of the pesticide affects the amount of volatilization. The deeper and more thorough the incorporation of the pesticide, the less volatilization. However, this translates into more potential for leaching into water bodies.

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The amount of pesticide applied also has direct affect on the amount that will volatilize. It stands to reason that 10 pounds of pesticide will have more volatilization than five pounds will. In addition, some pesticide formulations are more prone to volatilization than others. The thin layer of wettable powder left on the soil has the potential to be wind borne under dry soil and high winds conditions. Any irrigation will have the same effect as precipitation, namely, the

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water may carry the pesticide below the soil surface and reduce volatilization losses. Soil management can help greatly with pesticide retention. Agronomic practices that increase soil aeration, surface tillage and overall good soil structure may increase volatilization of pesticides.

Loss of pesticides through volatilization reduces the amount available for surface run-off or for leaching into the ground water. This is not without a trade-off. The volatilized pesticide could well end up someplace else where it is not wanted.

SLIDE 8:

ADSORPTION AND DESORPTION

Adsorption of pesticides is the process of chemical bonding of a solute, in this case a pesticide molecule, to soil solids. The adsorption is actually a chemical bonding onto the soil particle, [either mineral (sand, silt, clay) or organic (organic matter)]. There are many different types of bonds which occur, some of which are stronger than others, but all play a role in the adsorption of pesticides by the soil. Adsorption temporarily eliminates the pesticide molecule from transport through water or as a vapor.

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Desorption, on the other hand, is the return of the pesticide molecule to the soil solution by the breaking or disassociation of the chemical bond. The amount of adsorption and desorption plays a major part in the water contamination potential of a given pesticide. Tightly held pesticides are not a major threat to groundwater. They are, however, a threat to surface water. Pesticides that are tightly held enter surface water with soil run off and siltation of rivers and lakes. Conversely, pesticides that are not tightly held by soil particles have the potential to percolate through the soil with water drainage. The contamination of surface water with pesticides that are not tightly held can occur with heavy surface water run off into water bodies.

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The process of adsorption and desorption is arguably the most important factor affecting contamination of water by pesticides. The degradation of the pesticide and its movement into a water body is directly or indirectly affected by adsorption and desorption. These factors control the mobility and the persistence of pesticides in the soil. Soil characteristics, pesticide characteristics and environmental conditions are all factors that determine the amount of a pesticide that is adsorped by a soil at a specific time.

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Soil organic matter plays a significant role in adsorption of most pesticides; clay minerals can play a role specifically some herbicides. Clay content, cation exchange capacity, soil-water content, bulk density and pH also influence soil adsorption. In general, the more organic matter in the soil, the more adsorption of pesticide occurs. There is a relationship between some pesticides and the clay content of soils, but usually there is not direct correlation of increased clay content and increased adsorption.

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The exchange capacity (cation exchange) of the soil can also influence the adsorption of specific pesticides (paraquat, diquat, and others), but does not have a major effect on most agricultural pesticides. The soil-water content of soils has a dramatic effect on pesticide adsorption when soils are very dry. At this point, pesticide adsorption increases dramatically. The solution concentration of the pesticide increases in dry soils simply because there is little water present to dilute it. This raised concentration in the soil solution causes a concentration gradient between the soil solution and the concentration of pesticide present as adsorbed pesticide on the soil particles. There are always forces of equilibrium present in nature. So in this situation, more pesticide will become attached to soil particles in order to eliminate the concentration gradient. Obviously, addition of water can serve to flush off a lot of this newly attached pesticide, but this can lead to water contamination.

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Increased bulk density of a soil increases the amount of adsorptive sites available. This is true within a soil type, but not necessarily between soil types. A sandy soil with a higher bulk density than a clay soil does not necessarily have more adsorptive sites.

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The soil pH will have a strong influence on the adsorption of a pesticide which is either a weak acid or weak base. The soil pH has the most effect in cases where the pesticide tends to disassociate in solution. Adsorption of other pesticides are relatively independent of soil pH. In general, soil pH is not as important as soil organic matter in determining adsorption. Water solubility, structure (notably the electric charge of the molecule) and the solution concentration or rate applied are pesticide characteristics that influence the adsorption of a pesticide in a soil. With a couple exceptions, the more soluble the pesticide, the less likely it is to be

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adsorbed by the soil. The electric structure of the pesticide is extremely important in establishing how strongly adsorbed the pesticide will be. As the solution concentration of a pesticide increases, the amount of pesticide adsorbed on the soil particles increases. This is a matter of concentration gradients again.

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The primary environmental characteristic influencing the amount of pesticide adsorption is soil temperature. The majority of pesticides have decreased adsorption with higher temperatures. Generally, the more strongly adsorbed the pesticides, the more the temperature affects the adsorption rate.

