

**Title: Pesticide Research for Sustainability in Michigan Vineyards (791AgD8114)**

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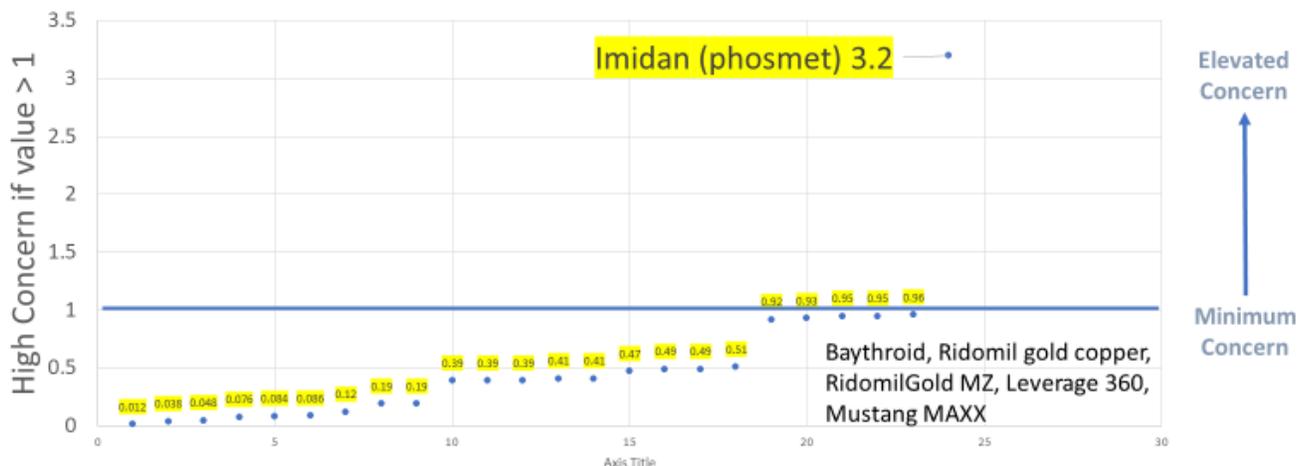
- I. **Overview:** We proposed to collect toxicity information for risk ranking of 71 ingredients in 59 pesticides for managing three diseases: grape berry moth, powdery mildew and downy mildew. We collected toxicity values for humans, fish, birds, bees, and other animals and insects of 77 active ingredients and 66 pesticides. A database has been designed for collecting 400 variables for each pesticide product. Thirty-eight pesticides have sufficient toxicity and exposure data to derive reliable risk values for human health. We have ranked the risk for dietary exposure and worker’s exposure, including oral risk, dermal risk and inhalation risk. We have developed methods for aggregating the risk of ingestion, dermal, and inhalation exposure. We have ranked the risk values for bees and the toxicity values for fish and birds.
- II. **Human Health Risk:** For assessing non-cancer risk, NOAELs (no-observed-adverse-effect levels) and amounts of exposure through ingestion, skin absorption, and inhalation were used. For cancer risk, potency factor (i.e. slop factor of the dose-response relationship), and dietary exposure were used.

**1. Dietary Risk:**

Dietary risk is assessment based on likely exposure to residues in food items, using the national dietary pattern for different age groups in the U.S. The highest exposure subpopulation is usually children between the ages of 1 and 3 years. Figure 1 shows the ranking of the dietary risk of 34 pesticides. Based on sources of a given pesticide in all food items, only one pesticide, Imidan (phosmet), has elevated risk concern for children. Baythroid, Ridomil Gold Copper, Ridomil Gold MZ, Leverage 360 and Mustang MAXX, although ranking top 2-5 on the list, their



**Figure 1. Dietary Risk Ranking of highest exposed subpopulation, Acute Risk**



Based national dietary pattern in the U.S., residues of a given pesticide in all food items

