PRELIMINARY ASSESSMENT OF ECOLOGICAL RISKS FROM PESTICIDES CURRENTLY USED IN THE ST. JOHNS RIVER, FLORIDA WATERSHED.

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Abstract

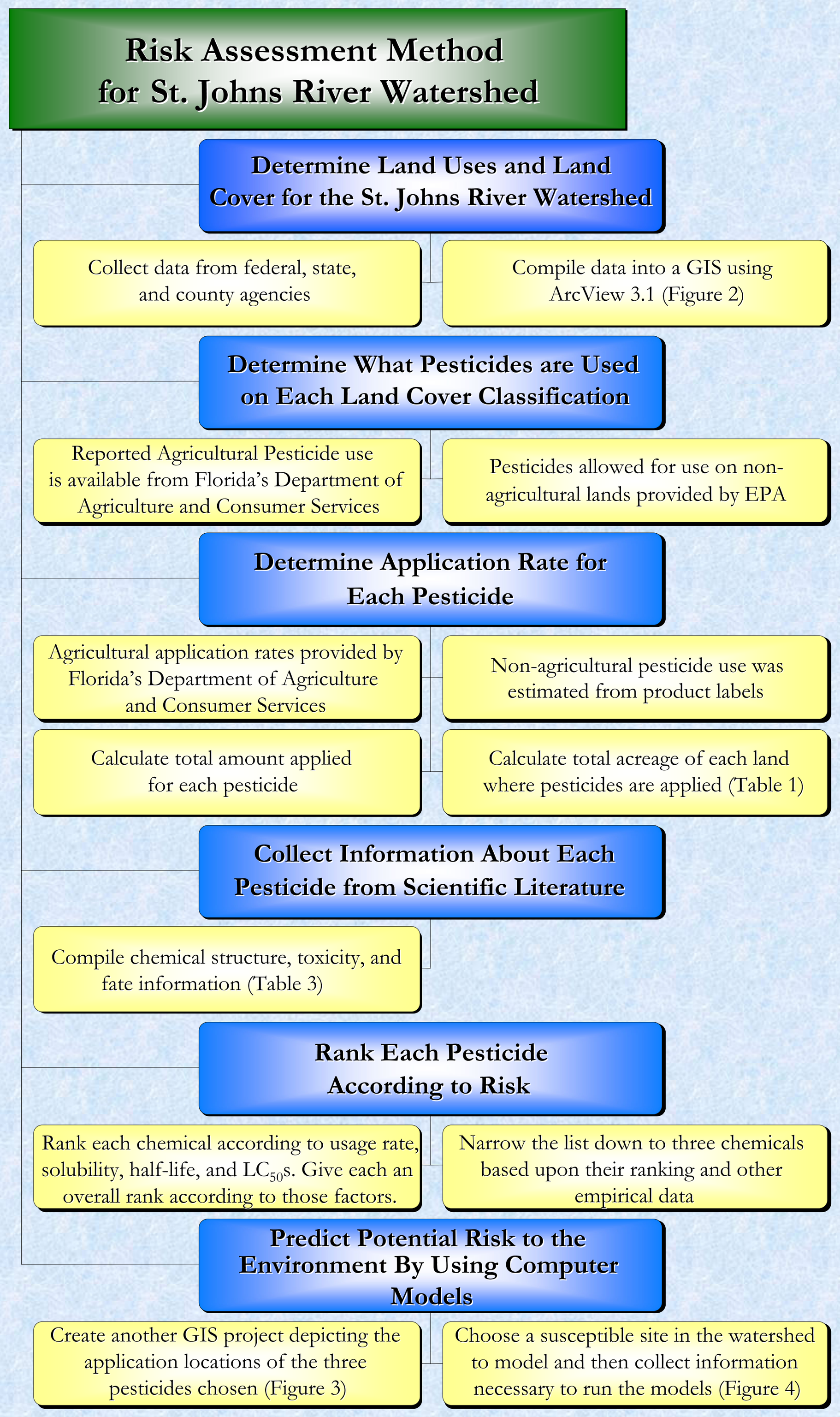
The National Oceanic and Atmospheric Association (NOAA) has recently implemented the Coastal Storms Initiative that will improve the use of its information, forecasts, tools, and training for protection of coastal communities. Although national in scope, it is being tested as a pilot program in the St. Johns River watershed in northeast Florida. One part of this initiative is the development of forecast models for ecological effects from storms. The effects that major storm events have on the movement of pesticides into nearby waterways are poorly understood. A risk assessment approach was used in order to identify the pesticides in the St. Johns River watershed that pose risks to natural resources and to minimize them by proposing risk reduction strategies. So far, approximately 170 pesticides have been identified for agricultural, residential and commercial applications within the watershed. The ecological risks were ranked using application amounts and locations, known toxicity thresholds, and chemical characteristics that affect each pesticide's transport and fate. This risk assessment approach identified the chemicals atrazine, fipronil and imidacloprid as three pesticides that pose significant hazards and may occur at significant levels in the St. Johns River and its tributaries after heavy rains. Detailed toxicological effects of these three chemicals on fish and shellfish are being characterized in ongoing research at NOAA's Center for Coastal Environmental Health and Biomolecular Research Laboratory in Charleston, South Carolina and the NOAA Fisheries Laboratory in Seattle, WA. Modeling to predict exposure levels during storm events is ongoing at NOAA/CCEHBR.