SLIDE 16:

Soil adsorption of pesticides reduces the amount available for leaching into groundwater. This does not mean that tightly adsorbed pesticides are the answer to ensuring pure water supplies. Compounds such as DDT are tightly held by the soil and do not contaminate groundwater. However, they are around for a long, long time. Additionally, the pesticides tightly held in soils can be found in surface water when soil erosion occurs.

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DECOMPOSITION

Pesticides can decompose either physically or chemically. Light most often causes physical degradation. Photo degradation, or breakdown by sunlight, can alter the chemical properties of a pesticide. Usually photo degradation of a pesticide makes it less toxic, and more susceptible to further breakdown. The rate of photo degradation of a pesticide relates directly to the amount of sunlight it absorbs. Once the pesticide is below the soil surface, however, photo degradation is not a factor.

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All soil-inhabiting organisms need carbon and nitrogen, among other elements, to support their growth and development. The amount of carbon and nitrogen present can limit the growth of soil microbes, particularly because the microbes seek nitrogen and carbon as they decompose pesticides, or any other compound. Nitrogen, phosphorous and potassium are needed for growth of microorganisms. The microbes will grow, and thereby degrade pesticides no faster than the availability of a rate-limiting nutrient. These microbes, are responsible for much of the decomposition of pesticides in soil.

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The second type of decomposition, chemical or biological, can occur at any time in the soil. However, the more chemically or biologically active the soil, the faster the degradation. The microbial population in the soil affects the rate of degradation so any influence on the microbial population affects it. Organic matter content, clay content, oxygen content, moisture, pH, nutrient availability and temperature also affect the soil microbial population, and therefore the rate of pesticide degradation. Similarly, the activity level, distribution and the amount of the microbial population, as well as the chemical properties and concentration of the pesticide have an affect on the degradation rate.

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Organic matter is the primary food source for the soil microbes, which help degrade pesticides. The amount of organic matter tends to regulate the size of the microbial population. Adsorption of pesticides into soil organic matter will remove the pesticide from degrading microbially. However, higher levels of organic matter adsorbing pesticides means higher populations of soil microbes, so the reduced availability of pesticides may be offset by the increased microbial population.

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The amount of clay in the soil has an indirect effect on the microbial population, and therefore an indirect effect on the degradation of pesticides. Clay attracts polarized or permanently charged cations (which include some pesticides), and tends to remove them from microbial attack. Clay content of a soil can affect the oxygen and water holding capacity of the soil, and therefore affect the microbial population. Oxygen-free or anaerobic conditions usually slow decomposition of pesticides. Most fungi, filamentous bacteria and some bacteria do not contribute to the chemical de-composition of the pesticides. However, some pesticides have chemicals which degrade best under anaerobic conditions. Interactions depend upon the compound. Different compounds, and even formulations of the same compounds will determine the sites available under aerobic or anaerobic conditions.

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Water, essential for growth of microbial organisms, if present in excessive amounts can lead to anaerobic conditions and slow pesticide degradation as well. Soil moisture conditions outside the range of 50 to 75 percent volumetric water content can reduce microbial activity, and therefore limit the degradation of pesticides. Additionally, decreased soil water levels tend to increase the soil adsorption of pesticides, further reducing the degradation.

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Soil pH affects microbial activity by limiting its enzymatic reactions. Most soil organisms grow within a highly specific pH range. A soil pH of five will favor filamentous bacteria over bacteria, although the opposite is true with a soil pH of 7.5. The particular microorganism most efficient at using the pesticide carbon as a food source varies with the pesticide.

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The soil temperature affects microbial populations by increasing or decreasing their chemical reactions. A traditional rule of thumb is that for each 18 degree F rise in temperature, the rate of the reactions doubles. A cold soil will not degrade pesticides as rapidly as a warmer soil. This condition holds for the range of temperatures tolerated by the soil microorganisms. Increased soil temperature increases the solute concentration of pesticides through desorption of the pesticides by the soil sites.

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Anything that increases the activity level or the size of the soil microorganism populations will usually increase the rate of pesticide degradation. However, there are exceptions to this. The make-up of the population can affect the rate of pesticide degradation. Some soils have populations that will decompose some pesticides faster than others, or faster than other soil microorganism populations. Some pesticides may need several different organisms for decomposition, while others may require a series of microbial attacks.

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In some cases, the majority of soil microorganism populations lack the enzyme or enzyme systems to degrade a pesticide. However, the presence of the pesticide as a food source tends to select that part of the population that can use it, especially with repeat exposures to the pesticide. This effect is well documented with some soil-applied pesticides.

