Screening of Selected Pesticides for Possible Future Consideration as Candidates for Biomonitoring in California

Glufosinate Ammonium, Glyphosate, Imidacloprid, Propanil

Materials for August 14, 2013 Meeting of Scientific Guidance Panel (SGP) for Biomonitoring California
Agenda Item: Chemical Selection Planning

The purpose of this document is to provide background information for the Scientific Guidance Panel’s (SGP’s) discussion of four pesticides for possible future consideration as candidates for biomonitoring in California. The four pesticides are glufosinate ammonium, glyphosate, imidacloprid, and propanil.

The SGP, the public and State staff have requested that the Program screen high use pesticides for possible biomonitoring in California. The four pesticides in the current screening document are all on the California Department of Pesticide Regulation’s (DPR) list of top 100 pesticides used in California in 2011. The pesticides were selected for screening because they are either high on the top 100 list (glyphosate, propanil), have shown recent increases in use (glufosinate), or have potential for residential/household exposure (glyphosate, imidacloprid).

This document includes a brief summary of information located so far on:

- Chemical identity and structure
- Type of pesticide and uses
- Volume applied in California
- Other data relevant to exposure
- Physical chemical properties
- Predicted bioaccumulation and persistence
- Some toxicity endpoints
- Pharmacokinetic factors
- Human biomonitoring

A comprehensive literature search was not conducted. Secondary sources and predictive tools were used for some of the information.

At the August 14 meeting, the Panel will recommend what next steps, if any, should occur. The SGP could recommend that the Program develop a document or documents to support consideration of one or more of the pesticides in this screen as potential designated chemicals. Another option would be for the SGP to recommend further screening of one or more of these pesticides. The Panel could also recommend no further action on any of these.

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1 California Environmental Contaminant Biomonitoring Program, codified at Health and Safety Code section 105440 et seq.
<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Structure</th>
<th>Type of pesticide and uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glufosinate ammonium</td>
<td><img src="image1.png" alt="Structure" /></td>
<td>Herbicide; crop desiccant &lt;br&gt;Used on conventional and genetically modified crops &lt;br&gt;<strong>Example crops:</strong> Corn, canola, soybeans, tree nuts (like almonds and walnuts), grapes, potatoes &lt;br&gt;<strong>Other:</strong> Rights-of-way; spot treatments on recreational fields and residential lawns</td>
</tr>
<tr>
<td>[77182-82-2]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glyphosate</td>
<td><img src="image2.png" alt="Structure" /></td>
<td>Herbicide; plant growth regulator &lt;br&gt;Used on conventional and genetically modified crops &lt;br&gt;<strong>Example crops:</strong> Corn (including forage/fodder), soybeans, cotton, tree nuts (like almonds), grapes, oranges &lt;br&gt;<strong>Other:</strong> Rights-of-way, landscape maintenance, residential garden maintenance</td>
</tr>
<tr>
<td>[1071-83-6]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Major salts: glyphosate isopropylamine salt [38641-94-0]; glyphosate potassium salt [39600-42-5])</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Screening of Selected Pesticides

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Structure</th>
<th>Type of pesticide and uses</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Imidacloprid</strong>&lt;br&gt;[138261-41-3]</td>
<td><img src="" alt="Structure of Imidacloprid" /></td>
<td><strong>Insecticide</strong>&lt;br&gt;<strong>Example crops:</strong> grapes, lettuce, citrus (like oranges), tomato (processing), potatoes, broccoli&lt;br&gt;<strong>Other:</strong> structural pest control, landscape maintenance, golf courses, pet pesticide, lawn and ornamental plant maintenance, invasive species control</td>
</tr>
<tr>
<td><strong>Propanil</strong>&lt;br&gt;[709-98-8]</td>
<td><img src="" alt="Structure of Propanil" /></td>
<td><strong>Herbicide</strong>&lt;br&gt;<strong>Food crop:</strong> rice</td>
</tr>
<tr>
<td>Chemical name</td>
<td>Pounds applied in CA</td>
<td>2011 Pounds sold in CA</td>
</tr>
<tr>
<td>-------------------------</td>
<td>----------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>Glufosinate ammonium</td>
<td>2007: 131,634</td>
<td>2008: 344,200</td>
</tr>
<tr>
<td></td>
<td>2011: 740,327</td>
<td>1,299,405</td>
</tr>
<tr>
<td>Glyphosate (all forms)</td>
<td>2007: 7,236,785</td>
<td>2008: 6,915,054</td>
</tr>
<tr>
<td></td>
<td>2009: 7,145,493</td>
<td>2010: 8,676,349</td>
</tr>
<tr>
<td></td>
<td>2011: 10,745,583</td>
<td>21,016,705</td>
</tr>
<tr>
<td>Imidacloprid</td>
<td>2007: 334,623</td>
<td>2008: 159,407</td>
</tr>
<tr>
<td></td>
<td>2009: 196,048</td>
<td>2010: 266,327</td>
</tr>
<tr>
<td></td>
<td>2011: 290,291</td>
<td>1,502,469</td>
</tr>
</tbody>
</table>

2 California Department of Pesticide Regulation (CDPR): [http://www.cdpr.ca.gov/docs/pur/purmain.htm](http://www.cdpr.ca.gov/docs/pur/purmain.htm)