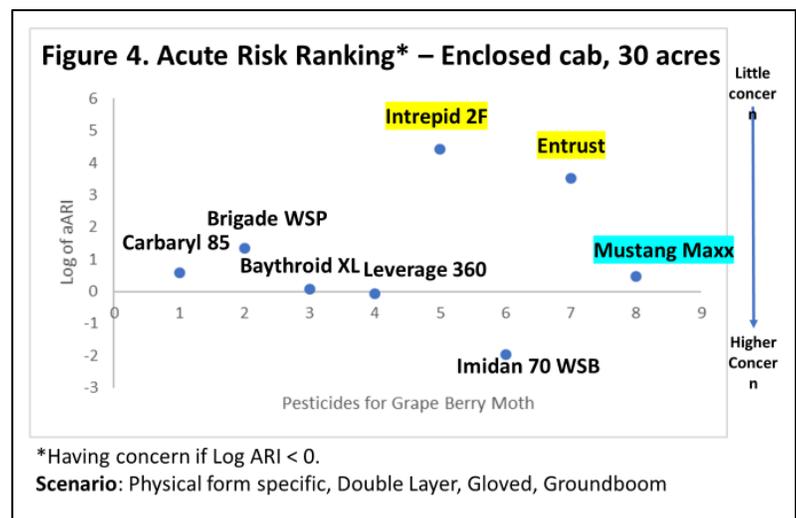
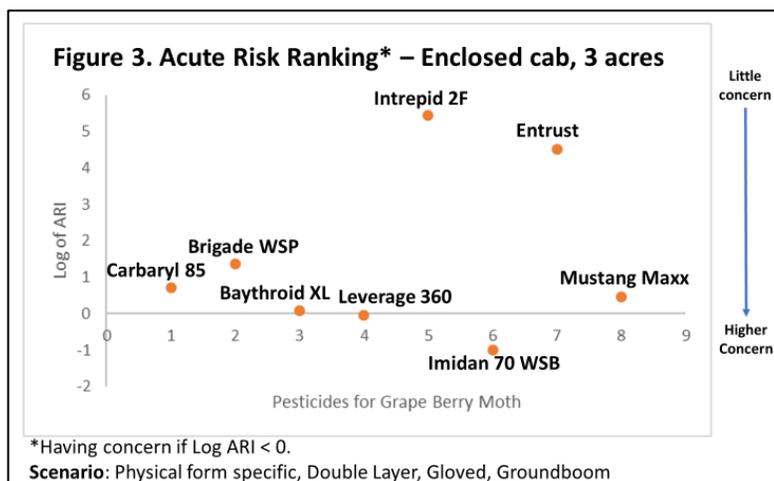
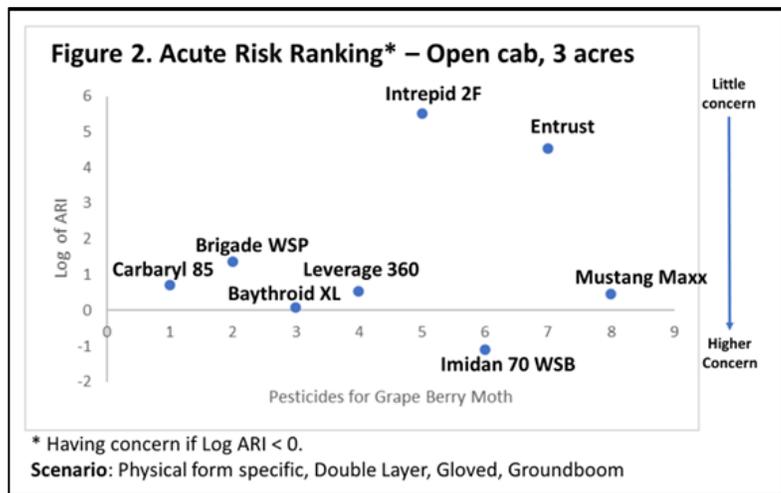
risk values indicate that they should be used judiciously. The rest of the pesticides, whose risk values are much lower than 1, are of minimal concern.

