# Chemical Selection Planning

## *Screening of four pesticides for possible future biomonitoring*

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*Presentation to Scientific Guidance Panel*
*August 14, 2013*

# Purpose of agenda item

- Review preliminary screen on four pesticides in CDPR* Top 100 list
  - Glufosinate ammonium
  - Glyphosate
  - Imidacloprid
  - Propanil
- Obtain Panel input on these as possible candidates for future consideration

*California Department of Pesticide Regulation

# Background

- Screening of pesticides as possible candidates for biomonitoring requested by:
  - Scientific Guidance Panel
  - State staff
  - Public

# Selection of pesticides for screening

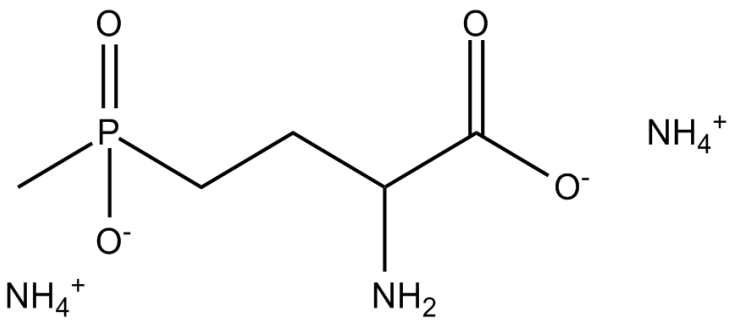
- Volume of use
- Marked increase in use
- Residential/consumer uses

# Screen briefly summarizes:

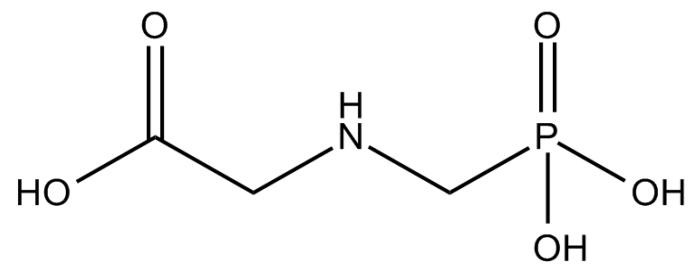
- Exposure sources
- Physical chemical properties
- Persistence and bioaccumulation
- Possible toxicity endpoints
- Key pharmacokinetic factors
- Past biomonitoring studies