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The actual concentration of the pesticide has an affect on the microbial population and therefore the rate of degradation. High concentrations of a pesticide may be very toxic to some or all of the resident soil microorganisms. The soil will then be recolonized with microbes from other areas, once the concentration is no longer toxic. The pesticide concentration may also be too low to select for microbial populations which would degrade it.

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A pesticide's chemical properties greatly influence its decomposition status. The solubility and electric configuration, among other factors, affect the rate of degradation. Halogenated hydrocarbon compounds are not as readily degraded as sulfur- or phosphorous-based compounds.

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SURFACE RUNOFF

Runoff is water and any associated dissolved or suspended matter that leaves an area. Pesticide runoff is that pesticide dissolved, suspended particulate, or absorbed on sediment that are transported by water from a treated land surface.

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On a large scale, pesticide runoff is affected by site-specific factors including slope, tillage patterns, soil residue, field topography, and actual crop in the field. Site-specific factors which determine the amount of surface runoff include the chemical properties of the pesticide (is it soluble or insoluble), the rate and the method of application of the pesticide, the soil characteristics and moisture conditions at present and during the recent past, ground cover, and the distance the runoff must travel to actually become runoff, and the rainfall pattern and intensity.

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On a smaller scale, contribution to pesticide runoff is pesticide washoff from plant surfaces, concentration of flow along the surface, and development of rills in which the runoff travels. Of course, volatilization, adsorption and desorption, and degradation of the pesticide have occurred and are likely still occurring. The surface runoff can include water flow in most of the top one half inch of soil. In general, the annual runoff of loss of pesticides are two to three percent of the total applied. The conditions of Maine, and even more over, farming in Maine would lead me to think that the surface runoff of pesticide would be even lower.

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On an even smaller scale, soil runoff starts with the removal of pesticide, in the suspended or dissolved form, from the soil pores to the runoff stream. There is desorption from the soil particles which occurs, releasing them into the runoff stream. Additional contributions to the soil runoff stream are from soil particles with attached pesticide, and actual physical movement of the pesticide particle into

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the runoff stream. Any incorporation of a pesticide will reduce the runoff, as will having the pesticide leach below the soil surface prior to a runoff episode.

SLIDE 33:

Rainfall parameters which affect pesticide transportation are numerous. The highest concentration of pesticide in runoff waters occurs in the first available runoff. Subsequent runoff events will have less pesticide included. When the rainfall intensity is greater than the infiltration rate, runoff will occur. The intensity of rainfall can affect the depth of soil surface interaction involved in runoff. A warmer rain tends to increase the solubility of pesticides and reduce the adsorption, therefore increasing the pesticide available to be included in runoff.

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Soil factors of texture, organic matter, compaction, moisture content, and slope all have an influence on the pesticide included in runoff water. Soil texture affects the soil erodability and the particle size influences how much of the soil fraction is available to be carried with the runoff water. Compaction and crusting of the soil increases the concentrations of pesticides available for runoff by decreasing the time to runoff and the severely decreasing the infiltration rate. The lowered infiltration rate accounts for the decrease in the water needed to exceed this rate and cause runoff. Similarly, the soil moisture content serves to decrease the amount of rain needed to cause runoff. Increased slope serves to increase the runoff rate. Increased rate of soil detachment and velocity of the runoff are resultant from increased slope.

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There are specific influences a pesticide will have on the amount which is susceptible to runoff. The more soluble the pesticide, the less likely it will appear in runoff, as it would be more readily leached into the soil, beyond the half inch or so of top soil which interacts in the water runoff. Some pesticides are strongly absorbed to the soil surface and would be more susceptible to runoff with soil erosion. The chemical charge and nature of the pesticide can play a large role in the amount of a pesticide is available to runoff. Tightly bound pesticides will tend to move with the soil particles, whether they are organic portions or mineral portions of the soil. Pesticide persistence at the soil surface increases the possibility that they will be included with runoff. Some formulations are more susceptible to inclusion with runoff reactions of water than are others. Wettable powders are likely to be included with the soil particle when they are transported with the runoff; granular formulations are less likely to be included with runoff than are liquid formulations. A more soluble formulation would less likely be included with

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runoff as it would tend to leach into the soil. The higher the rate of application, the more potential pesticide is available for runoff. Placement of a pesticide by incorporation reduces the amount available for runoff.

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Crop residues left on the surface can reduce the amount of runoff which occurs. They can also decrease the amount of soil erosion and thereby reduces transport of pesticides attached to soil particles. Any erosion control practices and especially those performed where irrigation is used, from contour farming to vegetative buffer strips will reduce runoff.

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