Propanil

<table>
<thead>
<tr>
<th>Chemical name</th>
<th>Pounds applied in CA</th>
<th>2011 Pounds sold in CA</th>
<th>Other data relevant to exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propanil</td>
<td>2007: 1,801,607</td>
<td>2008: 1,724,068</td>
<td>Residues of propanil or 3,4-DCA(^4) on tested rice samples ranged from 0.03 ppm to 8.7 ppm (US EPA). No residues were reported on polished rice. 1/435 detections in rice samples (USDA). Propanil or 3,4-DCA detected in ambient air and in surface and groundwater in some CA counties.</td>
</tr>
<tr>
<td></td>
<td>2009: 1,904,607</td>
<td>2010: 1,993,021</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2011: 2,221,773</td>
<td>2011: 2,743,410</td>
<td></td>
</tr>
</tbody>
</table>

\(^4\) 3,4-DCA (3,4-dichloroaniline) is the environmental degradate and plant metabolite of propanil.
### Screening of Selected Pesticides

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Molecular weight (g/mol)</th>
<th>Log $K_{ow}$</th>
<th>Vapor pressure (mm Hg)</th>
<th>Water solubility (mg/L)</th>
<th>BCF</th>
<th>Half-life (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Water</td>
</tr>
<tr>
<td>Glufosinate</td>
<td>181.13</td>
<td>-3.9</td>
<td>1.12E-10</td>
<td>1.0E06 ($^{(SRC)}$)</td>
<td>3.2</td>
<td>15</td>
</tr>
<tr>
<td>3-MPPA$^{10}$ (3-Methylphosphonicpropionic acid; MPP)</td>
<td>152.09</td>
<td>-0.8</td>
<td>1.3E-05</td>
<td>1.0E04 ($^{(PBT)}$)</td>
<td>3.2</td>
<td>15</td>
</tr>
<tr>
<td>Glyphosate</td>
<td>169.07</td>
<td>-5.4</td>
<td>1.6E-08</td>
<td>1.0E06</td>
<td>3.2</td>
<td>15</td>
</tr>
<tr>
<td>AMPA$^{10}$ (Aminomethylphosphonic acid)</td>
<td>111.04</td>
<td>-2.1</td>
<td>5.8E-05</td>
<td>1.0E04</td>
<td>3.2</td>
<td>15</td>
</tr>
<tr>
<td>Propanil</td>
<td>218.08</td>
<td>3.07</td>
<td>9.1E-07</td>
<td>1.5E02</td>
<td>49</td>
<td>60</td>
</tr>
<tr>
<td>3,4-DCA$^{10}$ (3,4-Dichloroaniline)</td>
<td>162.02</td>
<td>2.69</td>
<td>6.3E-03</td>
<td>9.2E01</td>
<td>28</td>
<td>38</td>
</tr>
<tr>
<td>Imidacloprid</td>
<td>255.67</td>
<td>0.57</td>
<td>1.7E-06</td>
<td>6.1E02</td>
<td>3.2</td>
<td>60</td>
</tr>
</tbody>
</table>

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5 Relevant chemical species listed
6 Values from PBT Profiler (http://www.pbtprofiler.net). Experimental values are shown in **bold** and estimated values are shown in plain text; all values at 25°C.
7 BCF = Bioconcentration factor. Values were estimated using PBT Profiler (http://www.pbtprofiler.net).
8 Half-life values were estimated using PBT Profiler (http://www.pbtprofiler.net). Orange indicates persistent (P) and red indicates very persistent according to U.S. EPA criteria.
10 Metabolite and/or environmental degradate
<table>
<thead>
<tr>
<th>Chemical</th>
<th>Some toxicity endpoints(^{12})</th>
<th>Pharmacokinetic factors (based on studies in laboratory animals)</th>
<th>Human biomonitoring</th>
</tr>
</thead>
</table>
| Glufosinate | Reproductive and developmental toxicity  
Neurotoxicity | 5-10% oral absorption  
Rapid excretion, primarily as parent compound in feces | Glufosinate and 3-MPPA reported in serum (Quebec, Canada).  
*Refer to Aris and Leblanc (2011) and Blacker et al. (2011) for more details.* |
| Glyphosate | Developmental toxicity  
Indication of endocrine activity (decrease in aromatase activity) | 30-36% oral absorption; poor dermal absorption  
Rapid excretion, predominantly as parent compound. Greater excretion in feces. | Glyphosate detected in urine:  
Farm (Iowa, S. Carolina, Minnesota) and non-farm families (Iowa)  
Adults from 18 European countries (unpublished study); also detected AMPA |
| Imidacloprid | Developmental neurotoxicity | >90% oral absorption  
Rapid excretion, primarily via urine. | No biomonitoring studies located |
| Propanil | Immunotoxicity | Rapid oral absorption of 3,4-DCA, plant metabolite and environmental degradation product of propanil.  
Rapid excretion, predominantly in urine | 3,4-DCA detected in urine.\(^{13}\)  
Adults, rural central Italy  
Farmers, Italy  
3,4-DCA-hemoglobin adducts detected in blood of 2 agricultural worker volunteers |

\(^{11}\) Many studies tested commercial formulations (including an adjuvant for example) or technical grade chemicals.  
\(^{12}\) This column provides information located so far on some toxicity endpoints, including from secondary sources. If any of these chemicals are chosen for further consideration, the known or suspected health effects will be reviewed and described in more detail.  
\(^{13}\) 3,4-DCA is also a metabolite of diuron and linuron.
Selected references consulted by OEHHA in preparing screening tables

**Glufosinate**


**Glyphosate**


**Imidacloprid**

Abou-Donia M, Goldstein L, Bullman S, Tu T et al. (2008). Imidacloprid induces neurobehavioral deficits and increases expression of glial fibrillary acidic protein in the


**Propanil**