# Chemical Structures

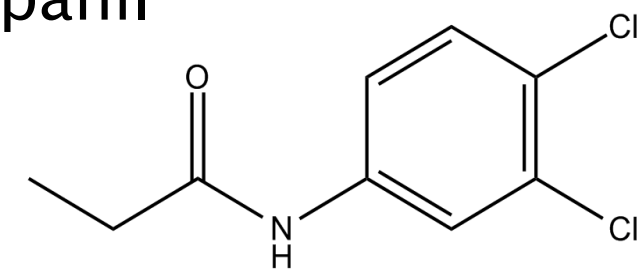
Glufosinate ammonium



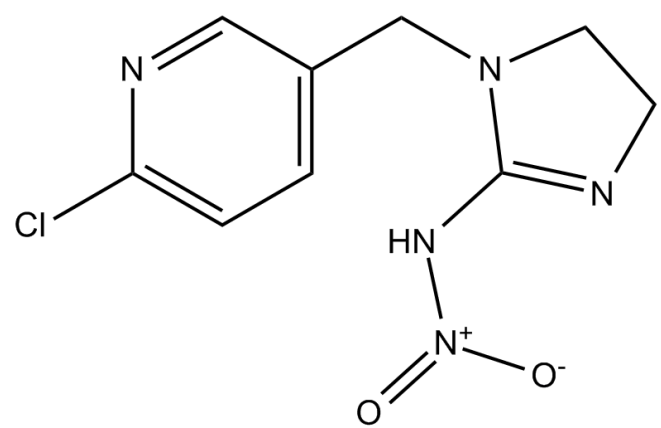

Glyphosate




Propanil




Imidacloprid



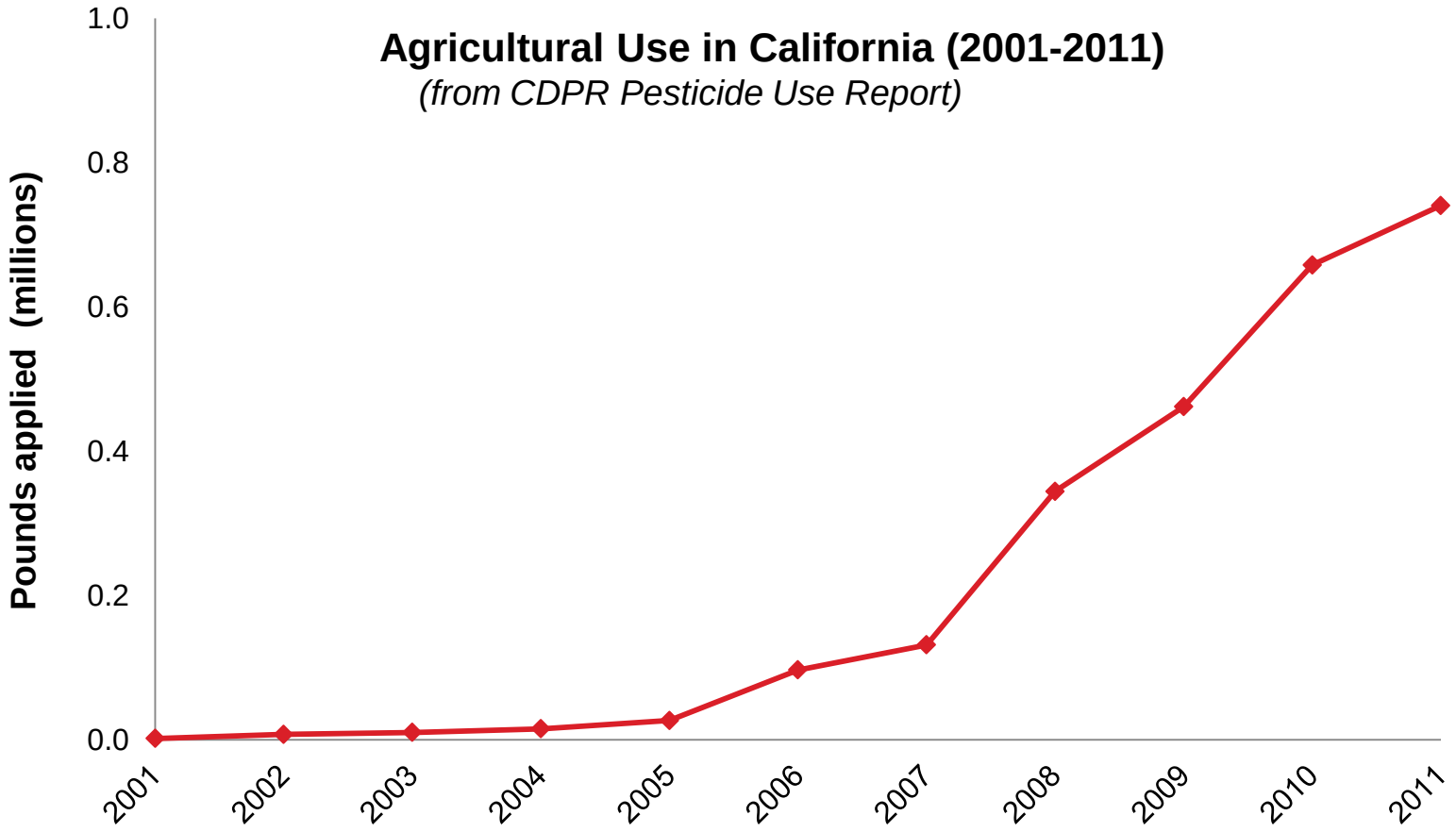
# Types of pesticides and uses

| Pesticides | Pesticide type and uses |
|---|---|
| Glufosinate ammonium | Herbicide; crop dessicant<br><br>Example crops: Corn, almonds, grapes, walnuts<br><br>Other: Rights-of-way, spot treatments on recreational fields and residential lawns |
| Glyphosate | Herbicide; plant growth regulator<br><br>Example crops: Corn, soybeans, almonds, grapes, cotton, pistachios, walnuts, oranges<br><br>Other: Rights-of-way, landscape and residential gardens |