Introduction

NOAA, with the cooperation of state and local agencies, has launched the Coastal Storms Initiative in a nationwide effort to improve forecasting and reduce the harmful effects of extraordinary weather events. This initiative is made up of nine projects that each address specific hazard-related issues and that collectively will result in the improvement of tools, data, information, forecast models, and training for the coastal communities within the study area. One of the nine projects is the Ecological Forecasting Project which will identify the locations within the study areas where toxic contamination will increase during and immediately following a large rain event. The National Ocean Service is developing a risk assessment model for the St. Johns River Water Management District (SJRWMD) in northeast Florida (Figure 1). If successful, this project may be used as a model for other coastal communities within the United States.

Figure 1 - ★Indicates Lake Bethel (See Figure 4)

Source: www.SJRWMD.org



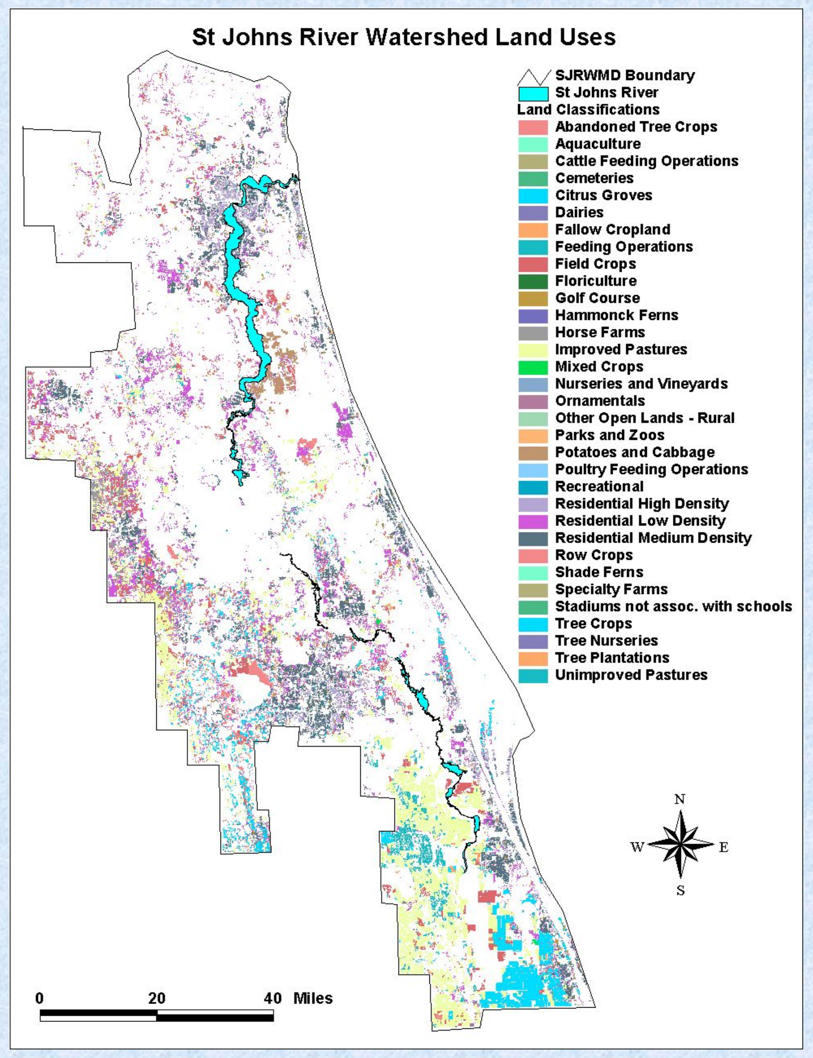


Figure 2 - SJRWMD Land Uses

Results and Conclusions

- A geographic information system (GIS) was created depicting the land uses and land cover in the SJRWMD upon which pesticides may be applied (Figure 2).
- The initial search for pesticides used in the SJRWMD resulted in a list of 170 different chemicals that included predominantly herbicides, insecticides, and fungicides (Table 2).
- The three chemicals chosen for the study were atrazine, fipronil, and imidacloprid. Initial toxicology compiled for these three pesticides is shown in Table 3.
- The GIS layout representing the areas of application for these three chemicals is shown in Figure 3.
- The region chosen to be represented in the Pesticide Root Zone Model (PRZM) and the Exposure Analysis Modeling System (EXAMS) was the region surrounding Lake Bethel and Bethel Creek in Volusia County. This region is shown in Figure 4.

