Rationale and Analysis for Residential Pesticide Relative Cumulative Ranking *(unpublished)*

***Note**: Ranking of pesticides is currently being recalculated; this overview is only of one approach*

Rationale

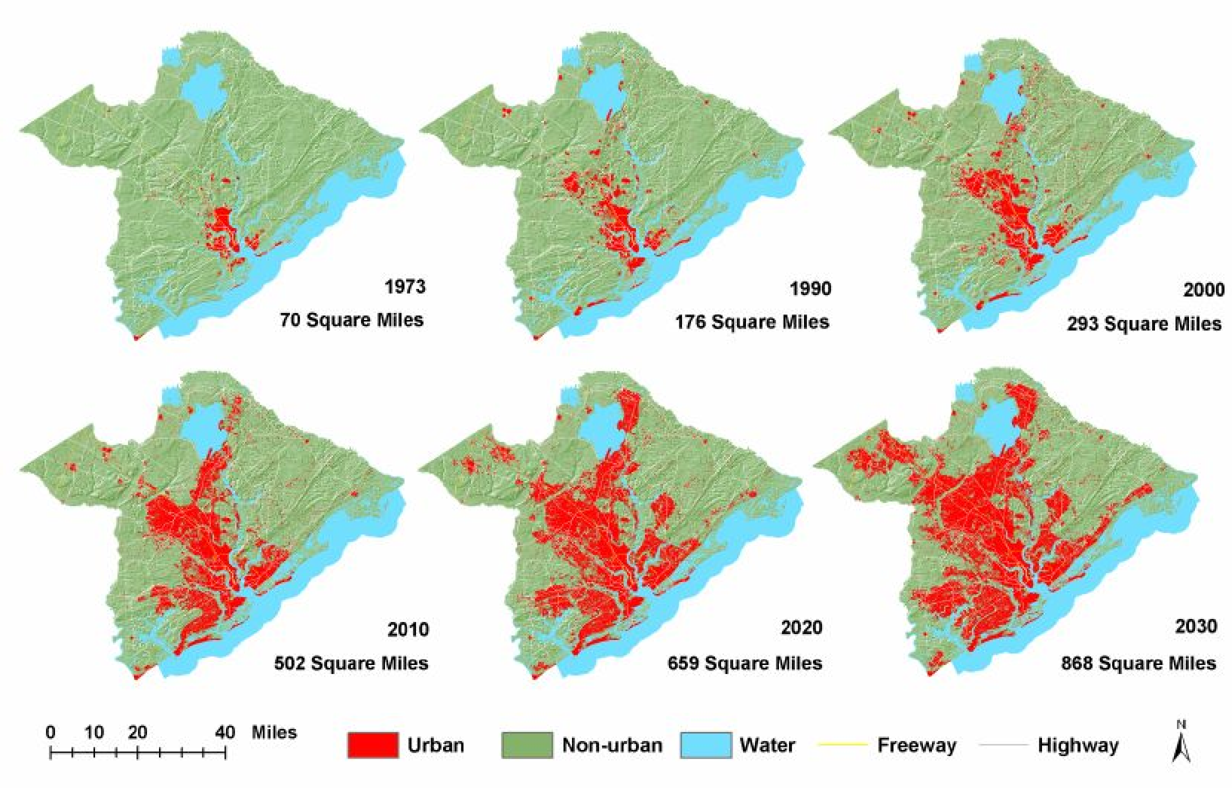
Pesticides and Urbanization

Approximately one billion pounds of conventional pesticides (i.e., herbicides, insecticides, fungicides, and a mixed group of fumigants, nematicides, and other pesticides) are used each year in the U.S. to contain or control weeds, insects, and various other pests (Gillom et al. 2006). As of 1997, approximately 900 pesticides were registered in the U.S. for use in more than 20,000 different products on the market (Gilliom et al. 2006, Aspelin and Grube 2006). Additionally, about 4 million pounds of non-conventional pesticides (e.g., chlorine disinfectants, wood preservatives, and other specialty products) are used each year in the U.S. (Gilliom et al. 2006). New pesticides – typically 10-20 per year as indicated by registration from 1967 to 1997 – are introduced as new pests-related problems arise, organisms gain resistance, and older products are determined to be more harmful than initially reported and are phased out (Aspelin and Grube 2006). The U.S. EPA estimates that approximately 75% of all pesticide usage in the United States is agricultural and the other 25% is for home, garden, industrial, commercial, and government applications (Hartwell 2011). Much emphasis has been put on pesticides and pesticide use in agricultural areas, as this usage category does account for the majority of use. However, as the nation's population continues to grow, it is imperative to learn which pesticides – as well as uses – should be accounted for in residential scenarios. This is particularly true in the South Carolina coastal zone, where rapid population growth is accompanied by urban sprawl (Figure 1 from Allen and Lu 2003).

Preceding the Civil War, South Carolina was an essential agricultural asset to the nation (Allen and Lu 2003). In the post-Civil War era, South Carolina's growth came to a halt for almost a century (Allen and Lu 2003) until urbanization and new suburban areas began to increase in the state in the 1950's and 60's (Frey and Speare 1988, Long 1988). In the 1970's immigration to the state resulted in changed population dynamics – with immigrants augmenting natural population increases (Brown and Wardwell 1980, Allen and Lu 2003). Acceleration of this changed population dynamic has occurred over the previous two decades – particularly within the South Carolina coastal zone (Allen and Lu 2003). From 1960 to 1990, urban growth well exceeded population growth at a ratio of 6.2:1 – almost triple that of the national average (2.3:1) (Allen and Lu 2003). Encroachment and overlap of urbanized areas into natural coastal environments potentially impacts the surrounding ecosystem and economically important commodities if proper management strategies are not integrated into developments and city planning.

Intricately linked to urban expansion is the use of pesticides within homes, on lawns and turf grass, in right-of-way easements, landscaped areas (ornamentals), and for vector control. As pest problems (e.g., severity of infestation, area of application, and type of application) are unique in many respects, educational efforts on overall toxicity, environmental fate and transport characteristics, and proper application of pesticide formulations needs to occur for the general population – particularly within the coastal zone given its continued population growth rate and development preferences. Suburban developments are potentially located near or downstream of agricultural areas as well and have close proximity to the estuarine and costal ecosystems. If residents understand the potential hazard improper use of pesticides presents – then efforts can be made by all to maintain the functionality, economic viability, and aesthetic appeal of a balanced estuarine ecosystem.

Figure 1 (From Allen and Lu 2003): The GIS figures illustrate predicted urban expansion over a portion of the South Carolina coastal zone with the current population growth to urban expansion ratio of 6:1. The model was built using a binomial logistic framework, along with a rule-based suitability module and focus group involvement, and is designed to predict land transition probabilities and simulate urban growth under different scenarios.



