

Pesticide Use Practices and the Impact on Water Quality in Oregon Communities

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There is a growing concern for the impact of chemical use in urban environments on surface and groundwater quality. Chemicals of the greatest concern are those being used in high volume, are persistent, bioaccumulative, and toxic to both humans and wildlife. In Oregon, Senate Bill 737 (2007) aims to encourage source reduction of persistent bioaccumulative toxins (PBTs) by directing the Department of Environmental Quality (DEQ) to produce a list of prioritized persistent pollutants that will be the target of Oregon communities for source reduction.

Types of pollutants of interest include polyaromatic hydrocarbons (PAHs), halogenated flame retardants, pesticides, pharmaceuticals and personal care products, perfluorinated surfactants, heavy metals, polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), dioxins and furans, and phthalate esters.

The community of Gresham in Oregon is the setting for this project. This research project evaluates just one class of pollutants commonly used in Oregon communities - pesticides. Pesticides are comprised of compounds with a wide range of chemistries with only one attribute common to all - efficacy in controlling pests. Pesticide use is ubiquitous in urban environments. Common uses include pest control in residences, businesses, public venues, and along rights of way (roads, rail lines, power lines, etc.). Outdoor pesticide use has the greatest potential to reach surface and ground water as well as the subsurface biosphere.

This project evaluates current pesticide use in the city of Gresham and what can be done to make sure those practices are in keeping with the city's current sustainability pledge as well as increasing eco-green practices. The city of Gresham's sustainability pledge is as follows:

Gresham will become a national model of sustainable planning, design, and development practices. Green practices will help form the image of the City, helping to attract sustainable industries, innovators, professional companies, new residents and a talented work force.

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The City of Gresham's website has a direct link to the Department of Environmental Quality (DEQ) website. The Oregon DEQ has several projects that they are working on in an effort to integrate pest management practices that are more sustainable and involve fewer pesticides. Their website on sustainability has a link to the Environmental Protection Agency's (EPA) web site. The EPA's website leads from urban areas to policies (in urban areas) to storm water best management practices (BMPs) as well as integrated pest management (IPM). All of these connections highlight how IPMs, BMPs, storm water discharge, and sustainability are all interconnected.

The EPA's website also touches on Low Impact Development (LID) as "an approach to land development (or re-development) that works with nature to manage stormwater as close to its source as possible. LID employs principles such as preserving and recreating natural landscape features, minimizing effective imperviousness to create functional and appealing site drainage that treat stormwater as a resource rather than a waste product. There are many practices that have been used to adhere to these principles such as bioretention facilities, rain gardens, vegetated rooftops, rain barrels, and permeable pavements. By implementing LID principles and practices, water can be managed in a way that reduces the impact of built areas and promotes the natural movement of water within an ecosystem or watershed. Applied on a broad scale, LID can maintain or restore a watershed's hydrologic and ecological functions. LID has been characterized as a sustainable stormwater practice by the Water Environment Research Foundation and others." This again ties in with sustainable practices.

The subsurface biosphere can play a major role in pesticide degradation and transformation to non-toxic products. The near surface soil horizon, particularly those with extensive plant root systems, create a nutrient and oxygen rich environment that can support a rich microbial community. In addition, plant uptake and metabolism may contribute to pesticide transformation and bioaccumulation. However, the contribution of the subsurface biosphere to pesticide degradation in urban landscapes is largely unknown.

The project was not finished in the time frame of the SBI and will continue on for the rest of my collegiate career. I will be expanding the list of pesticides to include all of the known pesticides that are being used in the city as they are reported. I will also continue to collect data on what types of organisms are most likely to be found in the different types of soil in the city.

The first task is to acquire a list of pesticides being used by the city of Gresham, outdoor pesticide use in the city, Tri-met, and other users when possible. The city of Gresham requires that the people who apply the pesticides in a commercial manner report what they use when and where. The city also has a volunteer reporting system that allows the citizens of the city to report private use, but they are not required to do so. This system is called the Pesticide Use Reporting System and can be found on-line. The data from this system was given to us by the city, it is sorted by zip codes in the city. The Tri-met data requires that a form be filled out and sent into the main office in writing with a signature. When I first tried to get the information on the net, on the phone I talked to several different people I was transferred to a lady that told me where to find the application that

I would need to fill out to receive the information that I was looking for. I was told that it had to be physically filled out and sent in.