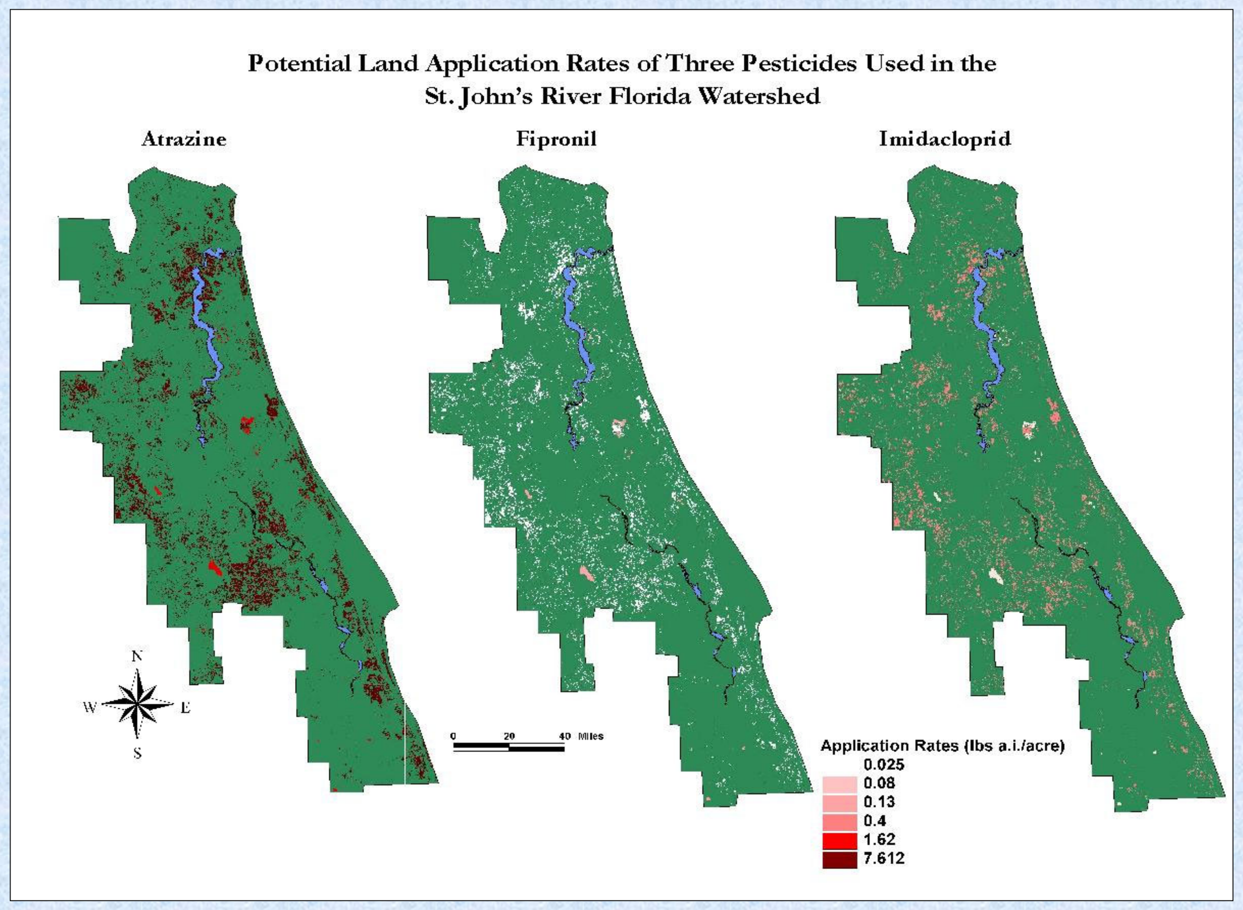


Figure 3

Attribute	Area (m²)	Area (acres)
Feeding Operations	122,480.6109	30.2656
Floriculture	408,833.3663	101.0248
Other Open Lands - Rural	580,583.7027	143.4651
Stadiums not assoc. with schools	759,424.5879	187.6576
Tree Plantations	1,527,095.3952	377.3529
Specialty Farms	3,171,027.1358	783.5787
Aquaculture	3,955,043.1153	977.3109
Nurseries and Vineyards	4,647,999.9533	1,148.5440
Dairies	6,250,568.9806	1,544.5468
Cattle Feeding Operations	6,252,405.9602	1,545.0008
Poultry Feeding Operations	7,389,954.0975	1,826.0946
Mixed Crops	9,379,922.0064	2,317.8256
Tree Nurseries	10,230,250.0722	2,527.9459
Cemeteries	10,630,688.5188	2,626.8963
Tree Crops	15,869,592.8087	3,921.4557
Parks and Zoos	16,165,703.9742	3,994.6263
Hammock Ferns	20,171,989.2820	4,984.5994
Shade Ferns	28,051,087.4864	6,931.5640
Recreational	30,376,440.7119	7,506.1704
Ornamentals	32,914,874.2297	8,133.4300
Fallow Cropland	33,779,220.0049	8,347.0142
Golf Course	111,869,788.0816	27,643.5840
Horse Farms	126,804,224.3424	31,333.9579
Potatoes and Cabbage	131,365,693.1472	32,461.1196
Row Crops	136,590,962.7202	33,752.3098
Abandoned Tree Crops	165,119,150.8075	40,801.7678
Unimproved Pastures	336,821,949.9661	83,230.3879
Residential High Density	465,879,526.9080	115,121.1605
Citrus Groves	898,504,309.1632	222,024.9073
Field Crops	985,985,006.1343	243,641.8249
Residential Med. Density	1,549,201,306.5636	382,815.3889
Residential Low Density	1,590,149,890.1510	392,933.9886
Improved Pastures	2,220,360,734.4182	548,662.2393
Total	8,961,287,728.4042	2,214,379.0041

Table 1 - Acreage of land classes that use pesticides

Further Study

The following are elements of this assessment that are in progress or are goals to be addressed as this study progresses.