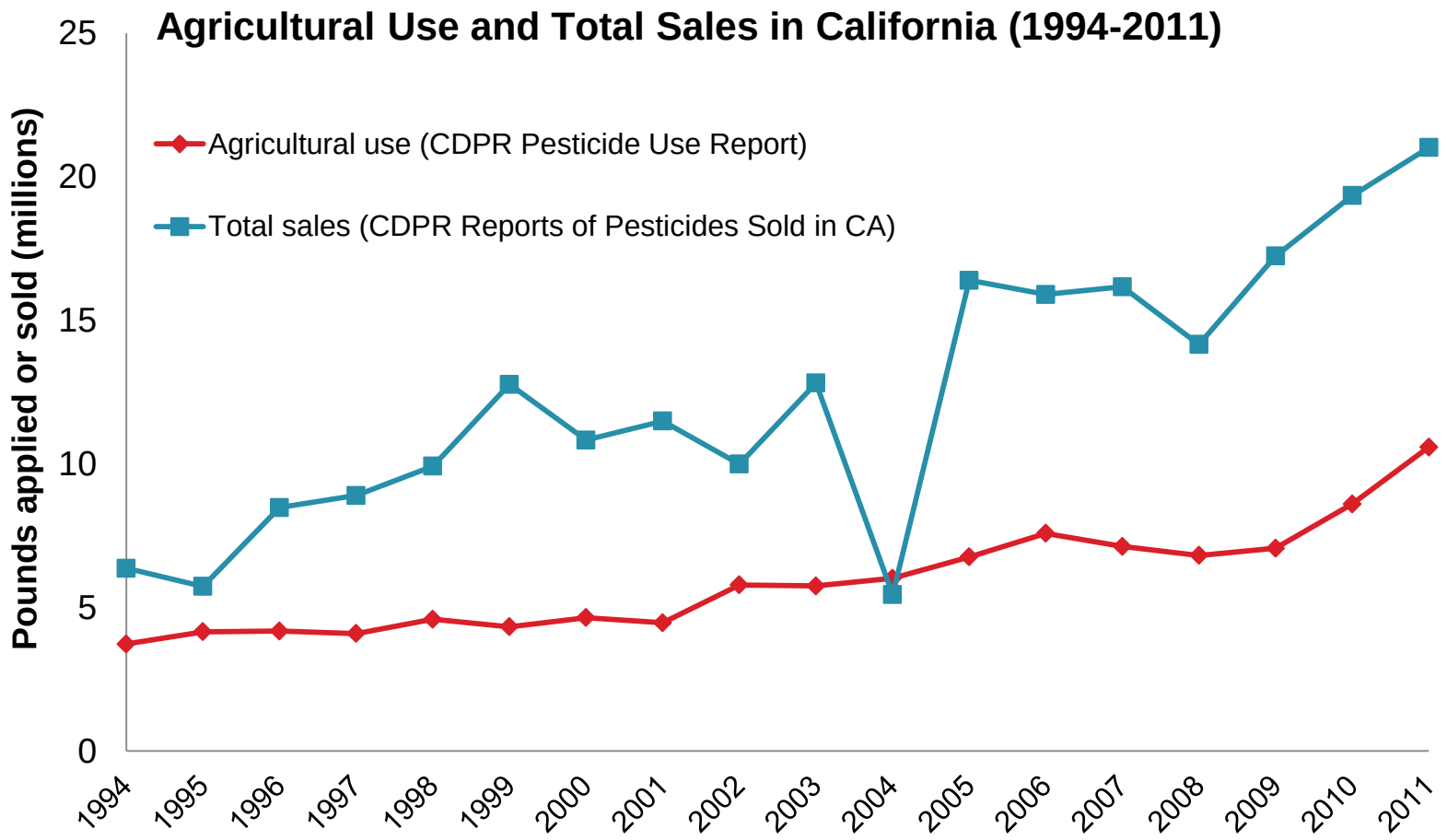
# Types of pesticides and uses

| Pesticides | Pesticide type and uses |
|---|---|
| Imidacloprid | Insecticide<br><br>Example crops: Grapes, oranges, lettuce, tomatoes, broccoli<br><br>Other: Structural pest control; landscape, lawn, ornamental plant maintenance; pet pesticide; invasive species control |
| Propanil | Herbicide<br><br>Crop: Rice |

