

Ecological Assessment of Storm Impacts on Marine Resources

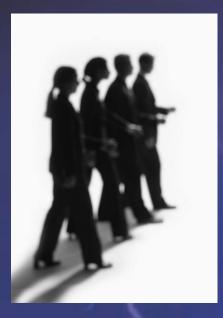
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NOAA National Ocean Service Center for Coastal Environmental Health and Biomolecular Research



## Acknowledgements

The authors wish to thank the following for their invaluable contributions to this research



**Katy W. Chung Michael Fulton Geoffrey Scott Thomas Pullaro Stacey McDaniel Robin Glenn Lou Ann Reed Florida DEP Dr. Ashok Shahane (FDACS) SJRWMD** 





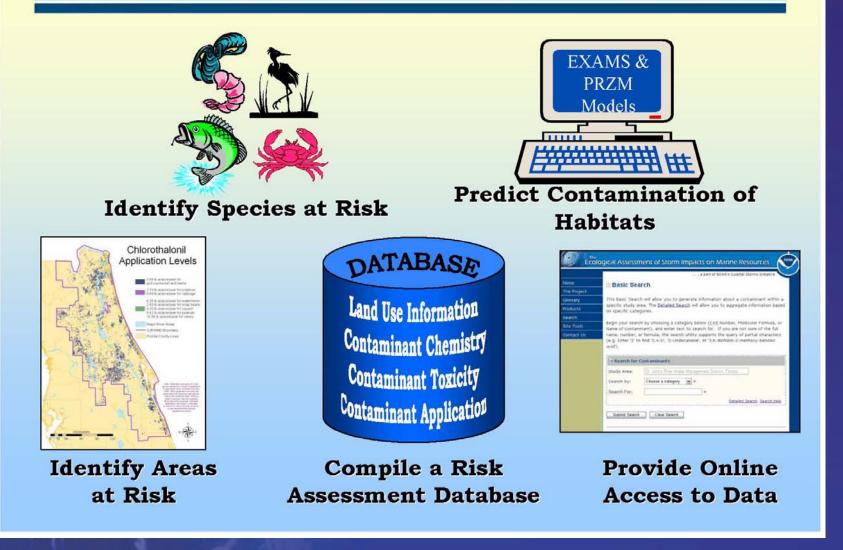
# **Project Purposes**

- Identify species at risk
- Identify geographic locations at risk
- Focus post-storm ecological assessments
- Assist mitigation planning
- Provide access to available risk information
- Promote responsible pesticide use



Some days all you can do is smile and wait for some kind soul to come pull your ass out of the bind you've gotten yourself into.

## Ecological Assessment of Storm Impacts on Marine Resources





# **Florida Pilot Area**

### **Risk Assessment**

- ° Land uses
- ° Toxicology
- ° Database

## Modeling

- ° Transport and Fate
- ° Lake Bethel

### Toxicology

- <sup>a</sup> Indigenous Species
- Developmental Model (NWFC)



Source: www.sjrwmd.org Coastal Storms Initiative



# **Risk Assessment**

### **Crop Information**

- Acreage of Each Crop per County
- Pounds of Active Ingredient per Crop Year Applied to Each Crop

### **Pesticide Information**

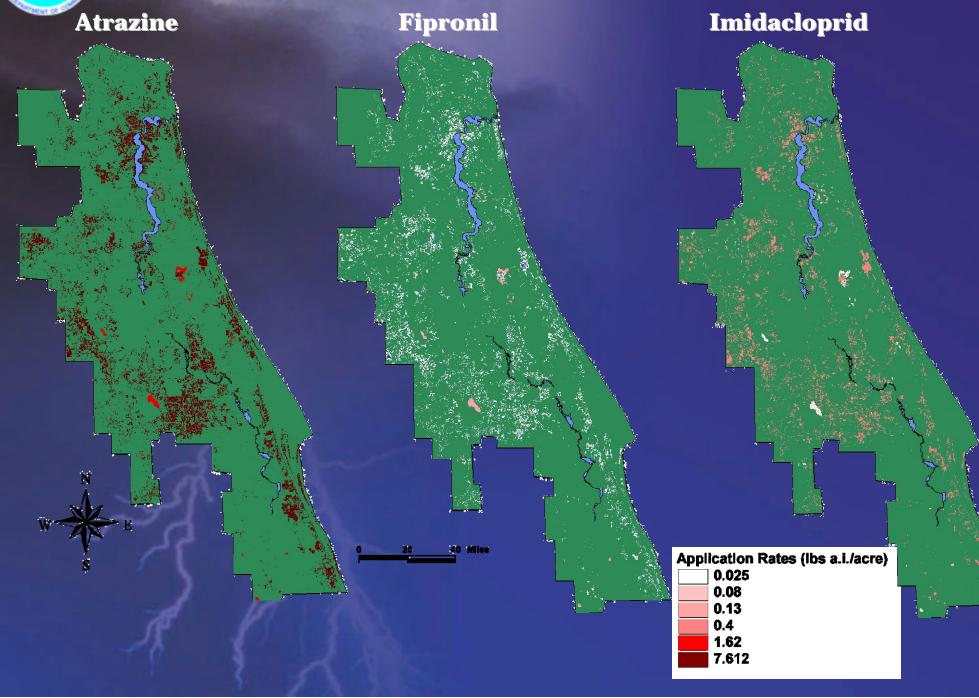
- ° Chemistry
- ° Toxicity
- ° Allowable Land Cover for Application