- Define the toxicology of atrazine, imidacloprid, and fipronil to sensitive estuarine organisms
- Run PRZM and EXAMS models to predict loading under different environmental conditions
- Make data available as an online database
- Use this risk assessment study as a model for other study areas

Acknowledgements

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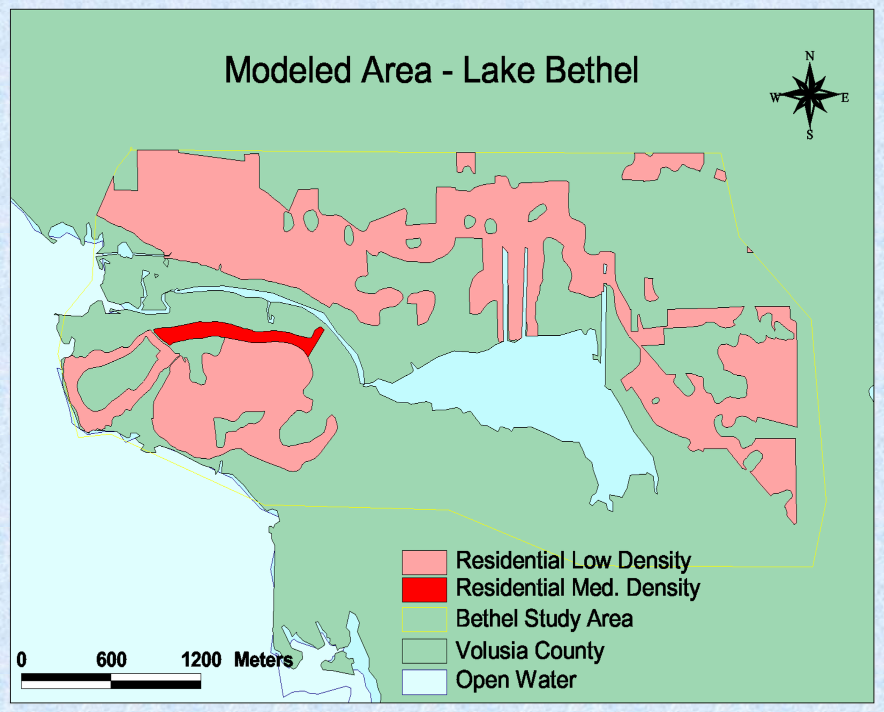
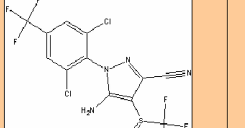
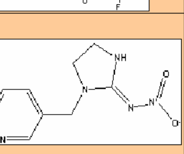
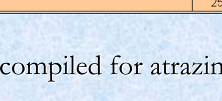