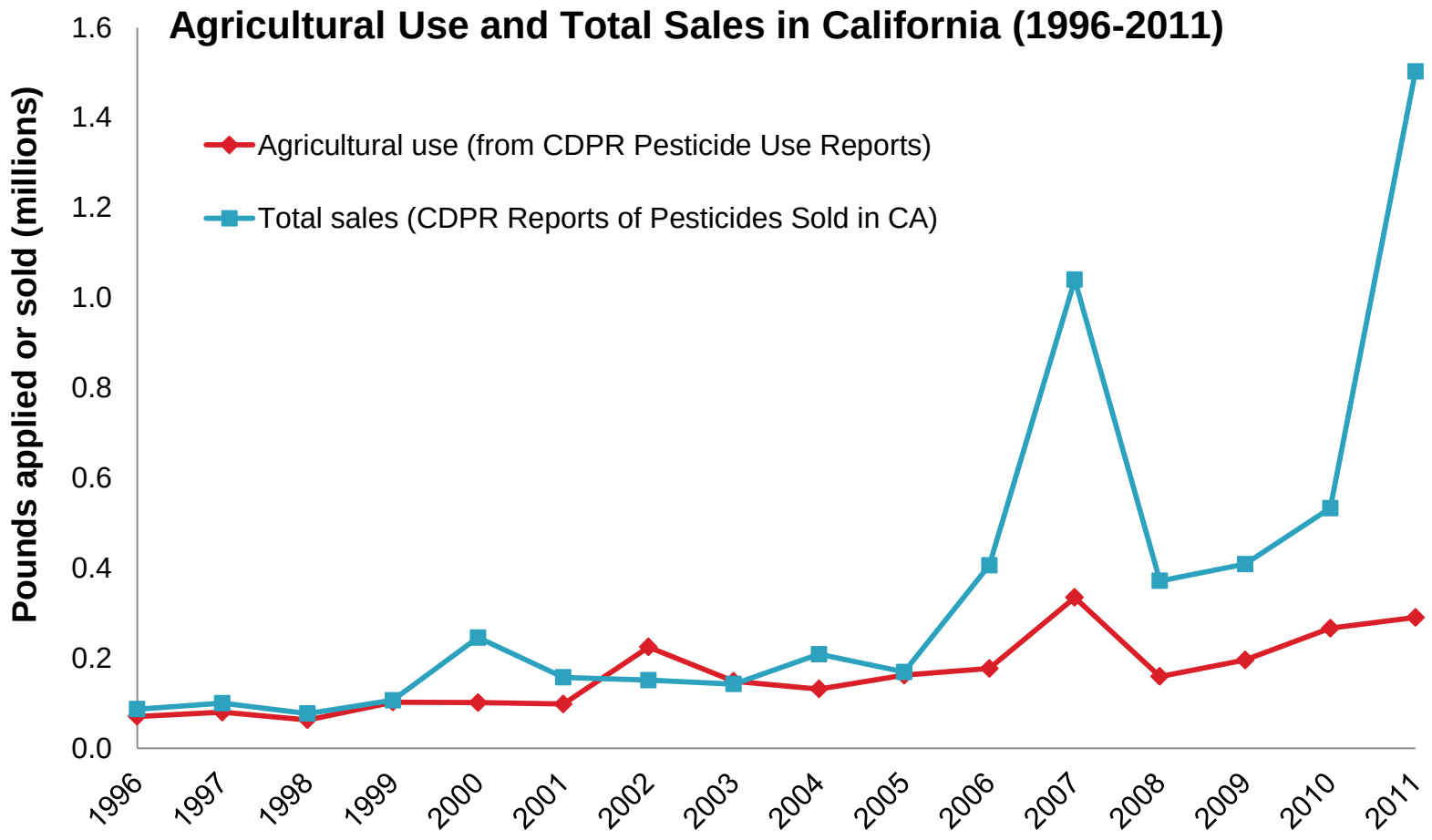
# Glufosinate Ammonium



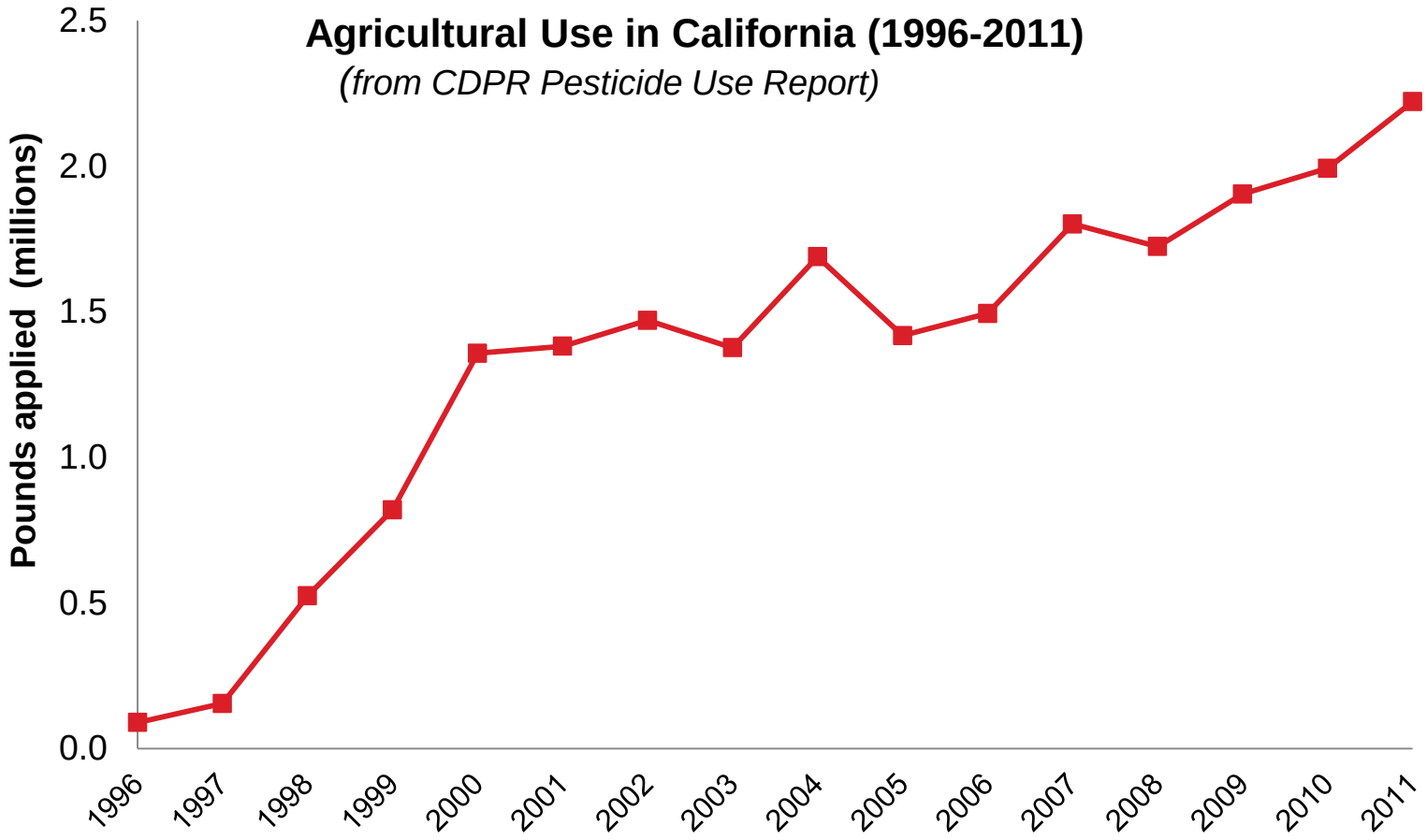
# Glyphosate


Agricultural Use and Total Sales in California (1994-2011)
Pounds applied or sold (millions)
25
20
15
10
5
0
Agricultural use (CDPR Pesticide Use Report)
Total sales (CDPR Reports of Pesticides Sold in CA)
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011