Web Accessibility

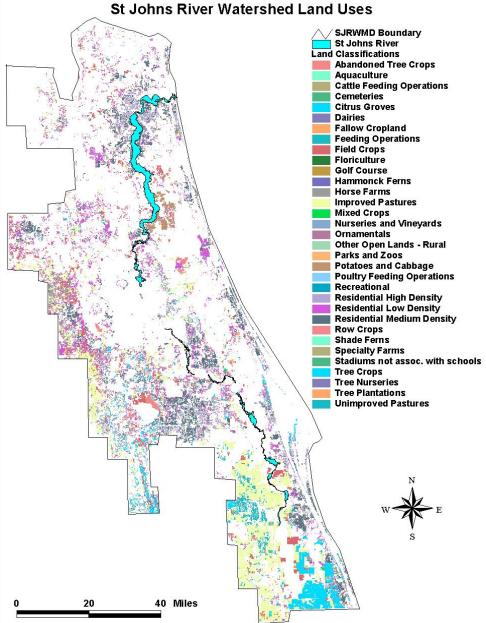


### Land Application Rates of Three Pesticides Used in the St. John's River Florida Watershed.

1088



# **Land Cover Data**



Coastal Storms Initiative

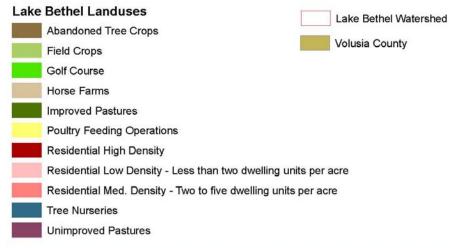
Abandoned Tree Crops Golf Course Poultry Feeding Operations Stadiums not associated with schools Tree Crops Horse Farms Recreational Aquaculture Tree Nurseries Cattle Feeding Operations Improved Pastures **Residential High Density** Tree Plantations Cemeteries Mixed Crops Residential Low Density **Unimproved Pastures** Nurseries and Vineyards Residential Med. Density Dairies Clay County St Johns County Fallow Cropland Ornamentals Row Crops Duval County Nassau County Specialty Farms Field Crops Parks and Zoos 6 12 18 24 Kilometers 3

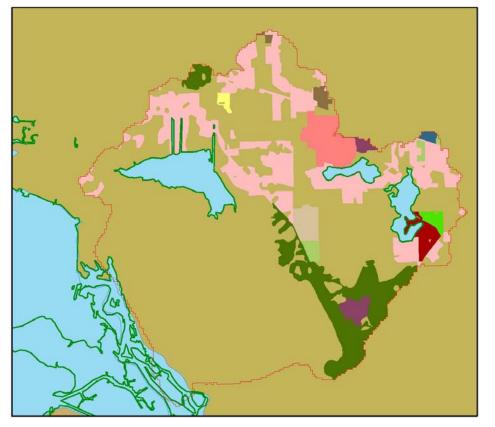
### **Duval County Land Use**

NORR



#### Lake Bethel Watershed







### **EASIMR Web Site**

### http://www.chbr.noaa.gov/easi/

**Coastal Storms Initiative** 

### Ecological Assessment of Storm Impacts on Marine Resources



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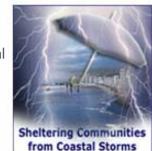
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#### Ecological Assessment Project: Home Page

Welcome to the website of the Ecological Assessment of Storm Impacts on Marine Resources. This project is a part of the Coastal Storms Initiative (CSI) and is designed to assess potential effects on fish and shellfish from non-point source pollution.

For more about this project, please click here.



#### Resources available on this website

This site includes a database of chemical and toxicological information on pesticides permitted for use in the St. Johns River Watershed, Florida. It will include other classes of chemical contaminants and other study areas in the future. You can search the database by contaminant name, Chemical Abstract Service registry number or molecular formula. It will provide estimates of application rates and locations derived from actual reported agricultural applications and USEPA-permitted nonagricultural applications. Locations were cross-referenced to available GIS data layers.

Queries will also provide available information on chemical structure, molecular weight, octanol-water partition coefficients, organic carbon partition coefficients, water solubility, persistence in soil, general toxicity information and specific toxicity levels, to five groups of organisms (algae, mollusks, finfish, crustaceans, and select terrestrial animals).

Toxicity to terrestrial animals is provided as a general comparison to a large body of available toxicological literature. All of this information was obtained from available scientific literature and is provided to assist identifying locations where risks to aquatic organisms might occur following storm events.

To begin querying the project's database, click here. To learn more about this

As part of NOAA's Coastal Storms Initiative, the <u>National Ocean Service</u> (NOS), <u>National Marine Fisheries Service</u> (NMFS), and the <u>Office of Response and Restoration</u> (ORR) are conducting research on the transport of contaminants, estimation of the risks to aquatic organisms, and mitigation approaches to reduce those risks. The project provides users with ecological assessment tools to identify areas of risks, and to mitigate impacts from coastal storms.

#### [ Top ]

#### **Geographic Locations**

There are currently two geographic areas being studied.

- 👪 The Florida Pilot
- The Pacific-Northwest Pilot

#### The Florida Pilot

The Florida pilot region is located along the northeast coast of Florida within the St. Johns River watershed.

If you are interested in learning more about the St. Johns River Water Management District (SJRWMD), please visit their official website at <u>http://www.sjrwmd.org</u>.

This region includes all or a portion of the following counties:



#### The Pacific-Northwest Pilot

The second pilot program is planned for the Pacific Northwest. This pilot region will focus on part of the Lower Columbia River, the northwest Oregon coast, and the southwest Washington coast. <u>NOAA</u> is currently working with state and local partners to identify the issues <u>CSI</u> will address in this pilot region. Chemical contaminants, in additions to pesticides will be included in the database.

St. Johns River Water Management District [Florida]



[ Ton ]



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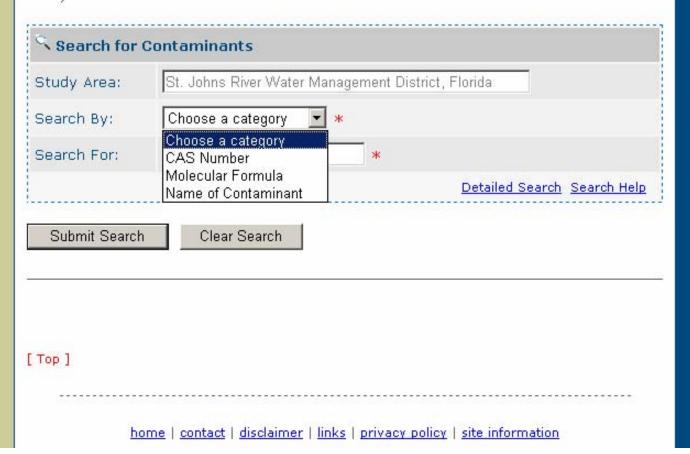
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#### Basic Search

This Basic Search will allow you to generate information about a contaminant within a specific study area. The <u>Detailed Search</u> will allow you to aggregate information based on specific categories.