Figure 4 – Lake Bethel Study Area

Pesticides Potentially Used in the SJRWMD						
Insecticides		Herbicides		Fungicides	Other Chemical	Multiple Use
abamectin	fipronil	2,4-D	linuron	(R)-2-{(2,6-dimethylphenylmethoxy) acetylamino}-propionic acid methyl ester	1,3-dichloropropene	2,4-D butoxyethyl ester
acephate	fonofos	2,4-D 2-ethylhexyl ester	methazole	alpha-(2-(4-chlorophenyl)ethyl)-alpha-phenyl-1H-1,2,4-triazole-1-propanenitrile (also found as Fenbuconazole)	1-Naphthalene acetic aci	fats and glyceridic oils, fish
aldicarb	imidaclorprid	3,6-dichloro-2-methoxy-benzoic acid, potassium salt	methyl 2,7-dichloro-9-hydroxyfluorene-9-carboxylate	basic copper sulfate	2-Undecanone	hydrogen peroxide
amorphous silica	lambdacyhalothrin	acifluoren (also found as actifluorfen and actiflourofen)	metolachlor	benomyl	adenosine, N-((2-hydroxyphenyl)methyl) (also known as Cytokinin R)	tall oil fatty acids, potassium salts
azadirachtin	lindane	alachlor	metribuzin	Binab T	allium sativum (garlic oil)	Tergitol 15-S-9 (***discontinued by Union Carbide Corp.)
benzoic acid, 4-chloro-, 2-benzoyl-2-(1,1-dimethylethyl)hydrazide	malathion	ammonium glyphosate	Metsulfuron Me (also found as metsulfuron-methyl)	calcium polysulfides	capsaicin	VM & Painters Naphtha
bifenthrin	methamidophos	ammonium salts of C8-18 and C18' fatty acids	MSMA	captan	chloropicrin	
bioresmethrin (also found as pyrethroids)	methomyl	atrazine	napropamide	carboxin	denatonium benzoate	
biotrol 4K	methoxychlor	benefn (also found spelled benefin, also found as benfluralin)	norflurazon	chitosan	dimethipin (*Harvade*)	
carbaryl	methyl parathion	bentazon (also found spelled bentazone)	oryzalin	chlorothalonil	ethephon	
carbofuran	mevinfos (also found as mevinphos and Phosdrin)	bromacil	oxadiazon	copper hydroxide	eugenol	
chlorpyrifos	myclobutanil	bromoxynil octanoate	oxyfluoren (found as oxyfluorfen)	copper octanoate	flurprimidol	
cyfluthrin	oxamyl	chloramben (also found as amiben)	paraquat	copper oxychloride sulfat	geraniol	
cypermethrin	oxythioquinox	chlorimuron	pebulate	copper sulfate	gibberellic acid	
cyromazine	permethrin	clopyralid	pendimethalin	cuprous chloride	indole-3-butyric acid	
deltamethrin	petroleum distillate	cyanazine	Pramitol	demosan	maleic hydrazide	
diazinon	phorate	dicamba	prometryn	flutolanil	mepiquat chloride	
dicofol (also found as kelthane)	profenofos	dimethylamine (R)-2-(2-methyl-4-chlorophenoxy)propionate	pyridate	fosetyl-al	metacetaldehyde	
dicrotophos	propargite	dimethylamine dicamba	Roundup (also known as glyphosate isopropylamine salt)	mancozeb	metam sodium (also found as methamsodium)	