The second task is to learn the ArcGIS system, how it works, how to input data, and what data was going to be needed for this particular project. The ArcGIS (geographic information system) is a unique system that has many different applications that can be used in various disciplines. This project uses ARC GIS as a platform to evaluate how different pesticides move in the soils. In addition this information is useful in evaluating pesticide fate as a function of soil types, pesticide degrading microbial community, weather patterns, land uses, pesticides chemical and physical properties.

<http://www.esri.com/> is a website that teaches people how to use the ArcGIS system.

There are many different site that trains people in the use of the ArcGIS program, with in the training system these are set up as there own lesson. Each lesson has a number of chapters that are needed to complete the lessons with tests at the end of each chapter to ensure a grasp of the material. These chapters can take between one to four hours to complete depending on the level of computer skills the individual has.

The third task— second and third tasks occur simultaneously — is to assemble a database on the pesticides of interest in the city. The focus was on eleven pesticides that the city uses 2,4 D, carbaryl, clethodim, dichlobenil, glysophate, isoxaben, metaldehyde, naphthalene, simazine, triclopyr, trifluralin. Collected were k_d/k_{oc} , half life, solubility, pka, vapor pressure and Henry's law constant. This data has been placed into an excel sheet.

The environmental fate in soils for the first eleven chemicals that we decided to start with is as follows:

2,4-D:

2,4-D amine salts and esters are not persistent under most environmental conditions. Typically, the ester and amine forms of 2,4-D are expected to degrade rapidly to the acid form. Soil half-life values have been estimated at 10 days for the acid, diethylamine salt, and ester forms. Another study estimated a soil half-life for the ester form EHE ranging from 1-14 days with a median half-life of 2.9 days. In aerobic mineral soils, a half-life of 6.2 days was estimated. A granular formulation of the BEE form was detected in aquatic sediments for 186 days post-application, perhaps due to either the formulation or slow de-esterification of the sediment-bound chemical. Microbial degradation of 2,4-D in soil involves hydroxylation, cleavage of the acid side-chain, decarboxylation, and ring opening. The ethyl hexyl form of the compound is rapidly hydrolyzed in soil and water to form the 2,4-D acid.¹ Other comparative studies demonstrated that ester and amine salt forms of 2,4-D have similar soil dissipation rates because they are converted rapidly to the same anionic form. (National Pesticide information Center)

Carbaryl:

Water:

In the environment, carbaryl breaks down primarily through hydrolysis and microbial degradation to 1-naphthol and carbon dioxide. Carbaryl degrades in distilled water with a half-life of 3.2 hours at pH 9 and 12.1 days at pH 7. Carbaryl is stable in acidic water

with a half-life of 1600 days at pH 5. Carbaryl is degraded by photolysis in water, with a half-life of 21 days. Scientists observed that carbaryl in river water (pH 7.3 - 8), exposed to natural and artificial light, degrades completely within 2 weeks. Carbaryl has low solubility in water and sorption to soil particles depends on the organic matter content of the soil. Carbaryl is moderately mobile in soils and can be found in the groundwater and surface water due to its widespread use and persistence under acidic conditions.

Air:

Carbaryl dissolved in water has low potential to volatilize. The low vapor pressure for carbaryl suggests that evaporation from treated surfaces will be minimal.

Soil:

The half-life of carbaryl ranges from 4 days in aerobic soils to 72.2 days in anaerobic soils. Carbaryl degrades more rapidly in aerobic soils due to microbial action. Carbaryl degrades nearly twice as fast in flooded soils compared to dry soils due to hydrolysis and microbial action.