Begin your search by choosing a category below (CAS Number, Molecular Formula, or Name of contaminant), and enter text to search for. If you are not sure of the full name, number, or formula, the search utility supports the query of partial characters (e.g. Enter '2' to find '2,4-D', '2-Undecanone', or '3,6-dichloro-2-methoxy-benzoic acid').



|            | Degin your search by choosing a category below (CAS Number, Molecular Formula, or              |
|------------|--|
| Site Tools | Name of contaminant), and enter text to search for. If you are not sure of the full            |
| Contact Us | name, number, or formula, the search utility supports the query of partial characters          |
|            | (e.g. Enter '2' to find '2,4-D', '2-Undecanone', or '3,6-dichloro-2-methoxy-benzoic<br>acid'). |
|            | Search for Contaminants  |
|            | Study Area: St. Johns River Water Management District, Florida                                 |
|            | Search By: CAS Number 💌 *  |
|            | Search For: 19 *   |
|            | Detailed Search Help   |
|            | Submit Search Clear Search   |
|            | Search Results   |
|            | Name: Atrazine   |
|            | CAS No.: 1912-24-9   |
|            | Formula: C <sub>8</sub> H <sub>14</sub> ClN <sub>5</sub>                                       |
|            | <u>View more detail on this item</u>   |
|            | Name: 2,4-D 2-ethylhexyl ester   |
|            | CAS No.: 1928-43-4   |
|            | Formula: C <sub>16</sub> H <sub>22</sub> Cl <sub>2</sub> O <sub>3</sub>                        |
|            | <u>View more detail on this item</u>   |
|            | Name: 2,4-D butoxyethyl ester  |
|            | CAS No.: 1929-73-3   |
|            | Formula: C <sub>14</sub> H <sub>18</sub> Cl <sub>2</sub> O <sub>4</sub>                        |
|            | <u>View more detail on this item</u>   |



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### Contaminant Details

#### Atrazine

CAS Number: 1912-24-9

Synonym(s): Atrazine; Atrazine 4L; Atrazine 80W;

Atrazine (Primatol); Atred; Atrex; Attrex; ATZ;

Azinotox 500; Candex; Cekuzina-t; Chromozin;

Crisamina; Crisatrina; Crisazine.

Formula: C<sub>8</sub>H<sub>14</sub>ClN<sub>5</sub>

Molecular Weight: 215.6851

Boiling Point (°C): 200

Melting Point (°C): 175

Pronounciation: Ah-trah-zeen

Contaminant Type: Atrazine is an herbicide.

Additional Information: 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.

#### Solubility (in water)

- Solubility: 33 mg/l <sup>9</sup> Temperature (°C): 25
- Solubility: 28 mg/l

#### Solubility (in water)

- Solubility: 33 mg/l <sup>9</sup> Temperature (°C): 25
- Solubility: 28 mg/l k Temperature (°C): 20
- Solubility: 33 mg/l k Temperature (°C): 27

#### Half-Life

t<sub>1/2</sub>: 30 days <sup>dd</sup> Environment: Estuarine conditions

```
■ t<sub>1/2</sub>: 60 days <sup>1</sup>
```

```
🏪 t<sub>1/2</sub>: 60-100+ days <sup>m</sup>
```

#### **Toxicity Effects**

- Type: Algae <sup>e</sup>
  Scientific Name: Microcystis aeruginosa
  Toxicity: 0.003 mg/l
  Test: 8d EC0
- Type: Algae <sup>e</sup>
  Scientific Name: Chlorococcum spp.
  Toxicity: 100 µg/l
  Test: 10d EC50
  Formulation (°C): Technical acid

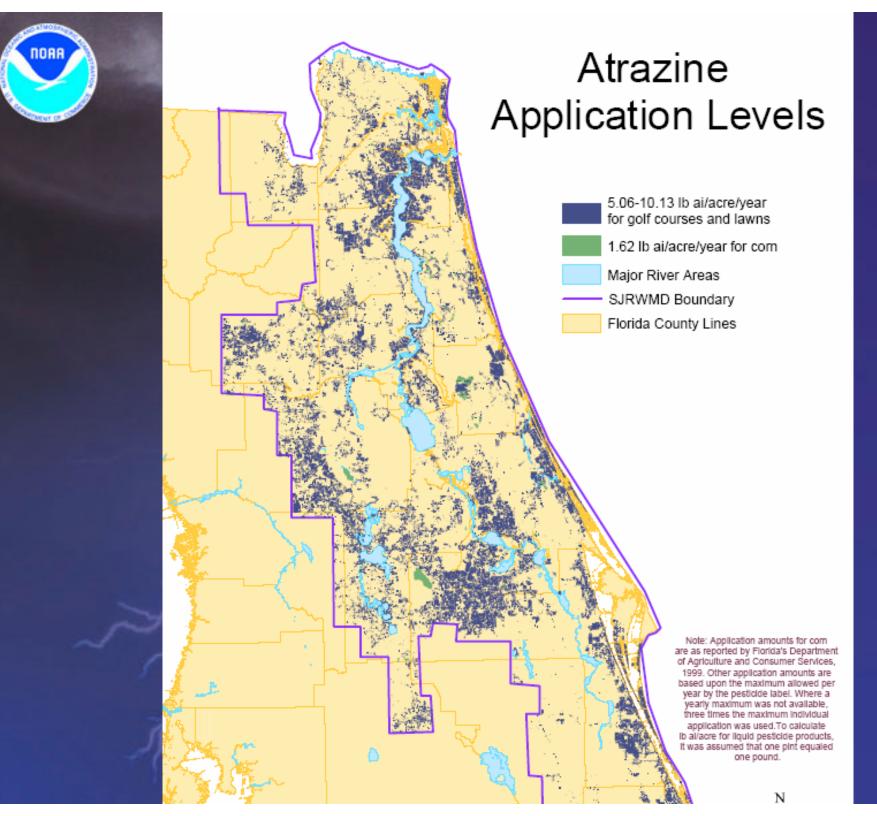
#### **Environmental Partition Coefficients**

PDF

Resource Map: Click below to open in a new window to view or print. Potential applications of this contaminant in the St. Johns Water River Management District

#### Bibliography

- Beyond Pesticides Fact Sheets. Washington, DC: Beyond Pesticides. (n.d). Retrieved November 2003, from http://www.beyondpesticides.org
- AQUIRE (AQUatic toxicity Information REtrieval) Database (As part of the ECOTOX Database) [Internet], Washington, DC:United States Environmental Protection Agency. [date unknown] - [updated February 2003, cited June 2002]. Available from http://www.epa.gov/ecotox/
- c EPR Professional 2002 CD
- d ChemFinder. Cambridge MA: CambridgeSoft Corporation. Retrieved November, 2003, from http://chemfinder.cambridgesoft.com
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- f Howard, P.H., Boethling, R.S., Jarvis W.F., Meylan, W.M., & Michalenko, E.M. (1991). Handbook of Environmental Degradation Rates. Chelsea, MI: Lewis Publishers.
- g Meister, R.T & Sine, C. (Eds.). (2003) Crop Protection Handbook (vol 86). Willoughby, OH: Meister Publishing Company
- h Extension Toxicology Network. Corvallis, OR: Oregon State University. (n.d). Retrieved November, 2003, from http://ace.orst.edu/info/extoxnet/