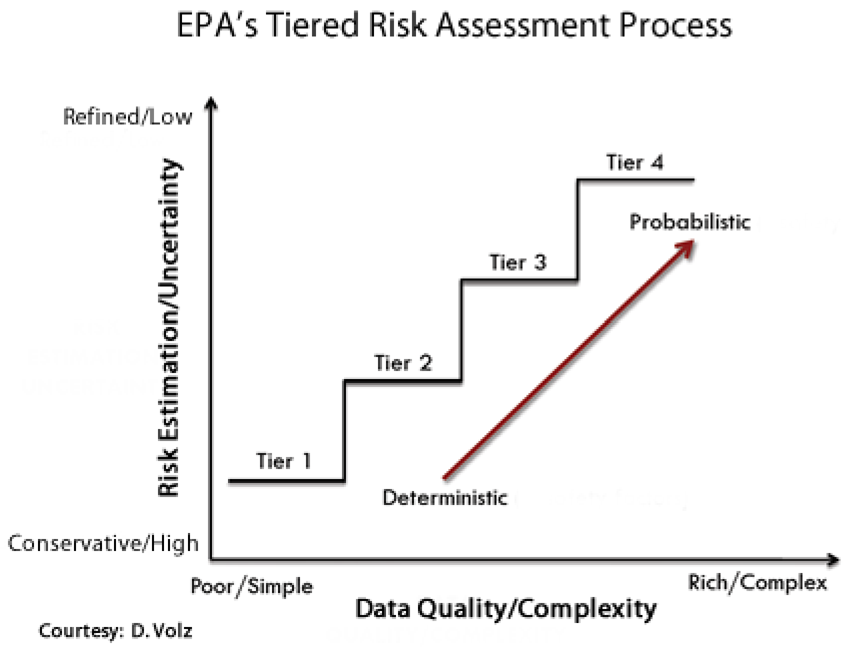
Ecological Risk Assessment for Pesticides *(Hazard and Exposure)*

The EPA takes a tiered approach to the Risk Assessment process conducted for pesticides (Figure 4) (EPA 2011). If a compound is found to likely to adversely affect the ecosystem then the risk assessment increases in complexity and refining the risk assessment and reducing uncertainties. For Tier I and II ecotoxicological bioassays, Risk Quotients ($RQ = EEC/LD_{50}$,

LC_{50}, EC_{50}) are generated for representative taxa from different trophic levels (e.g., non-vascular and vascular plants, aquatic and terrestrial invertebrates, warm and cold water fish species, avian species, and mammalian species). In most cases, a risk-based approach for cumulative assessment has been an effective methodology. In many cases for these types of analyses, pesticide use data was estimated or available to the developers so there was a measure of exposure. Using this approach RQs are compared to an established Level of Concern (LOC) that should not be exceeded. The RQ threshold (LOC) varies depending on acute and chronic endpoints, and endangered species. Often, a pesticide may exceed the LOC for the some toxicity endpoints being assessed, but not for other endpoints. In these cases, label changes and mitigation measures are tools the EPA uses to address exceeded LOCs. It is important to note when looking at the LD/LC_{50} for toxicity values, the lower the value the more toxic the compound is for the endpoint being assessed. Furthermore, for chronic toxicity, if the RQ value exceeds 1.0, then it exceeds the LOC set for chronic toxicity (Figure 5).

To determine the EEC used in the RQs for ecological risk assessment, the EPA uses the PRZM (Pesticide Root Zone Model) (Carsel et al. 1984) – EXAMS (Exposure Analysis Modeling System) (Burns et al. 1991) model to simulate environmental fate and transport of a compound. The PRZM model simulates chemical movement in soil within and immediately below the plant root zone and EXAMS is a surface water model that evaluates the fate, transport, and exposure concentration of pesticides. Together, the PRZM-EXAMS model simulates pesticide runoff scenario predominantly for agricultural applications. The model uses a 10 hectare field (crop area) with simulated runoff into a static 1 hectare pond that is 2 meters in depth. The output from the model provides daily pesticide concentrations (usually in ppb) referred to as Estimated Environmental Concentrations (EECs) in the standard farm pond over the thirty-six year period for which rainfall data is available. This became the Environmental Fate and Effects Division (EFED) of the EPA standard method for pesticide aquatic ecological exposure assessment as it was shown to also be a good predictor for concentrations in small but ecologically important upland streams (Effland et al., 1999). Importantly, the EPA's tier 2 assessment model contains golf course adjustment factors to account for percent acreage of a golf course that is labeled for treatment with an individual pesticide - creating better estimates for golf course scenarios.

Figure 2:



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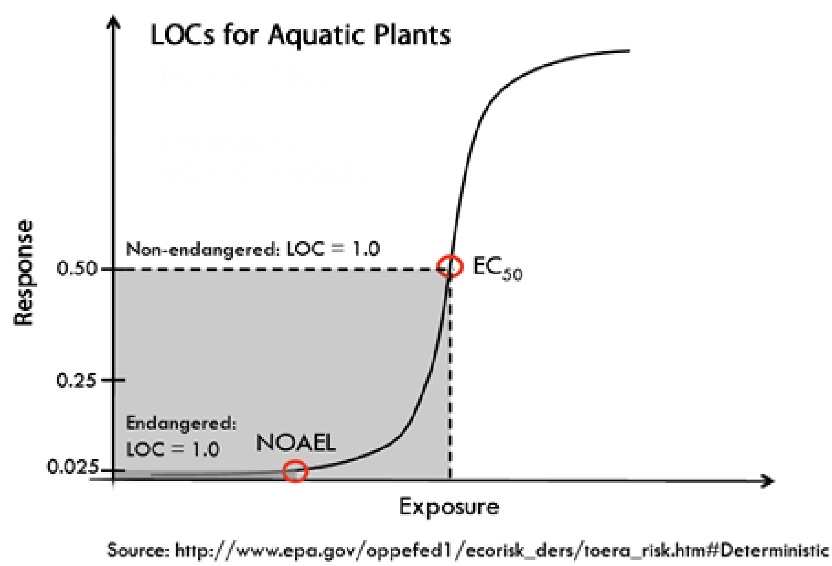

Increasing Complexity in Risk Assessment Approaches and Models

In order to estimate risk, one must also consider hazard and estimate of exposure. RQs give one measure of ecological risk, but still are based on deterministic quotients (i.e., RQs) and not necessarily accounting for effects distributions over space and time. While this method of risk assessment is an effective strategy, it is also filled with uncertainty. Taking a probabilistic approach generates distributions of exposure and effects decreasing uncertainty in the risk assessment. Using Monte Carlo analysis (Zolezzi et al. 2005) gives 10,000 simulations generating a distribution expressing the likelihood of quotients being exceeded. There are currently programs available used for taking the probabilistic risk approach including @Risk (Palisade – www.palisade.com/risk) or Crystal Ball (Oracle – www.oracle.com).

Project Goal and Objectives

Goal and Objectives: The goal of the proposed research is to provide an easily understandable synthesis of information available for pesticides used for six various situations (e.g., golf course maintenance) along the South Carolina coastline, specifically within the Port Royal Sound area. The objectives are to: 1) provide a technical section for each group (e.g., residential pesticides) of pesticides as well as a synthesis of information available and conveying it in terms that everyone can understand and 2) to provide useful, less toxic, cost-effective alternatives to conventional pesticides that may be currently in use.

