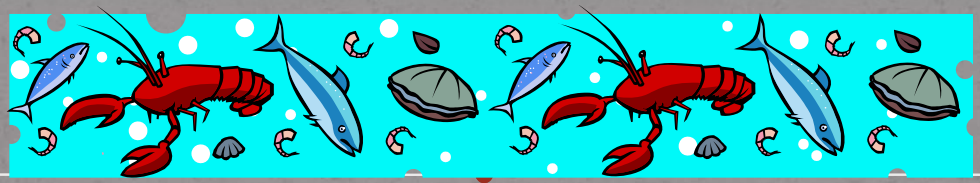
Proposed Method for Identification of Pesticide Active Ingredients which may Impact Lobster Health



Environmental Risk Advisory Committee

Maine Board of Pesticides Control

April 18th 2014

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Scope of the Project

- **Charge:** “Examine whether current pesticide residues have the potential to affect the lobster resource in Maine directly or via impact on other marine organisms”
- **Today’s Focus:** Identifying currently registered pesticides uses in Maine to which lobsters may be exposed and which may affect lobster health
- **Risks:** a mathematical function of exposure and toxicity
- **Selection of analytes:** Multi-step process

Step 1. Products and Ingredients

- Identify and characterize pesticides currently registered for use in Maine
  - Biological receptors
    - Target pest; those to be killed, repelled or otherwise mitigated (7 USC Chapter 125,FIFRA 2008)
    - Non-target species; all other species including man
  - “Active Ingredients”
    - Active against the target pest
    - Identified on the label
  - Some products have more than one active ingredient or more than one use

Step 1. Products and Ingredients

- Identify products and active ingredients (AI) as of 2-24-14
  - 9,471 Federally active pesticide products are registered in Maine
  - 724 Active ingredients
    - Grouped by chemical structure and/or mode of action (MOA)
    - One point in the proposed decision tree is groups of compounds with more than 50 products registered

Step 1. Products and Ingredients

- Characterize active ingredients
  - Type
    - Insecticide
    - Fungicide
    - Disinfectant etc.
  - Subtype
    - Chemical class,
    - Function (attractant, pheromone etc),
    - Mode of Action (MOA).

Types	"Active Ingredient-Products" as of 2-24-14		Active Ingredients (AI)	
	Number	%	# AI	%
Antifouling	333	2.22	6	0.83
Attractants and Repellents	389	2.59	49	6.77
Fungicides	1,225	8.16	140	19.34
Insecticides	4,873	32.47	177	24.45
Herbicides	2,660	17.72	192	26.52
Disinfectants-Slimacides	5,258	35.03	124	17.13
Miscellaneous	271	1.81	36	4.97
TOTAL	**15,009**	**100.00**	**724**	**100**

NOTE: Active ingredient-products, products with more than one active ingredient are double, triple etc. counted)

Step 2. Modes of Action (MOA)

- How a chemical interacts with a biological system
- Think in terms of a lock and key
  - Key is the chemical
  - Receptor in the biological system is the lock
    - If the key fits the lock the lock will open (response happens)
    - If the key nearly the fits in the lock, the lock is jammed (different response happens)
    - If the key doesn't fit the lock at all, there is no biological effect from this receptor

Step 2. Modes of Action (MOA)

- An herbicide (key) which interferes with photosynthesis will likely have low impact on aquatic invertebrates, unless the cellular target site (lock) has a commonality
- An insecticide (key) which acts as growth hormone in insects will like have high impact on lobster, If the biological receptor (lock) is the same in both groups of animals

Step 2. Modes of Action (MOA)