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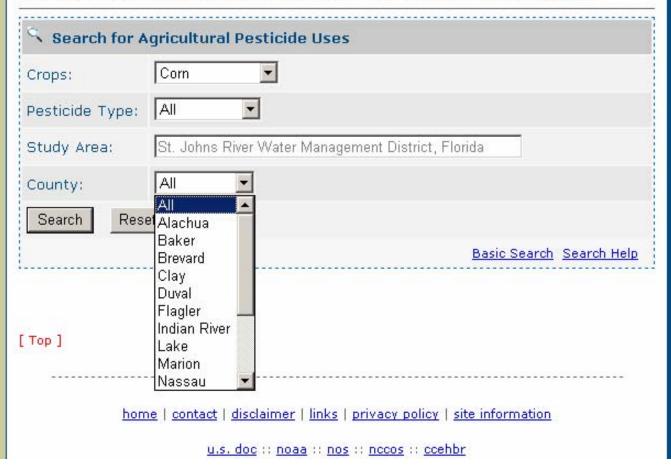
This utility will allow you to aggregate information based on three main categories. Choose one to begin your query:

- Agricultural Pesticide Use
- Toxicity Information

Detailed Search

Geographical Information

If you have a problem using this search utility, please look at our search help.



Detailed Search

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Your search for the relation between a crop: '**Corn**', a pesticide type: '**All**' and County: '**Alachua**' returned 22 records on 3 pages. You are currently viewing page 1, which has 10 records.

| County                           | Crop | Pesticide                    | Application *                            |  |
|----------------------------------|------|------------------------------|--|--|
| Alachua                          | Corn | <u>2,4-D</u>                 | <u>2,4-D</u> 4672 lbs ai/y <sup>cc</sup> |  |
| Alachua                          | Corn | Alachlor                     | 10585 lbs ai/y <sup>cc</sup>             |  |
| Alachua                          | Corn | Atrazine                     | 11826 lbs ai/y <sup>cc</sup>             |  |
| Alachua                          | Corn | <u>Dicamba</u>               | 3650 lbs ai/y <sup>cc</sup>              |  |
| Alachua                          | Corn | Metolachlor                  | 10220 lbs ai/y <sup>cc</sup>             |  |
| Alachua                          | Corn | <u>Pendimethalin</u>         | 5475 lbs ai/y <sup>cc</sup>              |  |
| Alachua                          | Corn | <u>Trifluralin</u>           | 4599 lbs ai/y <sup>cc</sup>              |  |
| Alachua Corn <u>Carbaryl</u>     |      | 29200 lbs ai/y <sup>cc</sup> |  |  |
| Alachua                          | Corn | <u>Carbofuran</u>            | 7300 lbs ai/y <sup>cc</sup>              |  |
| Alachua Corn <u>Chlorpyrifos</u> |      | 14600 lbs ai/y <sup>cc</sup> |  |  |
|                                  |      |                              | 1 <u>2</u> <u>3</u>                      |  |

\* Letters in red superscript indicate the source of the information for that record. <u>View entire bibliography</u>.



# Larval Grass Shrimp Toxicity Testing

- Grass shrimp common East Coast estuarine invertebrate.
- Larval stage most sensitive to pesticides.
- Pesticides tested singly and in mixture: Atrazine (ATZ), Fipronil (FIP), Imidacloprid (IMD)
- 96 hour LC50 tests with media changed every 24 hours.



# **Grass Shrimp**

- Palaemonetes pugio
- Common inhabitant of salt marshes along the Atlantic and Gulf Coasts.
- Important prey item for economically important fish and crustaceans.
- Used at CCEHBR as a model crustacean for toxicity assessments with contaminants in acute and chronic tests in aqueous and sediment exposures.







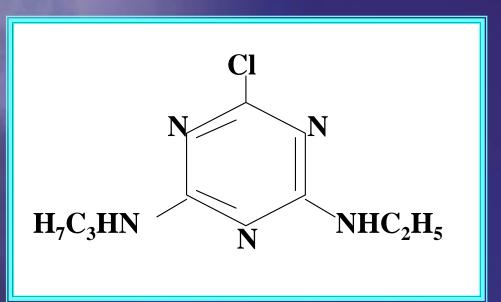
### MUD MINNOW Fundulus heteroclitus 24%



Dominant macrofauna in Southeastern estuarine creeks.



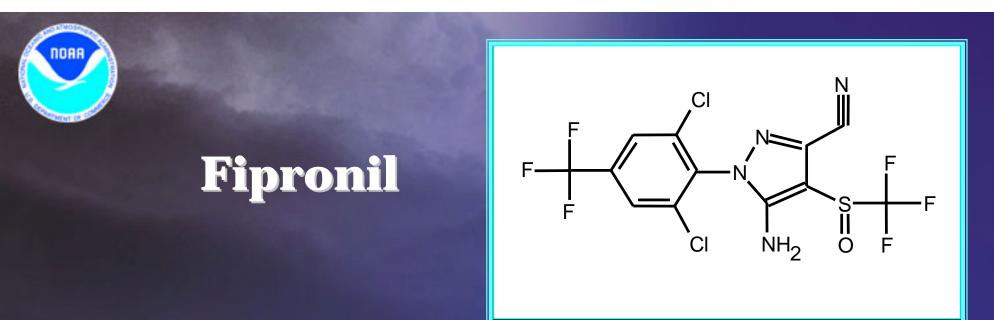
## Atrazine



• Herbicide

### • Second most widely used herbicide in U.S.

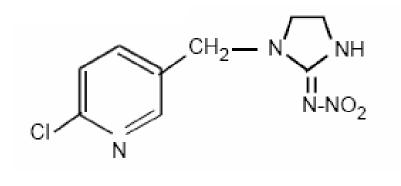
- 34,000 to 36,000 metric tons AI/yr (2001)
- Agriculture, turf grass and residential



- Insecticide
- Eight hundred metric tons produced for worldwide use in 2000.
- Active ingredient for control of termites, fire ants, fleas, ticks, agricultural pests.
- EPA lists it as a chemical alternative to chlorpyrifos.
- Widely marketed in Southeastern US for fire ant control (e.g., Over 'n Out)
- Reports of non-target aquatic animal kills



## Imidacloprid



- Insecticide
- Used on soil, seed and foliage to control turf and agricultural pests. Also controls termites and fleas.
- EPA lists it as a chemical alternative to chlorpyrifos.
- Like Fipronil, growing use.