In an effort to provide the residents of Beaufort, Jasper, and Hampton counties with a comprehensive evaluation of the hazard posed by commonly used residential pesticides, the ***goal*** of this project was to cumulatively evaluate pesticides commonly utilized for 1) residential applications (both indoor and outdoor), 2) golf courses, 3) vector control, 4) right of ways, 5) algae removal, and 6) tomato farms (Figure 2). The aforementioned categories were chosen based on the expressed areas of interest by the project funders, and do not necessarily address specific areas that have been identified as problematic within the region. For use category 1 – residential pesticides – the ***major objective*** (beyond the cumulative evaluation) was to make the decision-making process a dynamic one by way of an interactive website (sccoastalpesticides.org). This process required several steps discussed below.

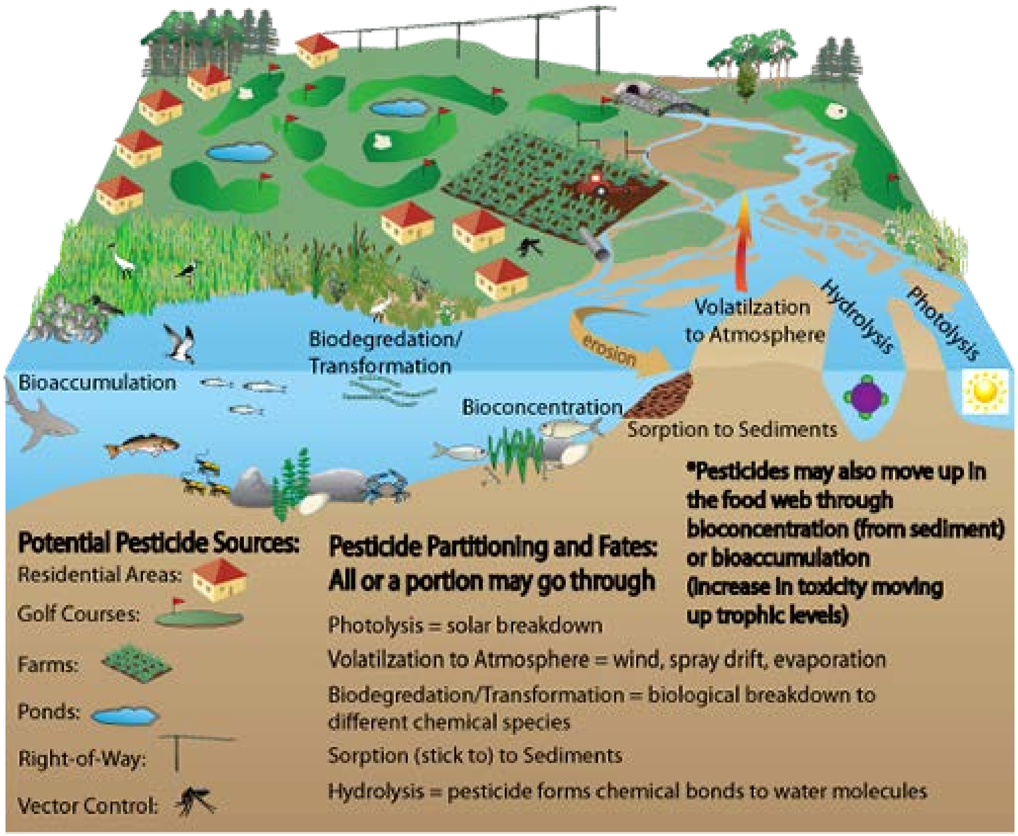

Figure 2: Conceptual Diagram of the potential sources of pesticides, and the environmental processes that potentially influence the final fate of pesticides in a South Carolina coastal suburban residential scenario.

Commonly-Used Residential Pesticides in the Tri-county Area

First, identification of the top one hundred pesticides (Table 1) had to be determined for the six identified use categories. Clemson University's Office of Pesticide Regulation and the Cooperative Extension office was an integral part of this process. Specifically, vector control agents specifically used within the tri-county area, were identified through records kept on spraying efforts (predominantly for mosquito control) to reduce vector populations. Next, Lowe's Home Improvement Store generously provided a comprehensive list of pesticide formulations that were most frequently purchased for in home pest control and lawn care. A list of pesticides registered for use on golf courses in South Carolina was obtained from the 2012 Clemson University Pest Control Guidelines for Professional Turfgrass Managers (http://www.clemson.edu/extension/horticulture/turf/pest_guidelines/) (McCarty 2012). Within this comprehensive list of pesticides herbicides, insecticides, fungicides, and algaecide data were compiled. Moreover, for algaecides the South Carolina Department of Natural Resources Nuisance Aquatic Species Program (http://www.dnr.sc.gov/invasiveweeds/homeowner.html) was also references to complete a comprehensive list of algaecides. For herbicides used in right-of-way areas, the local electric and gas company generously provided both information of pesticides uses and best management practices implemented in treated areas. Finally, Southeastern U.S. 2013 Vegetable Crop Handbook (http://www.thegrower.com/south-east-vegetable-guide/pdf/) was referenced for commonly used pesticides on tomato farms. Gathering these lists was time intensive and could not have been completed without collaborative efforts with multiple stakeholders.

Table 1: 100 active ingredient pesticides chosen for the relative-cumulative ranking of commonly-used pesticides in the Beaufort, Hampton, and Jasper counties, SC. Pesticide class is: A = algaecides, F = fungicide, H = herbicides, A = algaecides, and S = synergist. In total, 12 fungicides, 6 algaecides (strictly), 43 herbicides, 39 insecticides were included in the analysis.