## 2. Worker's Risk:

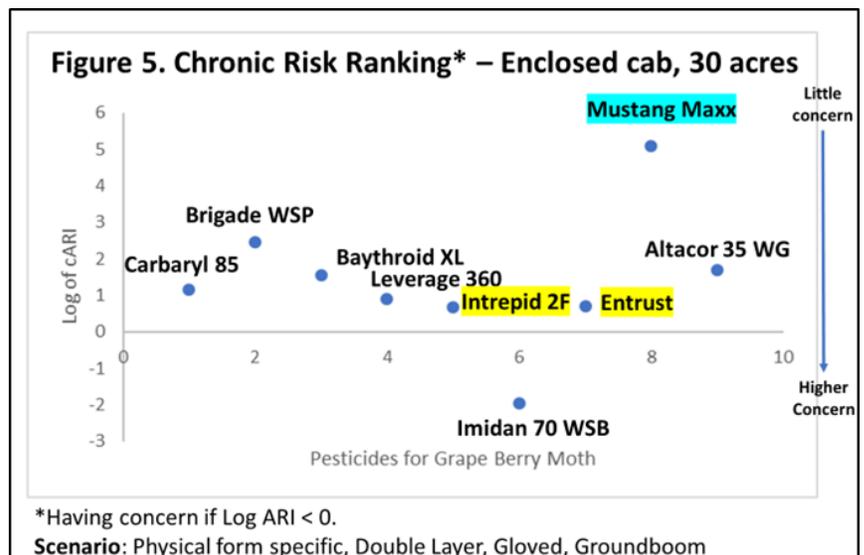
Potential worker's risks are assessed based on pounds of active ingredients applied per acre, the worker's tasks, (mixing, loading, or spraying), usage of closed-loading system, PPE (gloves, layers of clothing, and types of respirators), applicator (spraying methods, whether open or enclosed cab), and formulation of the pesticide products (i.e. dry flowable, granules, liquids, microencapsulates, wettable powders, with or without water-soluble packaging etc.). In combination, there could be 112 exposure scenarios for each pesticide.

We have ranked the risk for each of the three routes of exposure individually (i.e. ingestion, dermal, and inhalation). We have also used the Aggregated Risk Index (ARI) to rank the risk of total exposure. Presented in this report is a set of samples. Risk ranking of other scenarios will be made available to the Great Lakes Sustainable Wine Alliance.

For pesticides used for grape berry moth, the ranking of aggregate/total risks of all three routes of exposure is shown in Figure 2. based on the scenario of gloved, double layer clothing, using a power takeoff (PTO) with open cab, maximum application of a given pesticide per acre as indicated on the label, the same individual performing mixing, loading and applying the pesticide, and groundboom spraying 3 acres of vineyard. Lower ARI (Aggregate Risk Index) value is associated with higher concern over the risk of a given pesticide. When ARI value is around "0", there is minimum concern. Under this scenario, the risk of Imidan 70 WSB has the highest concern, while the concern over Interpid 2F and Entrust is more than 10,000 times less than that Imidan 70 WSB. Our results also demonstrated



that the total risk value for workers is mostly driven by dermal exposure, while dietary exposure and inhalation exposure have small influence on the total risk. The database and the embedded mathematical algorithm we established allow a user to examine risk and risk ranking of various scenarios based on the formulation of a given pesticide, worker's PPE, spray equipment and individual's task. For example, one may examine the difference in risk between open-cab and enclosed-cab PTOs. The



results of comparing the risk and rankings shown in Figure 2 and Figure 3 indicate that there is a slightly higher risk associated with using enclosed cab PTO, when compared with using open cab PTO. The slight difference is caused by the fact that workers using enclosed-cab PTO do not wear double-layer clothing and respirator during spraying. In addition, increasing the area of spray by 10 times, from 3 acres to 30 acres (comparing the 3-acre risk in Figure 2 with the 30-acre risk in Figure 4), does not change the ranking and only increases slightly the relative level of concerns. Increases in the length of exposure, however, does change the ranking of the risk, comparing Figure 4 (acute risk) with Figure 5 (chronic risk): the risk ranking of Intrepid 2F and Entrust decreased, while the risk ranking of Mustang Maxx increased.