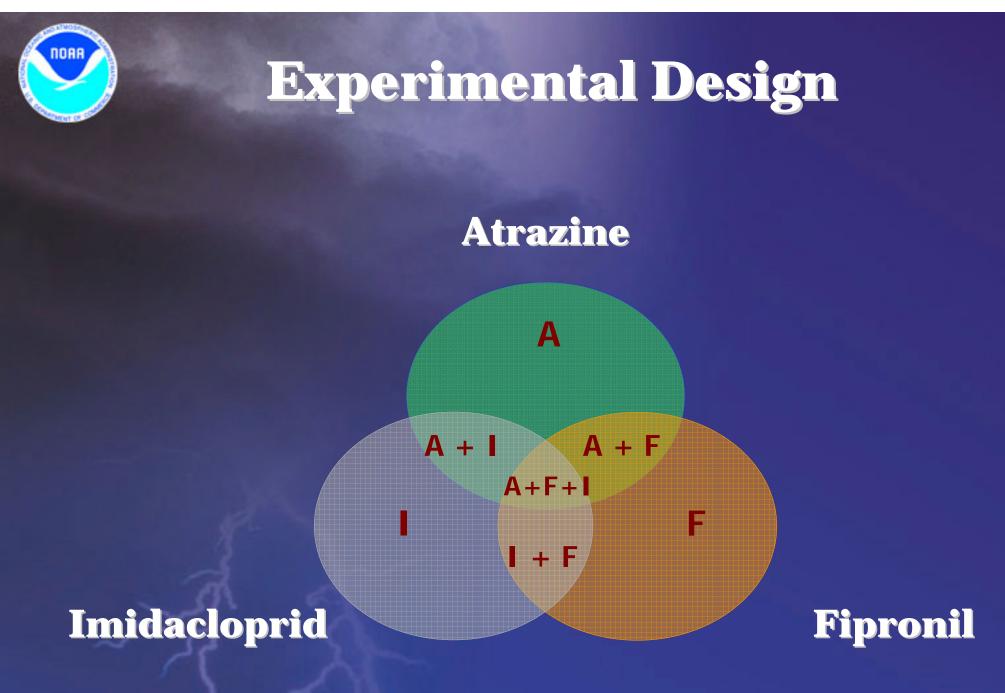


# Methods

### <u>Test Organism</u>

- Grass shrimp collected from Leadenwah Creek, SC.
- Acclimated in 75-L tanks at 25°C, 20 ppt salinity and 16-h light:8-h dark cycle.
- Fed Tetramin Fish Flakes and Artemia.
- Larvae pooled from at least 10 females.
- Newly hatched larvae exposed.







## **Results** <u>Individual Tests</u>

| PESTICIDE    | LARVAE<br>96-h LC50<br>(95% CI)<br>µg/L | ADULT<br>96-h LC50<br>(95% CI)<br>µg/L |  |
|--------------|---|--|--|
| Atrazine     | >10,000                                 | ND                                     |  |
| Fipronil     | 0.68<br>(0.57 – 0.80)                   | 0.32<br>(0.24 – 0.41)                  |  |
| Imidacloprid | 308.8<br>(273.6 – 348.6)                | 563.5<br>(478.1 – 664.2)               |  |





|                | 96-h LC50<br>(95% CI)<br>µg/L |                 |  |  |
|----------------|-------------------------------|-----------------|--|--|
| Contaminants   | Mixture                       | Individual      |  |  |
| Imidacloprid + | 287.6                         | 308.8           |  |  |
| Atrazine       | (241.8 – 341.9)               | (273.6 – 348.6) |  |  |
| Fipronil +     | 0.59                          | 0.68            |  |  |
| Atrazine       | (0.43 – 0.81)                 | (0.57 – 0.80)   |  |  |



## **Results** <u>Mixture Tests</u>

| Contaminants                             | Index<br>Range  | Mixture<br>Toxicity                     | Magnification<br>Factor |
|--|-----------------|---|-------------------------|
| Fipronil +<br>Imidacloprid               | -0.2050.0810.08 | Additive                                | ND                      |
| Fipronil +<br>Imidacloprid +<br>Atrazine | 0.3260.2080.082 | Greater than<br>Additive<br>(Synergism) | 1.21X                   |



# Conclusions

- Individual Tests
  - Fipronil most toxic to grass shrimp larvae with LC50 of 0.68 ug/L
  - Imidacloprid LC50 of 309 ug/L
  - Atrazine non-toxic at environmentally relevant concentrations.
  - Fipronil and Imidacloprid are additive
  - Fipronil, Imidacloprid and Atrazine are synergistic



# **Transport and Fate Modeling**

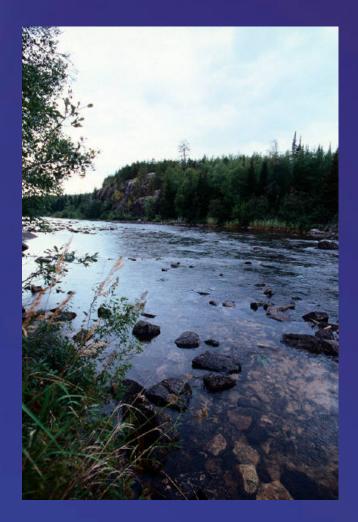
- Identify Locations of Concern
  - \* Florida Atrazine, Fipronil and Imidacloprid
- PRZM-3 (Pesticide Root Zone Model)
  - Groundwater Hydrology and Chemical Transport
  - ° Effects of Rain, Application, Transpiration, etc.
- EXAMS-II (Exposure Analysis Modeling System)
  - Surface Water Effects of Sorption, Biodegradation, Photolysis, etc.
  - <sup>o</sup> Uses Output of PRZM
  - Predicted Concentrations Compared to Aquatic Animal and Human Health Levels of Concern.