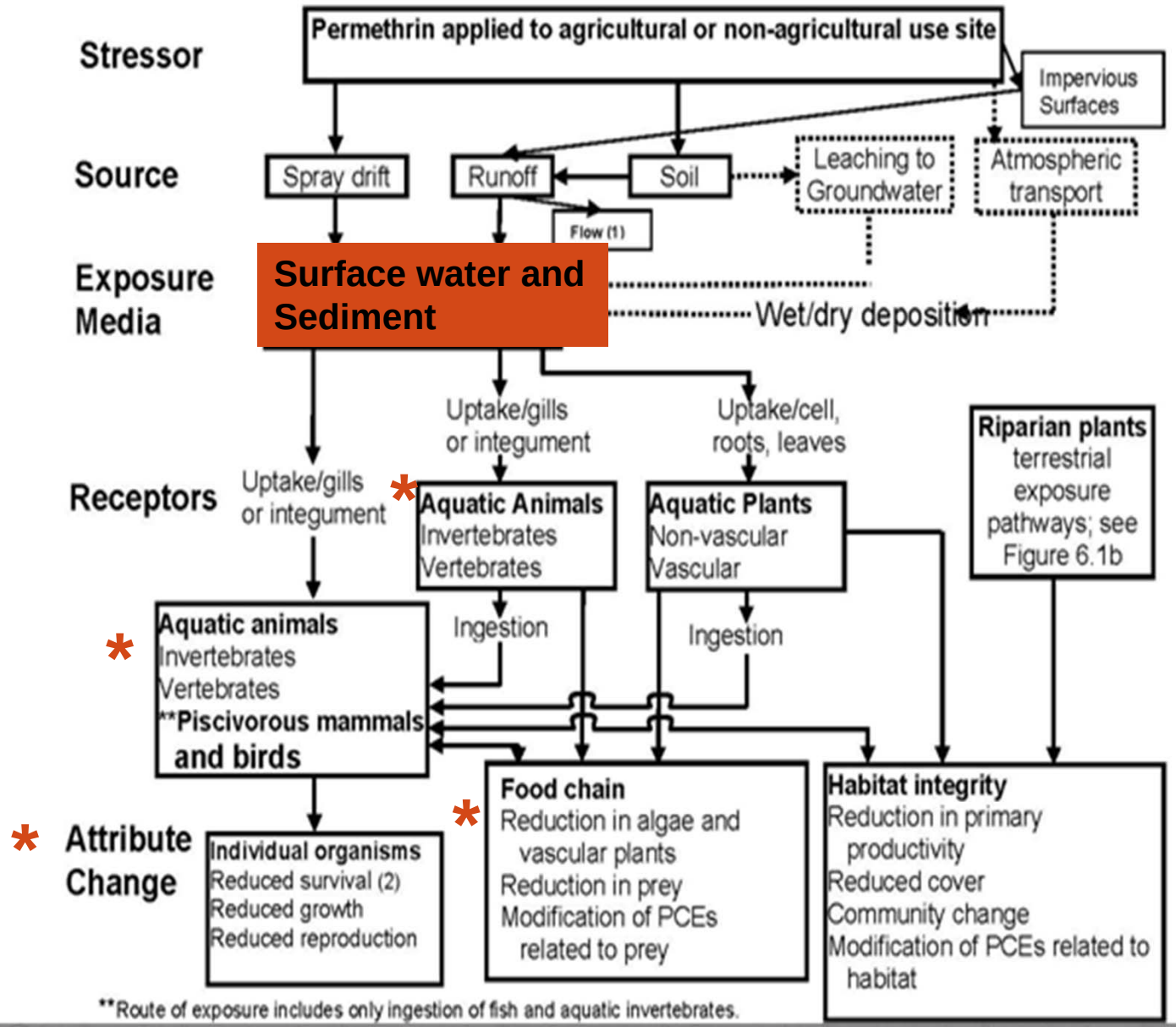
- MOAs are determined by scientific studies (laboratory and field) in target species
- The MOAs used here are based on the development of resistance in the pest population
- Pesticide active ingredients may have more than one MOA
  - The major MOA as identified by the various international resistance committees are used here
  - There may be other unknown MOAs

Step 2. Modes of Action (MOA)

- Identify known MOAs using
  - Insecticide Resistance Action Committee (IRAC) 2012 Report © found at: www.irac-online.org
  - Classification of Herbicide Site of Action (HRAC) 2014© , found at: http://www.hracglobal.com/
  - FRAC Code List © 2013: Fungicides, found at www.frac.info
  - Pesticide Manual 2003
  - Goldfrank et al.,1998
- Identify known MOAs of concern (common to target species and aquatic/sediment dwelling invertebrates)

Grouped Modes of Action of Concern (n = 724)	
Group	**Active Ingredients**
Affecting nervous system	67
Affecting cell metabolism	59
Quaternary Ammonium Chloride Disinfectants	28
Affecting cell structure	19
Chitin inhibitors	6
TOTAL	**188 (26%)**

Excluded MOA Group (n = 724)		
Group	**# Active Ingredients**	**Reason**
Reactive substances	169	Difficult or impossible to determine source
Physical	41	
Multisite/Others/ Unknown	60	
TOTAL	**270 (37%)**	
Plant Specific	163	Specific to target pests
Biological	54	
Attractants/Repellents	49	
TOTAL	**266 (37%)**	


Stressor
Permethrin applied to agricultural or non-agricultural use site
Impervious Surfaces
Source
Spray drift
Runoff
Soil
Leaching to Groundwater
Atmospheric transport
Flow (1)
Exposure Media
Surface water and Sediment
Wet/dry deposition
Uptake/gills or integument
Uptake/cell, roots, leaves
Riparian plants terrestrial exposure pathways; see Figure 6.1b
Receptors
Uptake/gills or integument
*
Aquatic Animals
Invertebrates
Vertebrates
Aquatic Plants
Non-vascular
Vascular
Ingestion
Ingestion
*
Aquatic animals
Invertebrates
Vertebrates
**Piscivorous mammals and birds
*
Attribute Change
Individual organisms
Reduced survival (2)
Reduced growth
Reduced reproduction
*
Food chain
Reduction in algae and vascular plants
Reduction in prey
Modification of PCEs related to prey
Habitat integrity
Reduction in primary productivity
Reduced cover
Community change
Modification of PCEs related to habitat
**Route of exposure includes only ingestion of fish and aquatic invertebrates.