### III. Risk and Toxicity of Ecological Species:

#### 1. Honeybee and Insect Risk:

Many pesticide active ingredients are toxic to bees and other beneficial insects. The risk of pesticide products in bees, expressed as RT25 (residual time to 25% mortality), is evaluated based on active ingredients, application rate, and the type of crop. The test insects can be honeybees, alfalfa leafcutting bees, and/or alkali bees. RT25 values could also be used as a surrogate index for assessing potential risk in other insects in the sprayed area.

We ranked the active ingredients with RT25 less than 6 hours as “low risk”; they are color coded in green. The residue level of these pesticides diminishes in less than 6 hours, therefore the risk in bees can be easily managed. Pesticides with RT25 greater than 6 and equal/less than 8 hours are ranked as “medium-low risk”, color coded in blue. The risk of pesticides in this category is manageable with calculated spray time. Those with RT25 greater than 8 hours and equal/less than 12 hours are categorized as “medium-high risk” and color coded in yellow, because their spraying time needs to be carefully managed to

Ranking	Active Ingredient Risk Ranking for Bees
<b>Very High Risk</b>	
1	cyfluthrin
<b>High Risk</b>	
2	cypermethrin
3	phosmet, 0.5 lb or greater
4	carbaryl
<b>Medium-Low Risk</b>	
5	Imidacloprid, if 0.5 lb/acre or greater
<b>Low Risk</b>	
6	chlorantraniliprole
6	spinosad
7	Imidacloprid, if 0.045 lb/acre or less
8	cymoxanil
8	famoxadone
9	All others

minimize the risk in bees. Those with RT25 greater than 12 hours and equal or less than 168 hours (7 days) are ranked as “high risk” and color coded in pink. Pesticides in this category are difficult to manage. Those with RT25 greater than 7 days are categorized as “very high risk” and color coded in red; their risk in bees and other insects is unlikely to be managed effectively.

We have also collected RT25 values generated from Valencia orange trees and citrus in the database for future references for other fruit trees.

## 2. Fish Toxicity:

Potential effect on freshwater fish is ranked based on the index NOAEC (no-observed-adverse-effect concentration). The top 6 “very high toxicity” pesticides and degraded ingredients include Baythroid XL, Mustang Maxx, degraded Topsin-M 70WDG, Merivon – Pyraclostrobin, Leverage 360 AI2, Pristine – Boscalid pyraclostrobin, and Flint, with NOAEC less than 5 ug of active ingredient/L (Table on the right).

The second group includes seven “high toxicity” pesticides: Sevin, Quintec, Merivon – Fluxapyroxad, Topsin-M 70WDG, Procure 480SC (TEP), Brigade WSB, and Sovran, with NOAEC between 5 ug/l to 10 ug/L.

The third group, ranked as “medium toxicity”, with NOAEC equal or greater than 0.1 mg/L and less than 0.5 mg/L, includes 10 pesticides: Procure 480SC (technical), Altacor 35WG, Endura, Vivando, Technical AC 375839, Luna Experience AI1, Abound, Quadris Top – Azoxystrobin, Torino, and Entrust.

The fourth group, ranked as “low toxicity” includes Leverage 360 A11, Rhyme, and Vivardo-BAS 560 00F. This group also includes the pesticides whose toxicity values in freshwater fish are not deemed to be of any concern based on the known properties of the active ingredients.

For a given pesticide, when multiple toxicity values from several fish species at different life stages are available, the value of the most sensitive species and at the most sensitive life stage is applied in the ranking.

<b>Pesticide Ranking for Freshwater Fish</b>	
<b>Ranking</b>	<b>Group 1 High Toxicity</b>
1	Baythroid XL*
2	Mustang Maxx*
3	Topsin-M 70WDG (degrate)
4	Merivon - Pyraclostrobin
5	Leverage 360 AI2*
6	Pristine - Boscalid Pyraclostrobin
7	Flint
<b>Group 2 Medium-High Toxicity</b>	
8	Sevin
9	Quintec
10	Merivon - Fluxapyroxad
11	Topsin-M 70WDG
12	Procure 480SC this NOAEC is lower than TGAI, TGAI is deleted from the ranking
13	Brigade WSB
14	Sovran
<b>Group 3 Medium Toxicity</b>	
15	Procure 480SC (technical)
16	Altacor 35WG
17	Endura
18	Pristine - Boscalid
19	Vivando, Technical AC 375839
20	Luna Experience AI1
21	Abound
22	Quadris Top - Azoxystrobin
23	Torino
24	Entrust
<b>Group 4 Low Toxicity</b>	
25	Leverage 360 AI1
26	Rhyme
27	Vivando, BAS 560 00F, for grapevine
28	Other pesticides of low toxicity concern