# Pesticide Root Zone Model (PRZM)

- Used by EPA and others to estimate groundwater contamination
- Shallow groundwater is major source of surface water contamination after rainfall
- Provides input to surface water model (EXAMS) to better estimate risks to aquatic organisms
- Available free to anyone





# **PRZM Methods**

- 3 pesticides identified by preliminary risk assessment (EASIMR)
- Published chemical parameters
- Florida meteorological data
  - Rainfall on June 1, July 1
  - 2-Yr, 25-Yr and 100-Yr storms





#### **PRZM Methods**

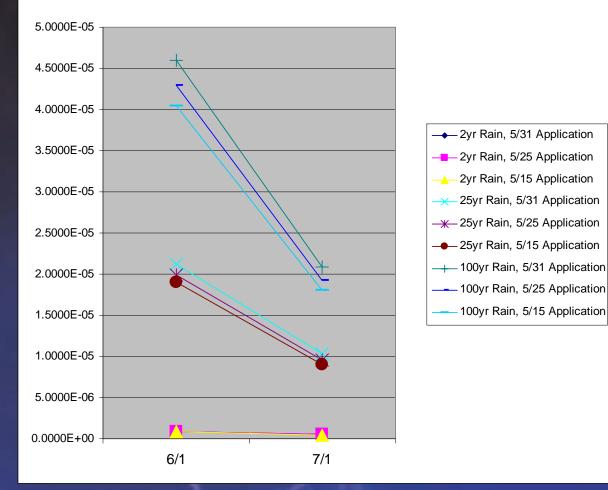
- Pesticides applied at maximum allowed rate
  - Atrazine 142 times Fipronil
  - Atrazine 4 times Imidacloprid
  - Imidacloprid 32 times Fipronil
- Pesticides applied 1, 6 or 16 days before storms
- Lake Bethel, Florida environment
  - Estuarine headwaters are most susceptible
  - Typical of Southeastern US changing adjacent land uses





#### **Soil Erosion of Atrazine**

#### **Total Erosion of Atrazine**



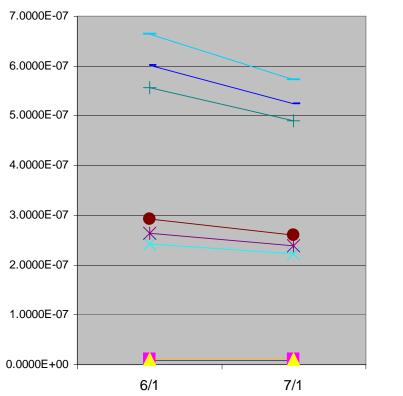
**Highest of the 3** pesticides **Storms:**  $\bullet$ 

•

- 100 Yr > 25 Yr > 2 Yr
- **Application:**  $\bullet$ 
  - 1-D > 6-D > 16-D
- **First storm > second**  $\bullet$ for 25-Yr and 100-Yr



#### **Soil Erosion of Fipronil**



**Total Erosion of Fipronil** 

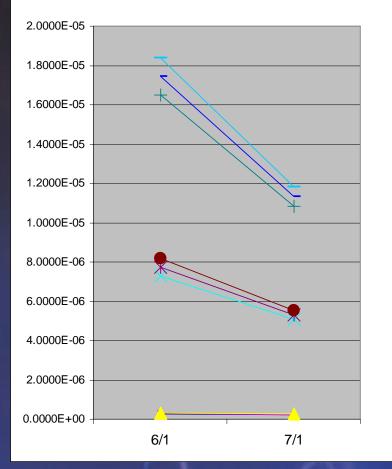


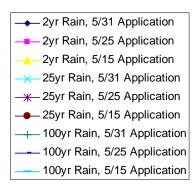
- Much lower than Atrazine or Imidacloprid
- Storms:
  - 100-Yr > 25-Yr > 2-Yr
- Application:
  - 16-D > 6-D > 1-D
  - Different than Atrazine
- First storm > second for 100-Yr



### **Soil Erosion of Imidacloprid**

#### **Total Erosion of Imidacloprid**



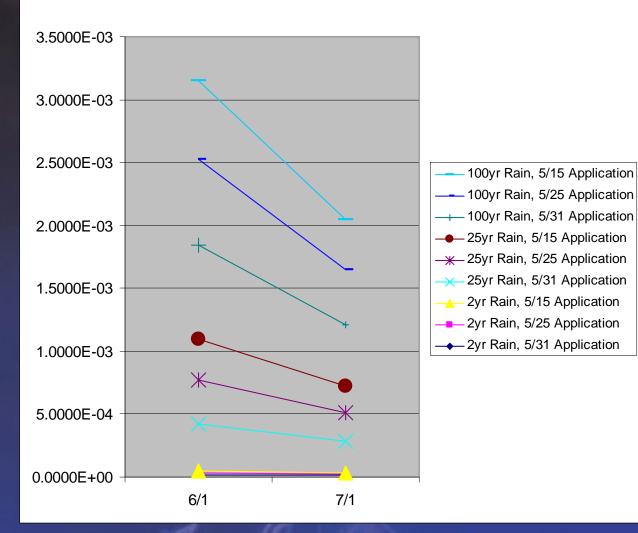


- Storms:
  - 100-Yr > 25-Yr > 2-Yr
- Application:
  - 16-D > 6-D > 1-D
  - **Like Fipronil**
- First storm > second for 100-Yr and 25-Yr



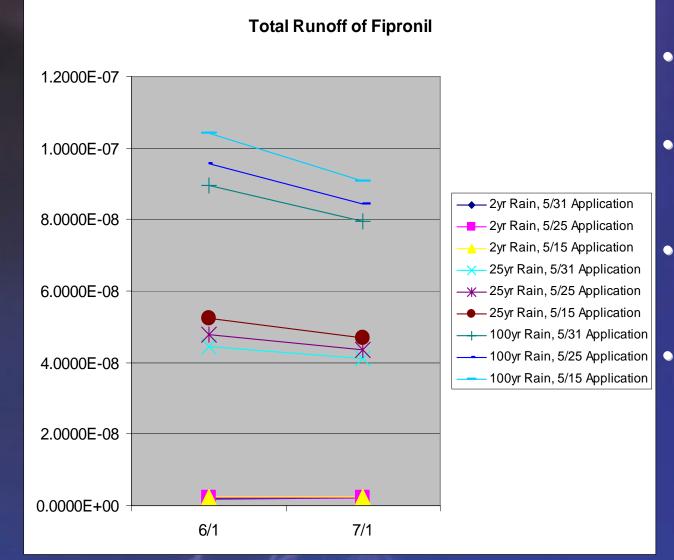
#### **Runoff of Atrazine**

Total Runoff of Atrazine



- Highest of the 3 pesticides
- Storms:
  - 100-Yr > 25-Yr > 2-Yr
- Application:
  16-D > 6-D > 1-D
- First storm > second for 25-Yr and 100-Yr