diflubenzuron	pyrethrum	dithiopyr	sethoxydim	maneb	methyl bromide	
dimethoate	resmethrin	diuron	simazine	metalaxyl	N-Methyl-2,4-dinitro-N-(2,4,6-tribromophenyl)-6-(trifluoromethyl) benzenamine (found as Bromethalin)	
disulfoton	spinosad #1	DSMA	sodium chloride	PCNB	sodium dichloroisocyanurate dihydrate	
endosulfan	sulfur	ethalfuralin	trifluralin	potassium bicarbonate	soy bean oil	
esfenvalerate	sulprofos	fenoxaprop	vernolate	propiconazole	thidiazuron	
ethion	terbufos	fluazifop (data for Fluazifop-butyl)		sulfur	tribufos	
ethoprop	thiodicarb	fluometuron		thiram		
ethyl parathion (found as parathion)	tralomethrin	glyphosate				
fenamiphos	trichlorfon	imazaquin ammonium				
fenbutatin oxide		imazethapyr				
fenvalerate		kerb (a.k.a. Pronamide)				

Table 2 - Pesticides potentially used in the SJRWMD

Pesticide	CAS Number CF	Mol Formula CF	Structure CF	MW CF	Activity ***	Log K_{ow}	K_{oc}	Solubility	Toxicity data	t1/2 in soil
Atrazine	001912-24-9	$C_8H_{14}ClN_5$		215.6851	Herbicide	(A) 2.33-2.80	LAR 45-63, (A) log 1.95-2.71, (UM) & ARS 100 ml/g	*** In water, 33 ppm at 25°C	(UM) Atrazine is moderately to highly mobile in soils, especially where soils have low clay or organic matter content. Because it does not absorb strongly to soil particles and it has a lengthy soil half-life, it is expected to have a high potential for groundwater contamination, even though it is only moderately soluble in water	PK 30 days, ARS 60 days, (UM) 60-100+ days
Fipronil	120068-37-3	$C_{12}H_4Cl_2F_6N_4OS$		437.1462	Insecticide			(M) As Regent 4SC: dispersible, Tech: 1.9 mg/l @ 20°C	*The photodegradate of fipronil, MB46513, is about 10 times more acutely toxic to mammals than fipronil itself	*122-128 days in oxygenated soil, 0.7-1.7 months on soil surfaces, and 3-7.3 months when incorporated into the soil. In anaerobic water and sediment, 116-130 days. In basic solutions, 28 days. When exposed to sunlight, 34 days in loamy soil.
Imidacloprid	138261-41-3	$C_9H_{10}ClN_5O_2$		255.6633	Insecticide	ESC 0.57	PK 411, DEP 132-310	(M) As Merit 75 WP: 9-10% of mixture, (UM) 0.51 g/l @200°C, PK 610 ppm, DPR 5.14 x 102 ppm (20oC at pH 7)	(UM) The chemical is moderately soluble, and has moderate binding affinity to organic materials in soils. However, there is a potential for the compound to move through sensitive soil types including porous, gravelly, or cobbly soils, depending on irrigation practices	(UM) 48-190 days depending upon ground cover