Plants:

Scientists observed 59.1% of carbaryl remaining 1 week after injection into bean plants and only 6.9% after 2 weeks. The mean foliar half-life of carbaryl on plants is 3.2 days. Carbaryl is slowly taken up by plants and breaks down through hydrolysis producing 1-naphthol, 4-hydroxycarbaryl, 5-hydroxycarbaryl, and methylol-carbaryl. (National Pesticide information Center)

Clethodim:

Soil and Groundwater:

Clethodim is of low persistence in most soils with a reported half-life of approximately 3 days. Breakdown is mainly by aerobic processes, although photolysis may make some contribution. Volatilization loss and hydrolysis are probably not important processes in the soil breakdown of clethodim. The main breakdown products in soils under aerobic conditions are sulfoxide, sulfone and oxazole sulfone. Clethodim and these degradates are weakly bound to soils, with reported soil K_d (soil-water partition coefficient unadjusted for soil organic matter) values of 0.05 and 0.23 over a range of five soils. Thus, while it may be somewhat mobile in the soil environment, it is very short-lived. EPA has stated "under present use patterns and under most circumstances clethodim does not appear to threaten groundwater". In field studies, no vertical movement of the parent compound or residues was observed below the top 20 cm of the soil.

Surface Water:

Clethodim may be highly persistent in the aquatic environment. Reported half-lives for clethodim in the aquatic environment are 128 days in the aqueous phase and 214 days in the sediment. The reported hydrolysis half-life at pH 7-9 is approximately 300 days. The main pathway for degradation of clethodim in the aquatic environment is anaerobic metabolism by microorganisms. However, due to the low persistence and mobility of the compound, it is unlikely to be found in surface waters.

Vegetation:

Clethodim is rapidly degraded on the leaf surfaces by an acid-catalyzed reaction and photolysis. Remaining clethodim will rapidly penetrate the cuticle and enter the plant. Little information is available regarding translocation and accumulation, but it is

hypothesized that it may translocate and accumulate at growing points. Within soybeans, cotton and lettuce it is rapidly metabolized.

Dichlobenil:

The half-life of dichlobenil in soil is about 60 days. It is moderately mobile in the environment and has the potential to contaminate groundwater. (Washington Department of Transportation)

Glyphosate:

Glyphosate is stable to hydrolysis and photodegradation. Metabolism of glyphosate to amino methylphosphonic acid (AMPA) by microorganisms is the major route of degradation in the environment, particularly in soil. The half-life of glyphosate in soils ranges from 3-130 days. Researchers evaluated the soil dissipation of formulated glyphosate products in field studies. They noted half-lives of 3-174 days. Glyphosate and its metabolite AMPA strongly adsorb to soil and have a low potential to leach to ground water. Researchers monitored glyphosate applied to a pond and calculated a water-dissipation half-life of 7.5 days. Binding to suspended sediment may influence aqueous dissipation of glyphosate. Glyphosate may adversely affect nontarget plants. Strong soil adsorption limits glyphosate's phytotoxicity in soil. (National Pesticide information Center)

Isoxaben:

A typical half-life for isoxaben in soils is 100 days. Microbes and sunlight break down isoxaben in the environment. Isoxaben's potential to leach to groundwater is low; surface runoff potential is high; and potential for loss on eroded soil is high. Isoxaben has moderate volatility and the potential for loss to the atmosphere is moderate. Isoxaben does not bioconcentrate (build up) through the food chain. Plants take up isoxaben primarily through the roots. Isoxaben is translocated (moved throughout) to other plant parts. (Washington Department of Transportation)

Metaldehyde:

Soil and groundwater:

Metaldehyde is of low persistence in the soil environment, with a half-life on the order of several days [8]. It is weakly sorbed by soil organic matter and clay particles, and is soluble in water. Due to its low persistence, it is not a significant risk to groundwater.

Water:

Metaldehyde undergoes rapid hydrolysis to acetaldehyde, and should be of low persistence in the aquatic environment.

Vegetation:

Many types of flowers lose their color when they come in contact with metaldehyde dust or spray.