Active Ingredient Pesticide	Pesticide Class	Active Ingredient Pesticide	Pesticide Class	Active Ingredient Pesticide	Pesticide Class
2,4-D	H, A	**Napropamide**	H	**Imidacloprid**	I
Copper compounds	A, F	**Pendimethalin**	H	**Malathion**	I
Glyphosate	A, H	**Fluroxypyr**	H	**Etofenprox**	I
Imazapyr	A, H	**Siduron**	H	**Trichlorfon**	I
Penoxsulam	A, H	**Benefin**	H	**Dicofol**	I
Carfentrazone	A, H	**Fenoxaprop-ethyl**	H	**Cyfluthrin**	I
Endothall	A, H	**Indaziflam**	H	**Temephos**	I
Flouridone	A, H	**Metolachlor**	H	**Hydramethylnon**	I
Triclopyr	A, H	**Oryzalin**	H	**Indoxacarb**	I
Simazine	A, H	**Bromoxynil**	H	**Chlorpyrifos**	I
Hydrothol	A, H	**Pronamide**	H	**Methiocarb**	I
Sodium-carbonate Peroxyhydrate (SCP)	A,H	**Diclofop-methyl**	H	**Endosulphan**	I
Fosetyl-Al	F	**Fluazifop-butyl**	H	**Abamectin**	I
Mandipropamid	F	**Paclobutrazol**	H	**Fipronil**	I
Thiophanate-methyl	F	**Dimetthenamid**	H	**Piperonyl butoxide (PBO)**	I, S
Pyraclostrobin	F	**Atrazine**	H	**Boric Acid**	I, F, A
Mancozeb	F	**Dithiopyr**	H	**Glufosinate**	H
Myclobutanil	F	**Oxadiazon**	H	**Clopyralid**	H
Trifloxystrobin	F	**Bensulide**	H	**Quinclorac**	H
Difenoconazole	F	**Bispyribac-sodium**	H, A	**Trinexapac-ethyl**	H
Iprodione	F	**Diquat**	H, A	**Clethodim**	H
Vinclozolin	F	**Metham-sodium**	H, F, I	**Ethofumesate**	H
Asoxystrobin	F	**DEET**	I	**Isoxaben**	H
Chlorothalonil	F, I	***Bacillus thuringiensis* (BTI)**	I	**Halofenozide**	I
Rimsulfuron	H	**Naphthalene**	I	**Permethrin**	I
Dicamba	H	**Dinotefuran**	I	**Cholorantraniliprole**	I
Asulam	H	**Thiamethoxam**	I	**Clothianidin**	I
Mesotrione	H	**Methoprene**	I	**Spinosad**	I
Metasulfuron-methyl	H	**Pyriproxyfen**	I	**Carbaryl**	I
Aminocyclopyrachlor	H	**Acephate**	I	**Hexaflumuron**	I
Foramsulfuron	H	**Sumithrin**	I		
Imazaquin	H	**Bifenthrin**	I		
Sethoxydim	H	**Deltamethrin**	I		

Sulfentrazone	H	**Lambda-cyhalothrin**	I

Data Mining

Values for each endpoint in toxicity and environmental fate tests being considered for each of the one hundred pesticides were mined from published documents from relevant governmental agencies. Data were gathered from US EPA Reregistration Eligibility Decisions (REDs), Interim REDs (IREDs), and the US National Library of Medicine's Toxicology Data Network (http://toxnet.nlm.nih.gov/index.html). Data were gathered from the OCSPP guideline assays conducted for registration or reregistration of an active ingredient pesticide under EPA guidelines (EPA 2013). Briefly, representative or (surrogate) species are chosen to represent a much larger community of organisms. For instance, the honeybee is used to represent all terrestrial insect species. Acute (short-term), sub-chronic (non-fatal endpoints), and chronic tests (long-term) are conducted for hazard assesment of pesticides. Within the relative cumulative ranking system we are using acute and chronic endpoints, but not sub-chronic, as these endpoints vary based on the pesticidial mode of action and were not consistently found for all the pesticides covered in the analysis. Sub-chronic endpoints should be considered when human health risk assessment and characterization is being conducted, but may not always be relavent to decision-making within an ecological assessment. Additionally, only *in vivo* tests are used in the cumulative ranking scheme, as *in vitro* assays are aimed more towards human health risk assessment. The terrestrial plants tests (OCSPP GLN #'s: 850.4100, 850.4150, 850.4230, 850.4300) (EPA 2013) were also excluded from the analysis as these data were not consistently found for all compounds. Figure 2.6 illustrates the endpoints considered for each pesticide. Each assay considered has an assigned Office of Chemical Safety and Pollution Prevention (OCSPP) guideline number for it (EPA 2013). The following representative bioassays for hazard assessment were used in the cumulative ranking of the chosen 100 residential pesticides:

- Acute Toxicity: Acute Oral Rat Toxicity – updated in 1996; GLN #: 870.1100 (EPA 2013)
- Chronic Toxicity: Chronic Feeding Study – updated in 1998; GLN #: 870.4100 (EPA 2013)
- Acute Toxicity: Avian Acute Oral Toxicity Test – updated 2012; GLN #: 850.2100 (EPA 2013)
- Chronic Toxicity: Avian Dietary Toxicity Test – updated 2012; GLN #: 850.2200 (EPA 2013)
- Acute Toxicity: Honey Bee Acute Contact Toxicity – updated 2012; GLN #: 850.3020 (EPA 2013)
- Acute Toxicity: Aquatic Invertebrate Acute Toxicity Test – updated 1996; GLN #: 850.1010 (EPA 2013)
- Chronic Toxicity: Daphnid Chronic Toxicity Test – updated 1996; GLN #: 850.1300 (EPA 2013)

- Acute Toxicity: Fish Acute Toxicity Test – updated 1996; GLN #: 850.1075 (EPA 2013)

- Chronic Toxicity: Fish Early Life-stage Toxicity Test – updated 1996; GLN #: 850.1400 (EPA 2013)

- Acute Toxicity: Algae Toxicity Test –updated 1996; GLN #: 850.5400 (EPA 2013)

There were also environmental fate and transport values considered that are also considered by the EPA during registration of a compound and include:

- ***n*-octonol-water partitioning coefficient (K_{ow})**

The *n*-octonol-water partitioning coefficient (K_{ow}) is used to predict the bioaccumulation potential in aquatic and terrestrial organisms and to estimate the amount of sorption to soil and sediment (Paustenbach 2002). The equation for the K_{ow} is:

$$Kow = \frac{\text{concentration of chemical in octonol phase}}{\text{concentration of chemical in aqueous phase}}$$

- **Soil Organic Carbon-Water Partitioning Coefficient (K_{oc})**

The Soil Organic Carbon-Water Partitioning Coefficient (K_{oc}) is a ratio of the mass of a chemical that is adsorbed in the soil per unit mass of organic carbon in the soil per the equilibrium chemical concentration in solution (EPA 1996). The K_{oc} acts as an important predictor of water mobility from the point of application. The K_{oc} is calculated by:

$$K_{oc} = K_d / f_{oc}$$

where: K_d is based on total soil mass and dependent on soil type and % organic matter and increasing K_d values result in decreasing mobility and decreasing values result in increasing mobility.

$$Kd = \frac{\text{concentration of chemical in soil}}{\text{concentration of chemical in water}} = \frac{\text{grams adsorbed / grams organic carbon}}{\text{grams / mL solution}}$$

and f_{oc} = weight fraction of organic carbon

- **Half-life ($T_{1/2}$)**

The half-life of a compound is a measure of persistence and is generally calculated for soil (aerobic and anaerobic), groundwater, and surface water.

Compound (Active Ingredient Pesticide)	Aquatic and Non-target Terrestrial Organism Parameters								Mammalian				
	Acute					Chronic			Acute	Chronic			
	Phyto toxicity EC50 (ppb)	Aquatic LC50 (ppm)		Avian LD50 (mg AI/kg)	Bee LD50 (µg/bee)	NOAEL or NOAEC (ppm)			Oral LD50 (mg/kg)	NOAEL (mg/kg/day)	log Kow	half-life (days)	Koc (ml/g OC)
		Invert	Fish			Avian	Invert	Fish					

Figure 2.6: For each of the 100 pesticides, 13 different endpoints (values) were mined in order to relatively cumulatively rank the active ingredient pesticides.