### **Runoff of Fipronil**

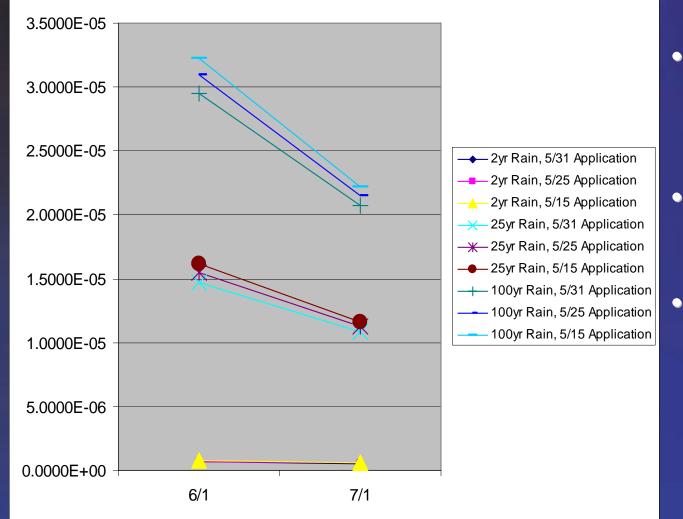


- Lowest of the 3 pesticides
- Storms:
  - 100-Yr > 25-Yr > 2-Yr
- Application:
  16-D > 6-D > 1-D
  - First storm > second for 25-Yr and 100-Yr



#### **Runoff of Imidacloprid**

#### **Total Runoff of Imidacloprid**



- Storms:
  - 100-Yr > 25-Yr > 2-Yr
- Application:
  16-D > 6-D > 1-D
  - First storm > second for 25-Yr and 100-Yr



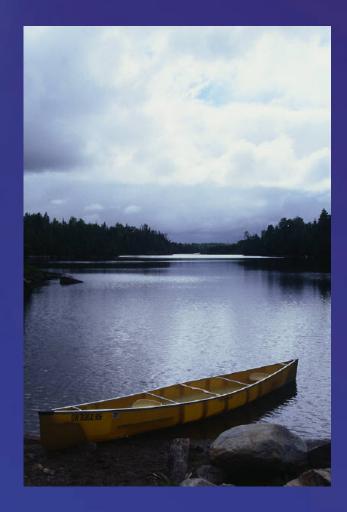
#### **PRZM Summary**

- Many other results
- Provides input to transport, fate and exposure model (EXAMS)
- Shallow groundwater loading:
  - Atrazine >> Imidacloprid > Fipronil
- Storm and application date dependent



### **Exposure Analysis Modeling System (EXAMS)**

- Used by EPA and others to estimate surface water contamination, transport and fate
- Estimates exposure and risk to aquatic fauna
- Available free to anyone





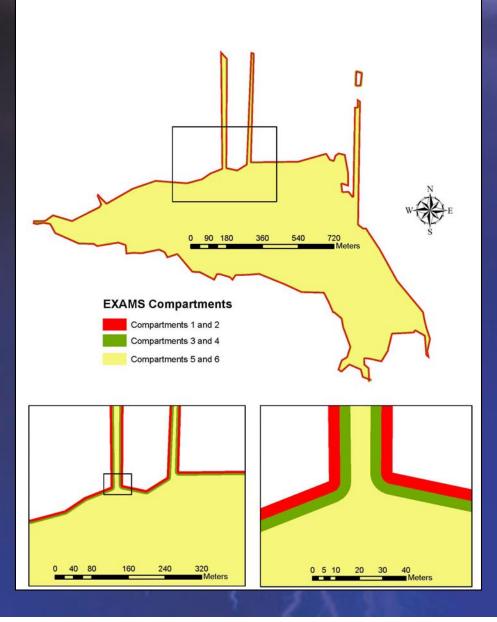
#### **EXAMS Methods**

- Same three pesticides used in PRZM
- Three pesticides identified by preliminary risk assessment (EASIMR)
- Used PRZM loadings and other inputs
- Published chemical parameters
- Jacksonville, Florida meteorological data
- Lake Bethel, Florida environment

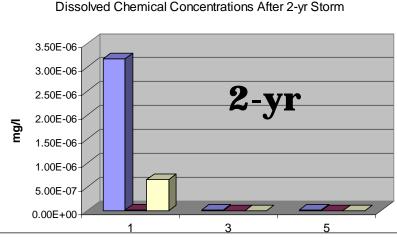


# RORR

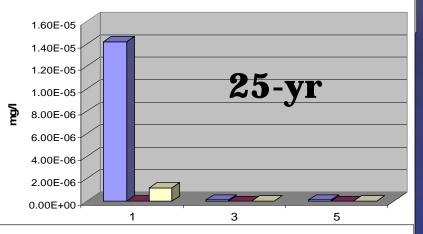
## Lake Bethel EXAMS Compartments (Conceptual)



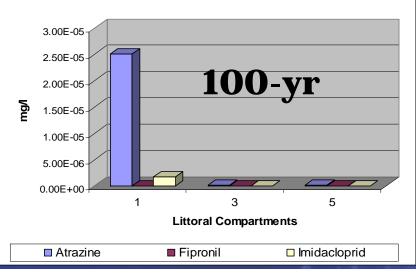
- Odd numbers are littoral
- Even numbers are benthic
- 1 and 2 are closest to shoreline
- 3 and 4 are next
- 5 and 6 are main lake body











Dissolved Chemical Concentrations in Littoral Compartments

**Storms:** 

100 - Yr > 25 - Yr > 2 - Yr

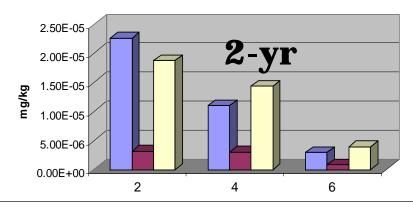
#### **Compartments:**

1>>3>5

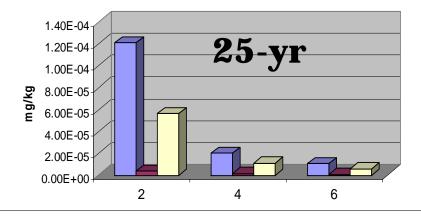
**Pesticides (concentration not toxicity): Atrazine >> Imidacloprid > Fipronil** 

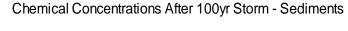
Note different Scales

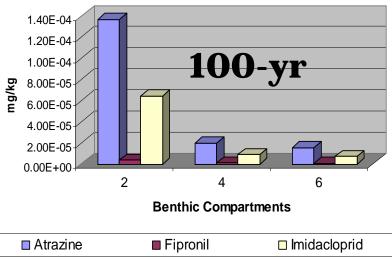
Chemical Concentrations After 2yr Storm - Sediments











#### Pesticide Concentrations in Benthic Sediment

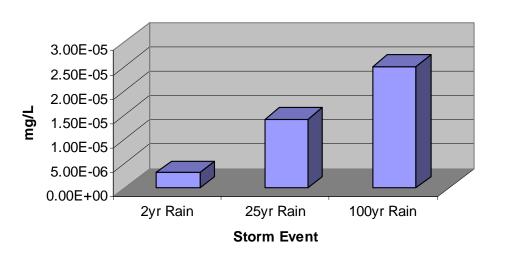
Storms: 100-Yr > 25-Yr > 2-YrCompartments: 2 > 4 > 6Pesticides (concentration not toxicity): Atrazine > Imidacloprid > Fipronil