# Imidacloprid



# Propanil


Agricultural Use in California (1996-2011)
(from CDPR Pesticide Use Report)
Pounds applied (millions)
2.5
2.0
1.5
1.0
0.5
0.0
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011

# Persistence & bioaccumulation

| Chemical | Persistence (P) Bioaccumulation (B) | |
|---|---|---|
| | P* US EPA | B** Log $K_{ow}$ |
| Glufosinate | — | -3.9 |
| 3-MPPA*** (3-Methylphosphinicopropionic acid) | — | -0.8 |
| Glyphosate | — | -5.4 |
| AMPA*** (Aminomethylphosphonic acid) | — | -2.1 |
| Imidacloprid | P | 0.57 |
| Propanil | P | 3.07 |
| 3,4-DCA*** (3,4-Dichloroaniline) | P | 2.69 |

* Conclusions of PBT Profiler (US EPA screening tool)
** Log $K_{ow} \geq 4$ considered evidence of possible bioaccumulation
*** Metabolite and/or environmental degradate

# Potential exposure sources

- Type of information:
  - Residues in food
  - Exposures from residential use
  - Detections in the outdoor environment

# Residue data (produce, crops)

| Chemical | Residue data located |
|---|---|
| Glufosinate | No crop/produce residue data located from US monitoring programs |
| Glyphosate | USDA produce monitoring (2010-2011) – US soybeans<br>Detected in 271/300 samples. Range: 0.26-18.5 ppm<br>AMPA detected in 287/300 samples. Range: 0.26-20 ppm |

# Residue data (produce, crops)

| Chemical | Residue data located |
|---|---|
| Imidacloprid | CDPR produce monitoring (2011)<br>Range: 0.012–0.516 ppm<br><br>USDA produce monitoring (2011)<br>Percent detects:<br>cherry tomatoes, 20%; lettuce, 36%; sweet bell peppers, 26% |
| Propanil<br>(or 3,4-DCA) | US EPA (2007) – Studies cited in modifying tolerances<br>Reported range of 0.03–8.7 ppm, but not in polished rice<br><br>FDA (2008) pesticide monitoring:<br>Reported in list of pesticides "detectable and found"<br><br>USDA (2009) produce monitoring:<br>1 detection in 435 rice samples |

# House dust: Glyphosate

| Type of household | Detection frequency | Residue in dust<br>Adjusted geo mean*<br>(ng/g dust) |
|---|---|---|
| **Non-farm**<br>(6 homes; 33 samples) | 85% | 110 |
| **Farm**<br>(5 homes; 31samples) | 100% | |
| No spray | | 1000 |
| Spray within 7 days | | 1300 |

*See Curwin et al. (2005) for details

# Imidacloprid exposure from pet pesticide use

- Six dogs treated with Advantage® (9.1% imidacloprid)
- Transfer from dogs' coats to cotton glove, through 4 weeks