### 3. Bird Toxicity:

Bird toxicity is ranked using NOAECs. The most frequently test species for assessing NOAEC are mallard duck and bobwhite quail. In general, the NOAEC in mallard ducks and bobwhite quails are similar. The differences in NOAEC of these two species are usually less than 3X. This toxicity ranking list, shown on the right, are based on the lowest NOAEC observed on all species tested. It is worthy of note that, based on the acute LD<sub>50</sub> value, red-winged blackbird (LD<sub>50</sub>, 56 mg/kg bw) could be much more sensitive to Sevin than bobwhite quails and mallard ducks (LD<sub>50</sub>, 1000 mg/kg bw). The NOAEC value for Sevin, however, is not currently available, it therefore does not appear on the list on the list on the right.

### 4. Earthworm Toxicity:

Assessing toxicity in earthworm was not in the original proposals. Because of Michigan grape growers' interest in soil quality, we provide a brief assessment in this report. Many pesticides that reduce earthworm populations have been removed from the market. Therefore, the pesticides frequently used in Michigan viticulture have minimal data available for toxicity or risk ranking. On our currently assessed pesticide list, Sevin and imicadacloprid in Leverage 360 are known to reduce earthworm populations. Chlorpyrifos, which is used to control mealybugs in viticulture, could also reduce the earthworm population in soil.

### IV. Discussions and Future Studies:

The divisions of the categories, narrative descriptions of the risk or toxicity, as well as color coding can be redesigned depending on the desire of the management approaches of the Great Lakes Sustainable Wine Alliance (GLSWA). The risk ranking lists for worker's health provided in this report are a small set of examples. The complete ranking lists may be delivered to GLSWA through a web-based platform.

In both birds and fish, Torino showed wide variations in different toxicological studies. The variations seem to be caused by study factors other than the differences between test species. For instance, the reported NOAEC in Mallard duck has two values, 99 ppm and 2224 ppm in two similar studies. Based on the NOAEC of 99, Torino is categorized in High Toxicity. Similarly, wide variations between study results are also observed for Vivando. Using the lowest NOAEC values available, Vivando is categorized in Medium Toxicity.

Beyond the scope originally described in the proposals, we have established databases to assess potential pesticide effects on aquatic plants and freshwater invertebrates. In addition, we are conducting surveys for constructing a database-user interface so that the relative risk and toxicity information can be extracted readily by grape growers, using a web-based platform for both Mac and Windows PCs. The relationship database could also be used to develop a mobile app for iOS and Android devices.

Pesticide Ranking for Birds	
Ranking	Pesticide Name
<b>High Toxicity</b>	
1	Leverage 360 AI1
2	Rhyme
3	Luna Experience AI1
4	Mustang Maxx
5	Brigade WSB
6	Torino
<b>Medium-High Toxicity</b>	
7	Merivon - Fluxapyroxad
8	Topsin-M 70WDG
9	Altacor 35WG
10	Quintec
11	Baythroid XL
12	Leverage 360 AI2
13	Endura
14	Pristine - Boscalid
15	Flint
16	Procure 480SC
<b>Medium Toxicity</b>	
17	Sovran
18	Vivando
<b>Medium-Low Toxicity</b>	
19	Merivon - Pyraclostrobin
20	Pristine - Pyraclostrobin
21	Abound
22	Quadris Top - Azoxystrobin
<b>Low Toxicity</b>	
23	Brigade WSB
	Imidan 70 WP
	Intrepid 2F