Note different Scales

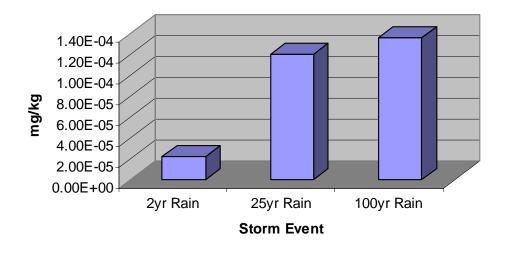


#### **Atrazine Near Shoreline**

**Dissolved Atrazine Concentration in Compartment 1** 



**Atrazine Concentration in Compartment 2 - Sediment** 

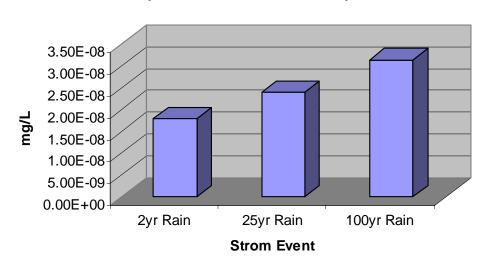


- Different Storm types
- Much higher than main lake
- Did not model feeder creeks, etc
- Increased exposure to both pelagic and benthic fauna

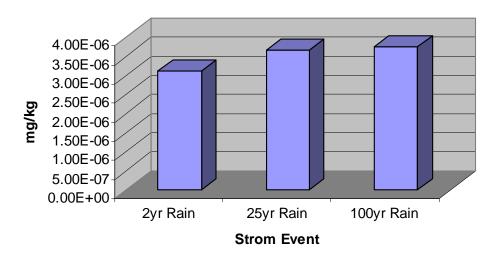


#### **Fipronil Near Shoreline**

**Dissolved Fipronil Concentration in Compartment 1** 



**Fipronil Concentration in Compartment 2 - Sediment** 

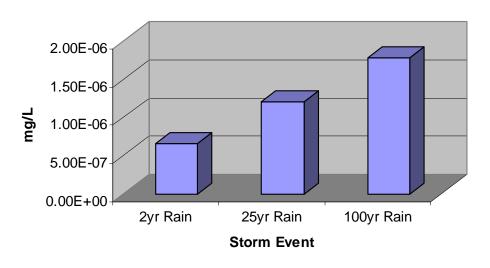


- Different Storm types
  - Not as much effect
- Much higher than main lake
- Did not model feeder creeks, etc
- Increased exposure to both pelagic and benthic fauna

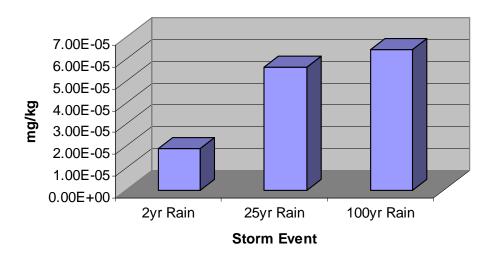


### **Imidacloprid Near Shoreline**

**Dissolved Imidacloprid Concentration in Compartment 1** 



Imidacloprid Concentration in Compartment 2 - Sediment

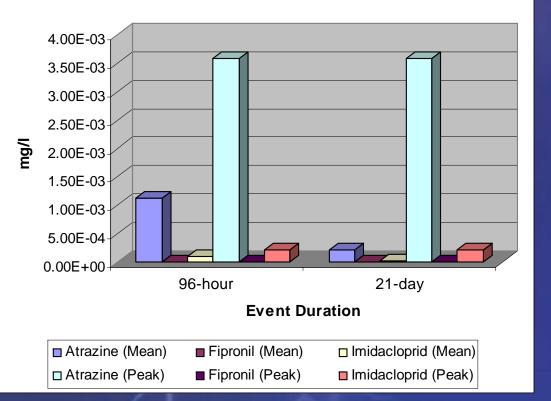


- Different Storm types
- Much higher than main lake
- Did not model feeder creeks, etc
- Increased exposure to both pelagic and benthic fauna



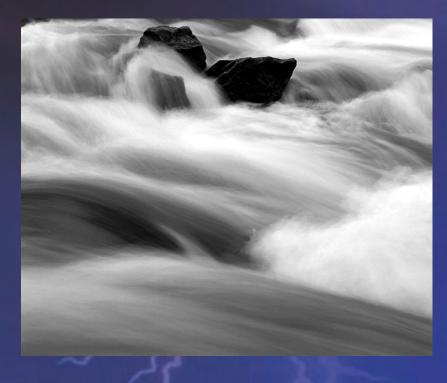
#### **Pesticide Concentrations: Mean vs. Peak**

Ecotoxicological Direct Exposure Concentrations Dissolved in Water Column



- 100-Yr Storm
- Short term peaks much higher than average
- High transient exposure

#### **EXAMS Summary**



- Shows vulnerability of areas nearest runoff
- Can be used to identify other areas of concern
- Compares effects of storm types
- Compares chemical contaminants
- Can be used to estimate risk without being there



### **Assessing Risk**

**It's Not Simple!** 

| Application | A > I > F  |
|-------------|------------|
| Exposure    | A > I > F  |
| Toxicity    | F > I >> A |





#### **Overall Summary**

- EASIMR
  - Web-accessible risk assessment database
  - Risk based upon landuses
  - Useful for preliminary risk estimation
- Toxicity testing
  - Estimates of toxicity of three pesticides
  - Heavily used pesticides in Southeastern US
  - Fipronil > Imidacloprid > Atrazine
  - Mixtures even more toxic
    - Mixtures rarely studied

#### **Overall Summary**

- PRZM Model
  - Estimates shallow groundwater and runoff contamination
  - Identifies effects of storm types, application date
  - Compares pesticides
  - Provides NPS inputs to exposure model



#### EXAMS Model

- Estimates surface water and sediment concentrations
- Used to identify sensitive areas/habitats
- Effects of storms types, application date
- Compares pesticides, other contaminants
  - Exposure: Atrazine > Imidacloprid > Fipronil





- Easy preliminary risk assessments based upon land use data
- Identify species at risk
- Identify geographic locations at risk
- Focus post-storm ecological assessments
- Assist mitigation planning
- Provide access to available risk information
- Promote responsible pesticide use