Naphthalene:

There are no acceptable fate studies for naphthalene. A single supplemental study has been provided which summarizes open literature data on adsorption/desorption and aerobic soil metabolism data (MRID 45346801). Other fate parameters needed to conduct

the ecological assessment have either been extrapolated from the open literature data (e.g., aerobic aquatic metabolism half life) or conservatively assumed to be stable (photolysis and hydrolysis). The lack of these data provides uncertainty to this assessment. Elimination of this uncertainty would require submission of additional data for these fate processes. However, the data used in the assessment are sufficient to allow evaluation of potential risk, and no additional environmental fate data are needed for current outdoor uses of naphthalene. (Naphthalene Reregistration Eligibility Decision, EPA)

Simazine:

Soil and groundwater:

Simazine is moderately persistent with an average field half-life of 60 days. Soil half-lives of 28-149 days have been reported. Residual activity may remain for a year after application (2 to 4 kg/ha) in high pH soils. Simazine is moderately to poorly bound to soils. It does, however, adsorb to clays and mucks. Its low water solubility, however, makes it less mobile, limiting its leaching potential. Simazine has little, if any, lateral movement in soil, but can be washed along with soil particles in runoff. Simazine is subject to decomposition by ultraviolet radiation, but this effect is small under normal field conditions. Loss from volatilization is also insignificant. In soils, microbial activity probably accounts for decomposition of a significant amount of simazine in high pH soils. In lower pH soils, hydrolysis will occur. Simazine residues have been detected in groundwater in at least 16 states. The range was from 0.00002 mg/L to 0.0034 mg/L.

Water:

The average half-life of simazine in ponds where it has been applied is 30 days, with the actual half-life dependent on the level of algae present, the degree of weed infestation, and other factors. Simazine may undergo hydrolysis at lower pH. It does not readily undergo hydrolysis in water at pH = 7.

Vegetation:

Plants absorb simazine mainly through the roots, with little or no foliar penetration. From the roots, it is translocated upward to the stems, leaves, and growing shoots of the plant. It acts to inhibit photosynthesis. Resistant plants readily metabolize simazine. Plants that are sensitive to simazine accumulate it unchanged. It is possible that livestock or wildlife grazing on these plants could be poisoned. (EXTOXNET)

Triclopyr:

Soil:

In soil, triclopyr has a half-life ranging from 1.1 to 90 days depending on soil type. Several resources have reported a 46 day half-life for triclopyr. The half-life of the major metabolite, TCP, is 30 to 90 days. • In soil, both forms of triclopyr degrade into several intermediates before ultimately degrading into carbon dioxide (CO₂).

Water:

Triclopyr in water is predominantly degraded by exposure to sunlight, with half-lives ranging from 1 to 10 days depending on water conditions, such as turbidity. Triclopyr is stable in water without sunlight.

Air:

The vapor pressure of triclopyr is 0.2 mPa at 25° C.

Plants:

Triclopyr's half-life in plants ranges from 3 to 10 days. The main metabolite is 3,5,6-trichloro-2-methoxypyridine. (National Pesticide information Center)

Trifluralin:

Breakdown of Chemical in Soil and Groundwater:

The substituted dinitroanilines do not move much in the soil, but remain where they are placed at application (Casarett & Doull's Tox. 2nd Ed. 1980). Trifluralin is strongly absorbed on soils ($K_{oc} = 7,000$ g/ml) and nearly insoluble in water. Therefore leaching and groundwater contamination by trifluralin is not expected to occur. Because adsorption is highest in soils high in organic matter or clay content and adsorbed herbicide is inactive, higher application rates may be required for effective weed control on such soils.

Trifluralin is subject to degradation by soil microorganisms. Trifluralin remaining on the soil surface after application may be decomposed by UV light or may volatilize.

Recommended application rates give season long weed control, but fall-seeded grain crops planted in soil treated with trifluralin during the preceding spring were not injured under warm, moist conditions. The half-life of trifluralin in the soil is 45 to 60 days or about 6-8 months (2.5 kg/ha). After six months to one year, 80- 90% of its activity will be gone. (EXTOXNET)

The following table (Table 1) is a table of the physical properties, half life, and key metabolites of the above list of chemicals.