The Pesticide-Support Tool Analysis

Previously Developed Pesticide Ranking Systems

In an effort to estimate the adverse impacts that pesticides potentially have on the environment and human health, several attempts have been made to develop indicator systems (e.g., Rues et al. 2000, Brown et al. 2003, Hart et al. 2003, Lewis et al. 2003, Whelan et al. 2005, Benbrook et al. 2007, Samuel et al. 2007). There is increasing consensus that such indicators should be based on risk (rather than hazard) and should be consistent with methodology utilized in the current regulatory framework (Whelan et al. 2005, Brown et al. 2003, Hart et al. 2003, Lewis et al. 2003). Often, the indicator systems to-date focus on identifying cases when pesticides are over used thereby making mitigation measures more effective (Whelan et al. 2005), or they focus on monitoring pesticide application over time to determine impacts to water quality. Many risk indicators and assessment tools that have been developed to date are predominantly intended for agricultural chemical applications alone, as these were the intended user groups. Ultimately, it must be decided by the system developer and based upon user group needs as to what should be considered in a multi-compartment pesticide risk indicator system. Measurement systems must find an acceptable balance between complexity and accuracy, and practicality and cost (Benbrook et al. 2007). The Low Country Pesticide Decision-Making Tool (PDMT) is unique in that this indicator system is not just for agricultural users of pesticides, but for other users as well (e.g., homeowners, golf course mangers, landscapers). Contrary to most indicator systems reviewed, the PDMT is also being applied to a smaller spatial scale (i.e. county, region) and is specifically tailored to residents within Beaufort, Hampton, and Jasper counties, SC.

There are many challenges in developing a cumulative ranking system for risk related to pesticides at any scale and for any user group. Challenges present themselves in several different areas. First, there are inherent uncertainties in toxicological data. There are many, but as an example, the honey bee acts as a surrogate species for all non-target terrestrial insects in the EPA's current regulatory ecological toxicity tests. However, there are many species of insects within the United States and there is likely species-to-species variability in susceptibility. In this example, uncertainty comes into play because you do not know if exposure to a pesticide will be more or less toxic to other non-target terrestrial organisms. Next, there is the issue of availability of pesticide use data, especially at smaller spatial scales (i.e., county level). One cannot truly calculate risk without accurate estimates of pesticide use. However, using the EPA's Risk Quotient (RQ) approach, allows projections of estimated environmental concentrations (EECs) and can provide insight into risk posed by specific active ingredient pesticides.

Developing a Relative Cumulative Ranking System for the Tri-County Area

Available Use Data and Residential Scenarios

Given the lack of pesticide use data (excluding general chemical usage on agricultural fields from NASS) in the three focus counties (for both agricultural and non-agricultural applications), it is difficult to estimate true risk of pesticides to the environment or to human health (Table 2) (NASS 2007). Farmers in South Carolina voluntarily submit use data to show proper use of pesticides (i.e., no improper use that potentially cause adverse effects to the surrounding ecosystem), but this still does not account for residential use of pesticides. The ratio of urban and suburban areas to agricultural areas is unknown to the author, but within the target counties residential pesticide use is an important consideration. Future studies plan to use a probabilistic approach and spatial analyses to model both surface water and groundwater EECs. We then reduce uncertainty in estimating risk in tri-county residential scenarios.

Table 2: Farmland (# acres) treated with various pesticides for control of insect, weed, nematode, and disease pests in South Carolina (SC), and in the three target counties for the PDMT: Beaufort, Hampton, and Jasper Counties, SC.

	Pest treated	Acres of farmland treated	% of total farm acres treated	Total acres in farms*
By County				
Beaufort				**49,401**
	Insects	2,912	**5.9%**	
	Weeds	2,417	**4.9%**	
	Nematodes	1,354	**2.7%**	
	Diseases	742	**1.5%**	
	$\text{Total}_{\text{Beaufort}}$	**7,425**	**15.0%**	
Hampton				
	Insects	21,876	**17.3%**	**126,753**
	Weeds	28,257	**22.3%**	
	Nematodes	10,801	**8.5%**	
	Diseases	7,712	**6.1%**	
	$\text{Total}_{\text{Hampton}}$	**66,646**	**52.6%**	
Jasper				**52,132**
	Insects	3,618	**6.9%**	
	Weeds	3,793	**7.3%**	
	Nematodes	142	**0.27%**	
	Diseases	D	**-------**	
	$\text{Total}_{\text{Jasper}}$	**7,553**	**14.5%**	

SC		**746,890**		**4,889,339**
	Insects	746,890	**15.3%**	
	Weeds	1,087,492	**22.2%**	
	Nematodes	222,707	**4.5%**	
	Diseases	175,644	**3.6%**	

*All Farms included in the National Agricultural Statistics Service (NASS) includes dairy farms, ornamentals, as well as vegetable and fruit farms; D = Withheld to avoid disclosing data for individual farms

Here, our goal was to develop a ranking system for commonly-used residential pesticides that anyone can use and implement. While recognizing the importance of risk estimates in ranking systems, we use a binning approach (ANOVA with tertiles of frequency distribution as grouping thresholds) to easily convey information to the public. The evaluation for all 100 pesticides for the pesticide-decision making tool is based on acute and chronic toxicity values (i.e., hazard data) and physical and chemical properties (i.e., environmental fate and transport characteristics) of pesticides. The amount of information available varied from AI to AI, thus a more hazard-based approach was taken due to the lack of availability of data – particularly concerning estimated environmental concentrations (EECs). According to the EPA, all AI pesticides currently on the US market are safe (from a risk perspective) if applied as instructed on the label. We must make the assumption that mixtures of AI pesticides within formulations does not increase or decrease toxicity.

Cumulative Scoring

Thresholds for the toxicity values were set according to the EPA hazard ranking system and environmental fate and transport values (EPA 2013) (Table 2.2). It is important to note when looking at the LD/LC_{50} for toxicity endpoints, that the lower the value the more toxic the compound. Furthermore, for toxicity data, values used for each endpoint are the most conservative values (e.g., lowest LD_{50}/LC_{50}). In the ranking process, the most conservative value from acute and chronic toxicity aquatic non target species (i.e., invertebrates or fish species) was used in the analysis for each pesticide. Relative cumulative rankings are based on eleven different but equally weighted endpoints. Each endpoint being assessed was given numeric values (1= low, 5= moderate, 10= likely) based on the given thresholds for that endpoint set by the EPA test guidelines (Figure 2.7). Once numeric values were assigned to each endpoint for a pesticide, a summation was taken across all endpoints and averaged. Cumulative values were assigned for all 100 pesticides. It is important to note that occasionally data for all thirteen endpoints was not generated (i.e., data gaps) or could not be located by the author for all one hundred pesticides; in these cases a null value of 5 was assigned to that endpoint for that pesticide. To create an easily understandable outcome of the analysis for end users, the cumulative scores were used to divide the pesticides into subcategories (low, moderate, and likely hazard to the ecosystem) and were given a corresponding color as an indicator of each category of the three categories – these are termed bins (Figure 2.8).