Step 3. General Use Patterns

- Pesticide products are registered for particular uses on certain sites at given rates according to the labels
  - What sites (where)
  - How much (rate),
  - Which equipment may be used?
- How pesticides get into the water
  - Intended to be put in the water (1st cut; type of product)
  - Surface water runoff (2nd cut; environmental fate, See step 4)
  - Misuse or accident

Step 3. General Use Patterns

- Misuse; indoor products used outdoor or agricultural products at your home etc. are illegal
- Accident; spill, fire etc. are not highly predictable or controllable
- **Do we want to address these in this project? If so, How?**

Step 3. Direct Applications to Water

Type of Use	Number of Active Ingredients
	Known aquatic uses
Antifouling	6
Disinfectants-Slimacides	30
Fungicides	?
Herbicides	25
Insecticides	12
Others	0
Total	**73**

Step 4. Environmental Fate Parameters

- Independent of MOA and use site concerns, compounds will be further reviewed, if there are more than 50 products in that chemical-type-MOA class registered
  - Environmental fate
  - Registered sites of interest
    - Aquatic herbicides
    - Antifouling paints

Step 4. Environmental Fate Parameters

Parameter	Definition	EPA's criteria [(a)]
Log K_{ow}	Log of Water-octanol partition coefficient	≥ 3
K_{oc}	Soil organic carbon sorption coefficient	≥ 1,000
K_d	The ratio of sorbed to solution pesticide concentrations after equilibrium of a pesticide in a water/soil slurry (USDA 2013c)	≥ 50
Water solubility	ug/L (ppb) or mg/L (ppm) @ 25 °C (77 °F) Standard temperature	

(a) Criteria for requiring toxicity testing on sediment invertebrates

Step 4. Environmental Fate Parameters

- Data to be reviewed
  - Log Kow and Koc, EPISUITE program (EPA SRC 2014)
    - USDA WIN-PST program (USDA 2013c)
    - Experimental data was given preference over modeled
  - Kd
    - Not used for selection, because it is soil type dependent
    - Koc/100 can be used to approximate unknown Kds (USDA WIN-PST 2013c)

Step 4. Environmental Fate Parameters

- Data sources EPISUITE (EPA SRC 2014) and WIN-PST (USDA 2013c)
- Temperature Dependent
  - Partition coefficients
  - Solubility in water
- How does the ambient water temperature in Maine marine waters alter these parameters?
- Has EPA published estimated environmental concentrations in marine water?

Step 5. Environmental Toxicity Data

- Review EPA's most recent environmental risk assessments for toxicity endpoints for marine invertebrates
- Evaluate acute and chronic toxicity to aquatic invertebrates
- If available evaluate the data for marine sediment dwelling invertebrates

Step 6. Detailed Use Patterns by Product

- Determine the number of unique parent products for AIs of concern registered in Maine
- Use the NSPIRS database to identify general use patterns
  - Indoor only
  - Outdoor only
  - Products which may be used indoor and outdoor
- Review the most recent federally approved label for the parent products, if necessary to verifiy
  - Indoor only
  - Outdoor only
  - Products which may be used indoor and outdoor

Step 7. Risk Assessment

- Risks to aquatic species is currently estimated using the risk quotient method
  - **Acute risks;** Ratio of the peak estimated environment concentration to the median lethal concentration (LC50) or median effect concentration (EC50)
  - **Chronic risks;** Ratio of the mean estimated environment concentration to the chronic no observable adverse effect concentration (NOAEC)
- Factors to consider
  - Age of the exposed animals
  - Concentration in the water
  - Duration of residues in the water

Step 7. Risk Assessment

- In addition to the factors for aquatic organisms
- Sediment dwelling invertebrates
  - May be exposed in sediment or pore water
  - Concerns may be acute or chronic, depending on the half-life of the compound in sediment
  - Aquatic invertebrates have been used as a surrogate for sediment dwelling invertebrates

Underway

- **Step 4. Environmental Fate Parameters**
- **Step 5. Environmental Toxicity Data**
- **Step 6. Detailed site review by product**
- **Step 7. Risk Assessment**
- **Step 8. Laboratory Analysis**

Step 8. Laboratory

- Can the laboratory quantify the selected active ingredients in sediment?

On to Mary's topic