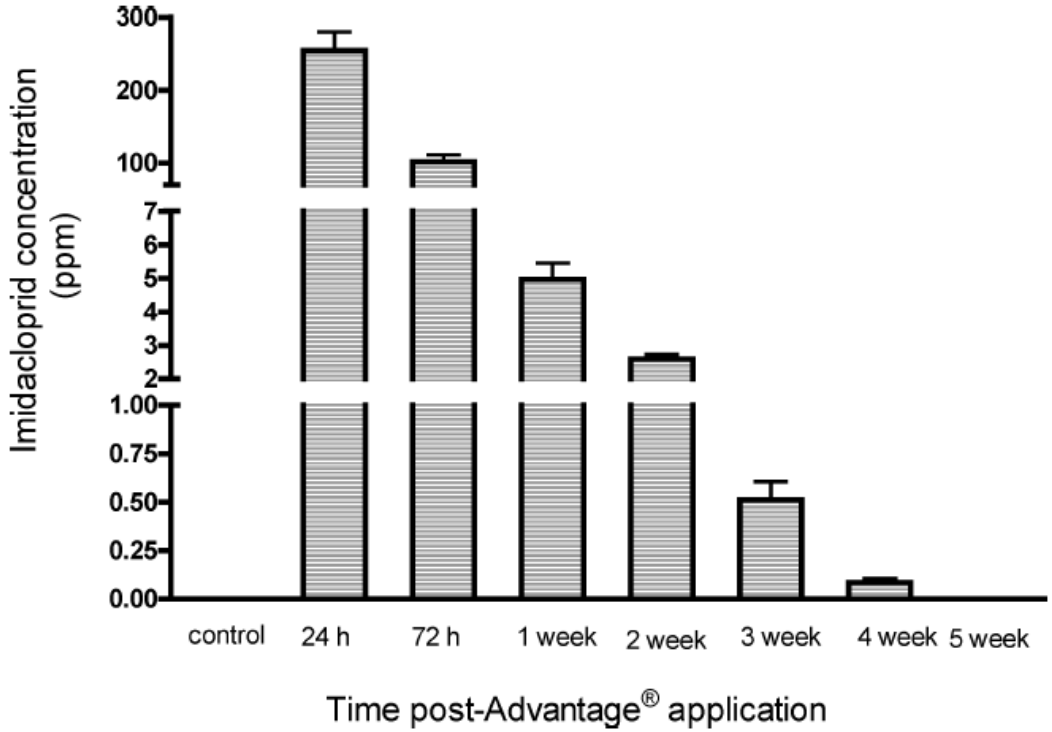



*Figure from Craig et al. (2005)*

# Detections in outdoor environment

| Chemical | Environmental media |
|---|---|
| Glufosinate | Detected infrequently in monitoring of US surface water<br>Not detected in California |
| Glyphosate | Some US surface water and groundwater samples (AMPA also detected)<br>Surface water in some California counties |
| Imidacloprid | Surface water in some California counties |
| Propanil (or 3,4-DCA) | Ambient air, surface water and ground water in some California counties |

# Ability to biomonitor

- Extent of absorption?
- Rate of elimination and by what route (e.g., urine or feces)?
- Is there a biomarker that is specific for the chemical?
- Is there an analytical method?
- Has the chemical been found in humans?

# Pharmacokinetic factors

| Chemical | Pharmacokinetic factors (studies in laboratory animals) | |
|---|---|---|
| | Absorption (oral) | Excretion rate (primary route) |
| Glufosinate | 5–10% | Rapid (feces) |
| Glyphosate | 30–36% | Rapid (feces, urine) |
| Imidacloprid | >90% | Rapid (urine) |
| Propanil (3,4-DCA) | Rapid | Rapid (urine) |

# Human biomonitoring studies

| Chemical | Detected in* |
|---|---|
| Glufosinate | Serum |
| Glyphosate | Urine |
| Imidacloprid | ---- |
| Propanil (3,4-DCA) | Urine |

**Studies of non-occupationally exposed individuals*

# Preliminary screen summary

| Chemical | Use Increasing (↑) Residential (✓) | Predicted to be Persistent | Detected in | | | Other notes |
|---|---|---|---|---|---|---|
| | | | Crops/ produce | House dust | Humans | |
| Glufosinate ammonium | ↑ | | | | ✓ | EU phase-out |
| Glyphosate | ↑ ✓ | | ✓ | ✓ | ✓ | |
| Imidacloprid | ↑ ✓ | ✓ | ✓ | | | |
| Propanil | ↑ | ✓ | ✓ | | ✓ | EU phase-out |

# Options for the Panel

The Panel can recommend that the Program:

- Gather additional screening information on any of these pesticides
- Prepare document(s) to support consideration of one or more of these pesticides as potential designated chemicals
- Continue tracking these pesticides
- Not consider these pesticides further

# Other chemical selection activities

- Potential designated chemicals:
  - Synthetic musks
  - Organotins
- Additional metals that EHL can measure as potential designated/priority chemicals
- Continuing to track possible target analyte(s) for diesel exhaust