Pesticide	Algae			Molluscs	Fish			Crustaceans			Rats
Atrazine	(#) *Microcystis aeruginosa* *Chlorococcum* sp. *Dunaliella tertiolecta* *Isochrysis galbana* *Phaeodactylum tricornutum*	8d EC0 10d EC50 10d EC50 10d EC50 10d EC0	0.003mg/l 100 ppb technical acid 300 ppb technical acid 100 ppb technical acid 100-200 ppb technical acid		(#) bluegill bluegill fathead minnows fathead minnows brook trout brook trout	2y LC50 MATC 1y LC50 MATC 1.5y LC50 MATC	5.4-8.4 mg/l at 27°C 0.09 mg/l at 27°C 11-20 mg/l at 25°C 0.21 mg/l at 25°C 4.0-6.0mg/l at 9-16°C 0.06 mg/lat 9-16°C	EPA mysid shrimp	NOAEC	80 µg/l	*** 1780 mg/kg, 1600-3800 when in mixture (UM) 672-3,000 mg/kg
Fipronil				PK Oyster (*C. virginica*) EC50? 770 (180-1700)	* Highly toxic (M) As Regent 4SC: bluegill rainbow trout PK sheepshead minnow (*C.variegatus*)	 96h LC50 96h LC50 96h LC50	 85 µg/l 248 µg/l 130 (110-280) µg/l	(M) As Regent 4SC: *Daphnia magna* PK Mysid (*M. bahia*) grass shrimp (adult) grass shrimp (larvae) grass shrimp embryo crayfish (*P. clarkii*) crayfish (*P. zonangulus*)	48h EC50 EC50 ? 96h LC50 96h LC50 96h LC50 96h LC50 96h LC50	190 µg/l 0.14 µg/l 0.32 µg/l 0.68 µg/l >512 µg/l 63.7 µg/l 65.1 µg/l	* 97 mg/kg (M) As Regent 4SC: 336 mg/kg
Imidacloprid					(UM) rainbow trout carp golden orfe DEP rainbow trout	96h LC50 96h LC50 96h LC50 96h LC50	211 mg/l 280 mg/l 237 mg/l >83 ppm	(UM) Daphnia DEP *Daphnia magna* Mysid shrimp	48h EC50 48h LC50 96h LC50	85 mg/l 85 ppm 34 ppb	(M) As Merit 75 WP: 2591 mg/kg (male), 1858 mg/kg (female) (UM) 450 mg/kg (96h?)

Table 3 – Toxicology data compiled for atrazine, fipronil, and imidacloprid

Chart Sources			
(#)	*Handbook of Environmental Data on Organic Chemicals*, Karel Verschueren, 3rd Edition, 1996	ARS	The ARS Pesticide Properties Database, http://wizard.arsusda.gov/acsl/ppdb.html
(A)	*Agrochemicals Desk Reference: Environmental Data*, Montgomery, John H. 1993	CF	http://chemfinder.cambridgesoft.com/
(M)	According to MSDS Provided by EPR Professional 2002 CD	DEP	"Environmental Fate of Imidacloprid", Juanita Bacey,
(UM)	The University of Manchester, http://www.man.ac.uk/umec/extra/i/listi.html	EPA	Provided by EPA Pesticide Database
*	http://www.beyondpesticides.org	ESC	http://esc.syrres.com/interkow/kowdemo.htm
***	*Farm Chemicals Handbook 2000*, vol 86	LAR	Data provided by Lou Ann Reed of NOAA/NOS/CCEHBR
		PK	Data provided by Pete Key of NOAA/NOS/CCEHBR

Herbicide	(green)
Insecticide	(orange)