Table 1 Physical properties of pesticides used in Gresham

Name	Vap press at 25 °C	solubility	pka	Log Kow	Koc	half-life	Key Metabolites	Source
2,4-D	1.9 x 10 ⁻⁵ Pa 1.4x 10 ⁻⁷ mmHg	8.6 x 10 ⁻⁶ atm·m ³ /mol	2.8 (PPD)	0.001 M sol'n pH 5: 2.14 pH 7: 0.177 pH 9: 0.102	20-136	13 days (I)	2,4- dichlorophenol	NPIC
Carbaryl	<5.3 mPa	40 mg/L	10.4 (I)		211 (I)	12 days (I)		NPIC = (N) (I) IUPAC footprint
Clethodim	<1 x 10 ⁻² mPa	5450 (I)	4.47 (I)		40 (I)	5.5 days (I)		EXTOXNET (I) IUPAC footprint
Dichlobenil	88 at 25oC (mPa) (I)	14.6 at 20oC (mg l-1) (I)				70 days (I)		(W) = WA DOT (I) IUPAC footprint
Glysophate			2.3 (PPD)			69 DAYS (I)		NPIC = (N)
Isoxaben	5.50 X 10 ⁻⁴ (I)	0.93 (I)	9.78 (I)			601 (I)		(W) = WA DOT (I) IUPAC footprint
Metaldehyde	Negligible at room temperature	260 mg/L @ 30 C			85 (I)	stable in aquious 4.4 days in soil (I)		EXTOXNET

Napthalene	8.0 x10 ⁻² mm Hg (PPD)	3.0 mg/L (PPD)						
Simazine	0.000810 mPa	5 mg/L	1.6 (PPD)		130 (I)	60 days (I)		EXTOXNET (I) IUPAC footprint
Triclopyr	0.168 mPa (E)	440 mg/L (E)	2.7 (PPD)		48 (I)	0.1 days (I)		NPIC = (N) EXTOXNET = (E) (I) IUPAC footprint
Trifluralin	1.99 x 10 ⁻⁴ mm Hg	0.0024% at 27 degrees C water Acetone > 50 g/100 ml Methanol 2 g/100 ml Xylene 81 g/100 ml	7.0 (50% suspension)		7000 g/ml	0.4 days (I)		EXTOXNET

The fourth task is to gather land use data. The city of Gresham has GIS map of the land uses in the city, how water flows through the city including storm water discharge, and where in the city pesticides are being applied; other GIS sources will also be used. In the city there are features called bio-swells, these are pit like structures that are meant to slow the flow of water through the landscape so that the pesticides have time to settle out of the water and into the soil if the bio-swells are able to do this then the pesticides are not likely to be in the public water ways such as Johnson Creek that eventually feed into the Willamette River.

Some obstacles to this project include non-compliance in reporting of pesticide use, largely unknown soil microbial community, and incomplete data on the pesticides chemical and physical properties. The city itself will let us know what active ingredients they are using. Landscape companies are required to report their usage. The city has a voluntary reporting system for its residents; however private residents are not required to report to the system. The living organisms in the soil are largely unknown, and can only be guessed at. Some of the pesticides that are in use now do not have a lot of data in the literature.

When I asked about a list of microbes that would be found in the different soil types, given their current land use, I was told that types and amounts is largely unknown. This information would be helpful since it is believed that most pesticide degradation is due largely to the microbial community in the soil. It is thought that pesticides are metabolized by various fauna in the soils to their most basic structures. These structures are then taken up by the plant life. If we knew what organisms were in the soil and how the metabolized various compound then we would have a much better understanding of why some pesticides persist in some soils but not in others. We would also be able to design pesticides that controlled the pest and supported the microbial community. It would also be good to know what and how much of these pesticides are doing to the microbial communities.

Given what we do know, there is some certainty that most microbes live in the area of the soil termed as the rhizosphere. The rhizosphere is a very diverse layer of the soil that holds the root system of the plants that one sees on the surface of the soil. The roots hold nutrients that microbes can access either in a symbiotic or parasitic relationship. It is therefore thought that this very small area holds the largest amount of organisms that break various compounds, such as pesticides, down in the soil. Unfortunately there is relatively little data in this field.