Statistical Analysis for Categorical Grouping (3 bin approach)

A cumulative frequency distribution was generated to obtain a final cumulative ranking (i.e., potential relative ecosystem hazard) for all pesticides. The cumulative frequency distribution starts from the lowest and goes to the highest summed values - with the lowest values falling into the low hazard category (“low” bin) and the highest values in to the “likely” bin. Once normality and variance were checked (Normality = Shapiro-Wilk test, Variance = Levene’s test; $P < \alpha$), cumulative scores were statistically separated into one of three bins using tertiles (33% and below, 33 -67%, and 67-100%) of the distribution. A one-way ANOVA procedure ($\alpha = 0.05$) was performed to determine if significant differences were present between the three bins. Using the post hoc Tukey's Studentized Range (HSD) test to indicate significant differences among all three categorical bins ($\alpha = 0.05$), each tertile (comprising a bin) was checked against the others to confirm that means among bins were significantly different.

Table 2: Cumulative values assigned for each category being considered for each pesticide. A numeric value (1, 5, or 10) was assigned to each categorical level, with the numeric value increasing with increasing toxicity or environmental fate characteristic. Corresponding color codes to the final cumulative ranking are applied based on summation and then average of the values from each category. This process normalizes the endpoints being considered for each pesticide in the analysis – equally weighing each endpoint. Thresholds were based on EPA thresholds set during ecological hazard or environmental fate assessment (EPA 2013).

I. Acute Aquatic Organism Toxicity Thresholds (invertebrates and fish) **(units** = ppm**)**

10 = $LC_{50} \leq 1$ (very highly to highly toxic)

5 = $LC_{50} > 1$ to 10 (moderately toxic)

1 = $LC_{50} \geq 10$ (slightly to practically non-toxic)

II. Chronic Aquatic Organism Toxicity Thresholds (units = ppm**)**

10 = NOAEC ≤ 1 (very highly to highly toxic)

5 = NOAEC > 1 to 10 (moderately toxic)

1 = NOAEC ≥ 10 (slightly to practically non-toxic)

III. Acute Avian Toxicity Thresholds (units = mg/kg**)**

10 = $LD_{50} \leq 50$ (very highly toxic to highly toxic)

5 = $LD_{50} > 50$ to 2000 (moderately to slightly toxic)

1 = $LD_{50} \geq 2000$ (practically non-toxic)

IV. Chronic Avian Toxicity Thresholds (units = mg/kg**)**

10 = NOAEL ≤ 500 (very highly toxic to highly toxic)

5 = NOAEL > 500 to 5000 (moderately to slightly toxic)

1 = NOAEL ≥ 5000 (practically non-toxic)

V. Acute Mammalian Toxicity Thresholds (based on rodent oral LD_{50}) (units = mg/kg**)**

VI. Chronic Mammalian Toxicity Thresholds (units = ppm**)**

10 = NOAEL ≤ 500 (very highly toxic to highly

10 = LD_{50} ≤ 50 (very highly toxic to highly toxic)

5 = LD_{50} > 50 to 2000 (moderately to slightly toxic)

1 = LD_{50} ≥ 2000 (practically non-toxic)

VII. Acute Honey Bee Toxicity Thresholds (oral or topical application) (units = µg/bee**)**

10 **=** LD_{50} ≤ 2 (highly toxic)

5 = LD_{50} > 2 to 11 (moderately to slightly toxic)

1 = LD_{50} ≥ 11 (practically non-toxic)

IX. Bioaccumulation Potential

10 = log K_{ow} ≥ 4 (high bioaccumulation potential)

5 = log K_{ow} > 2 to 4 (moderate bioaccumulation potential)

1= log K_{ow} ≤ 2 (low bioaccumulation potential)

XI. Soil/Water Mobility (Units = ml/g_{oc})

10 = K_{oc} ≤ 1000 (highly to moderately mobile)
5 = K_{oc} >1000 to 10000 (slightly mobile)
1= K_{oc} ≥ 10000 (hardly mobile to immobile)

toxic)

5 = NOAEL > 500 to 5000 (moderately to slightly toxic)

1 = NOAEL ≥ 5000 (practically non-toxic)

VIII. Plant Phytotoxicity Thresholds (units = ppb**)**

10 = EC50 ≤ 1100 (complete control)

5 = EC50 > 1100 to 10000 (complete to selective control)

1 = EC50 ≥ 10000 (practically non-toxic)

X. Estimated Half Life (from water or soils, whichever is longest)

10 = $t_{1/2}$ ≥ 180 days (persistent)

5 = $t_{1/2}$ > 45 to 180 days (moderately persistent)

1 = $t_{1/2}$ ≤ 45 days (nonpersistent to slightly persistent)

Compound (Active Ingredient Pesticide)	Aquatic and Non-target Terrestrial Organism Parameters								Mammalian				
	Acute					Chronic			Acute	Chronic			
	Phyto toxicity EC50 (ppb)	Aquatic LC50 (ppm) Invert	Aquatic LC50 (ppm) Fish	Avian LD50 (mg AI/kg)	Bee LD50 (µg/bee)	NOAEL or NOAEC (ppm) Avian	NOAEL or NOAEC (ppm) Invert	NOAEL or NOAEC (ppm) Fish	Oral LD50 (mg/kg)	NOAEL (mg/kg/ day)	log KOW	half-life (days)	Koc (ml/g OC)
fosetyl-Al	6790	188	141.4	8000	100	1500	17	100	5400	250	-2.1	5.7	20
fosetyl-Al	5	1		1	1	5	1		1	1	1	1	10

Cumulative Score = 2.545

Figure 2.7: The process of taking the raw value given for an assay (top row) and assigning it a numerical value (bottom row) based on the set thresholds for each endpoint included in the relative cumulative ranking of pesticides. The cumulative value is outlined in blue and is the average of the values. The most conservative of the aquatic assays – acute and chronic – were based on the most conservative (i.e. most toxic) raw values and then assigned a single value for the final ranking.

$AVG_{ranking}(n_1 + n_2...)$ (> 67% in cumulative scoring) = likely =

$AVG_{ranking}(n_1 + n_2...)$ (> 33% < 67%) = moderate =

$AVG_{ranking}(n_1 + n_2...)$ (> 0% < 33%) = low =

Figure 2.8: Cumulative Scoring of frequency distribution on parameters/pesticide. Thresholds = tertiles of distribution (i.e., lower 33% = highly safe to the ecosystem)

2.4 RESULTS

Relative cumulative ranking values ranged from 2.182 to 9.091. Descriptive statistics indicated that the overall mean ranking value was 5.453 for all pesticides. The distribution of values was statistically divided into significantly different tertile regions (e.g., safety bins). Significant differences were found between the mean value for each of the three bins ($F = 2, 205.5$, $P < 0.0001$) (Figure 2.9). The mean for the compounds between 0 – 33% (highly safe) of the relative cumulative ranking was 3.90. The means for the 33% - 67% (moderate) and 67% (likely) and above were 5.67 and 7.21, respectively. For the 100 active ingredient compounds covered, 35 fell into the low category, 39 were in the moderate category, and 26 were placed in the likely to be a relative potential ecosystem hazard bin (Figure 2.9). The three different representative colors were then assigned to each corresponding bin based significantly on differences of low, moderate, and likely relative potential ecosystem hazard (Figure 2.9). The thresholds set by the tertile binning system of the distribution of relative cumulative ranking analysis were set at ≤ 4.545 as low (dark green), > 4.454 ≤ 6.128 as moderate (light green), and above 6.128 as likely (orange) (Figure 2.10). Pesticides (AI) and pesticide class, and the distribution of cumulative ranking values are found in Figure 2.11. The slope of the distribution indicates 3 distinct regions. The steepness of the slope is highest in the low and likely compartments and flattens out for the moderate compounds. This indicates there is a portion of pesticides that on average rank about the same when the eleven endpoints cumulatively scored per pesticide.

For the eleven endpoints considered for each of the one hundred pesticides, acute avian toxicity (68 pesticides – low), honey bee toxicity (68 pesticides – low), and acute mammalian toxicity (59 pesticides – low) were the endpoints with the most pesticides falling into the "low" bin (Figure 2.12). Both acute (46 – likely) and chronic (58 – likely) aquatic toxicity values, along with phytotoxcity (43 – likely) endpoints, contained the higher numbers of pesticides with "likely" classifications (Figure 2.12). Chronic mammalian toxicity also had 58 compounds in the "likely" bin. The endpoint with the most pesticides in the moderate category was for chronic avian toxicity.

For the environmental fate endpoints considered, 61 pesticides fell into the likely to be hazardous to the ecosystem (i.e., scored a numberical ranking of 10 based on EPA EFED thresholds for soil/water mobility) categories based on K_{oc}. High runoff rates are a concern for these pesticides. Fifteen pesticides fell into the high soil binding category (i.e., scored a 1 on the numerical ranking based of set thresholds by the EPA), where erosion (i.e., potential soil loss) should be taken into consideration if water quality impairments occur in surrounding waters. For the log K_{ow} values determined, 33 pesticides fell into the "likely" bin, 30 in the "moderate" bin, and 37 in the "low" catergorical bin. Most compounds had a low ranking for half-life with only 20 in the "likely" bin, 28 in the "moderate" bin, and 52 in the "low" bin.

Based on pesticide class, herbicides had the most AIs in the low group with insecticides having the most AIs in the likely category according to cumulative ranking (Figure 2.12). Notably, these two classes also had the most pesticides falling into the moderate category as well. Algaecides largely fell into the low category, while fungicides had the highest number of rankings falling into the moderate category.

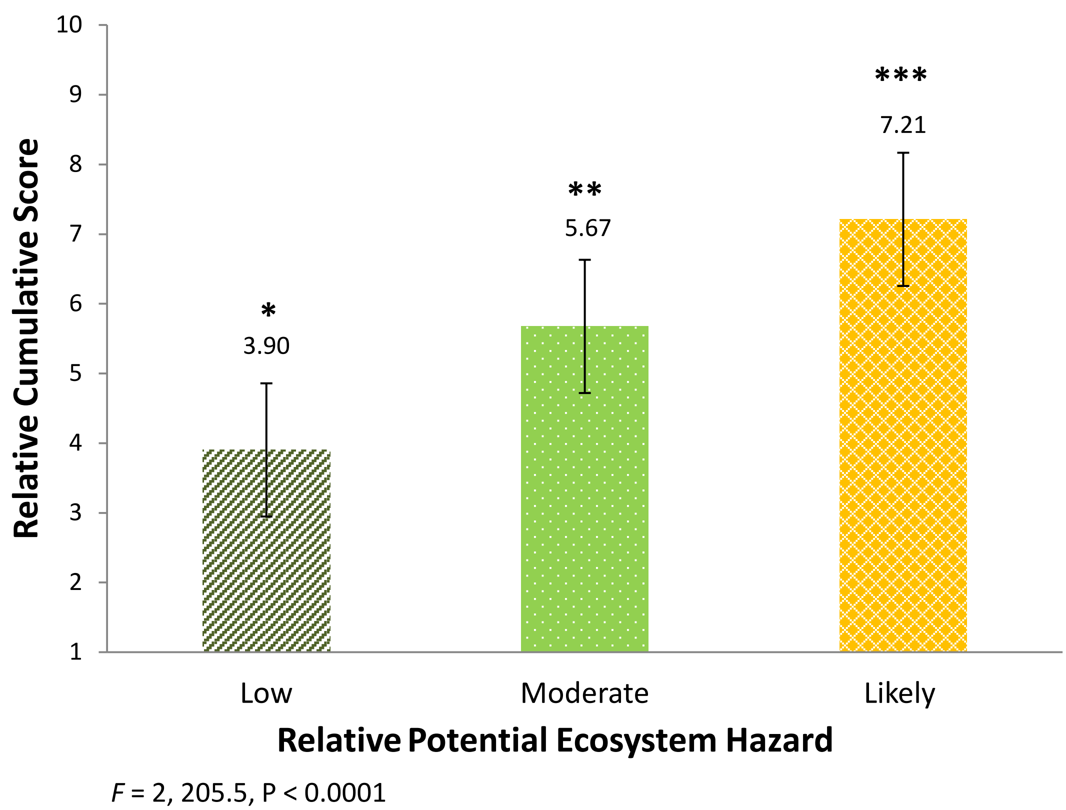

Figure 2.9: Means and significant differences (α = 0.05) among the three different binning compartments (low, moderate, likely – relative potential ecosystem hazard). A one-way ANOVA procedure indicated significant difference among means (immediately above each bar) within each binning compartment (F = 2, 205.5, P < 0.0001). Using the post hoc Tukey's Studentized

Range (HSD) Test (α = 0.05) indicated significant difference among all three binning croups and are indicated by asterisks at the top of each bar.

$\text{AVG}_{\text{ranking}}(n_1 + n_2 ...)$ (> 67% in cumulative scoring) = likely =

$\text{AVG}_{\text{ranking}}(n_1 + n_2 ...)$ (> 33% < 67%) = moderate =

$\text{AVG}_{\text{ranking}}(n_1 + n_2 ...)$ (> 0% < 33%) = low =

Figure 2.10: All three groups (low, moderate, likely) were significantly different from each other at the α = 0.05 significance level. Each bin was assigned a representative color.

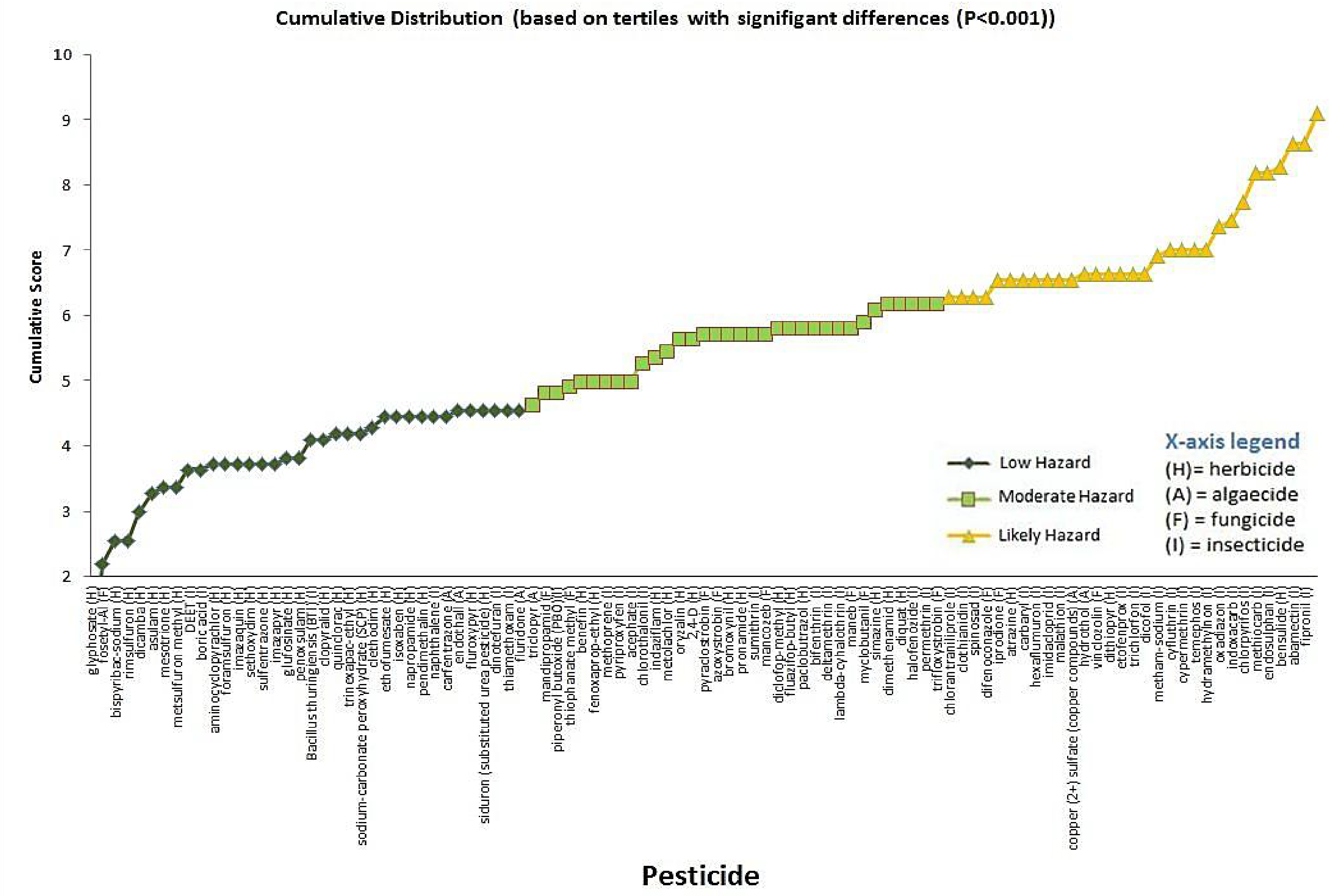

Figure 2.11 The 100 pesticides covered in the relative cumulative ranking system separated by color based on tertiles from the frequency distribution of values.

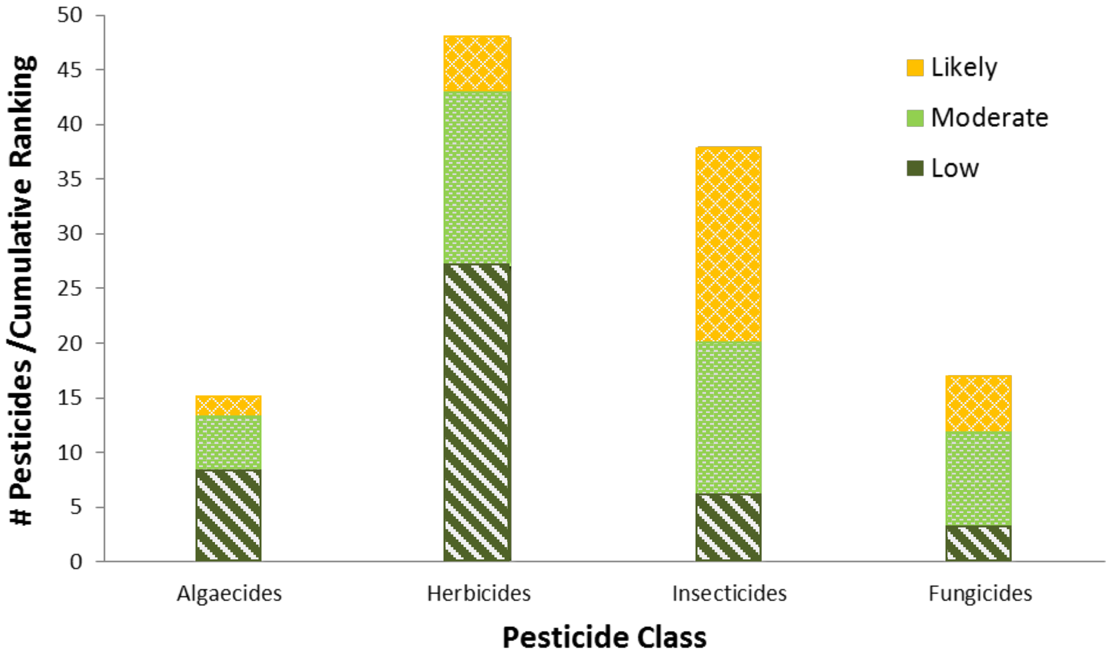

Figure 2.12: The number of pesticides – based on relative cumulative ranking score – that fell into each categorical bin.

Limitations and Future Work: ***In continuing to better the ranking scheme for public use, all environmental fate parameters will be considered and RQs will be calculated for toxicity assays.*** EECs will be calculated and then results of the initial analysis will be compared to the later used the risk-based approach. Clustering – based on different endpoints for each AI – will also be clustered to determine which pesticides have similar environmental concerns. The current ranking system is biased towards hazard therefore not taking into account application rates and therefore exposure. Some AIs are very toxic, but used at such low rates that they will almost never exceed the Level of Concern (LOC) set by the EPA. The ranking system in place may give users the idea that one AI is worse than another because it is more toxic. However, it may be applied at a much lower rate than an AI that is relatively less toxic, but is applied at a much higher rate – giving rise to the concept that even though something is more toxic, it may have less of an environmental impact given its low application rate. Even though the target counties within this study consist of regions of estuarine ecosystems where diurnal tidal events create dynamic systems of exposure, using an EEC should give the intended users a better idea about the "acceptable risk" when pesticide application does occur. The current ranking system is useful to the public from the perspective of looking at hazard and environmental fate of the 100 covered pesticides.

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