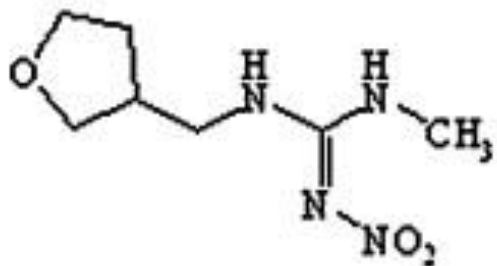


Neonicotinoid Insecticides

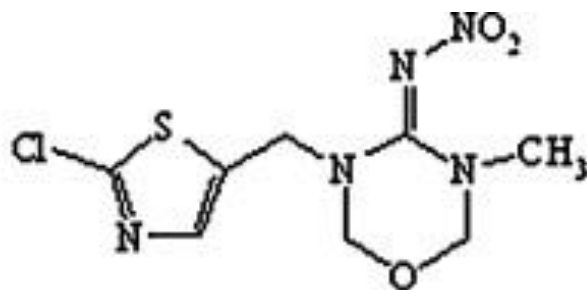
- Who are they? (Common compounds)
- How are they used?
- What are their characteristics?
- Current issues
 - Persistence
 - Solubility / transport
 - Toxicity (to bees)
 - Need for use, impact, return on investment

References

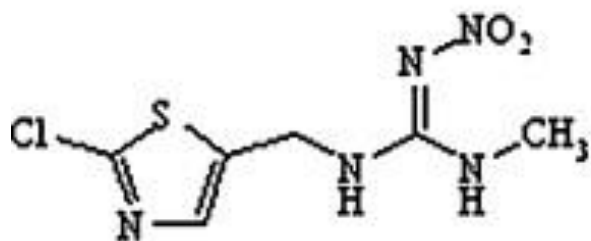
- Krupke, C.H., G.J. Hunt, B.D. Eitzer, G. Andinao, and K. Gvien. 2012. Multiple Routes of Pesticide Exposure for Honey Bees Living Near Agricultural Fields. PLOS ONE: <http://www.plosone.org/article/info%3Adoi%2F10.1371%2Fjournal.pone.0029268>.
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- Hopwood, J., M Vaughan, M. Shepperd, D. Biddinger, E. Mader, S. Hoffman-Black, and C. Mazzacano. Are Neonicotinoids Killing Bees? Xerces Society. http://www.xerces.org/wp-content/uploads/2012/03/Are-Neonicotinoids-Killing-Bees_Xerces-Society1.pdf
- The Effectiveness of Neonicotinoid Seed Treatments in Soybean. <https://www.extension.umn.edu/agriculture/soybean/pest/docs/effectiveness-of-neonicotinoid-seed-treatments-in-soybean.pdf>



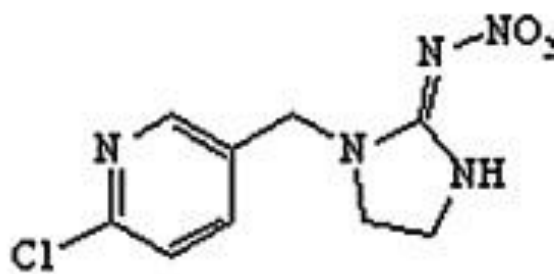
Dinotefuran



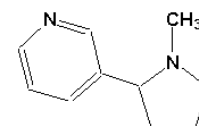
Thiamethoxam



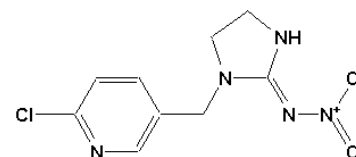
Clothianidin



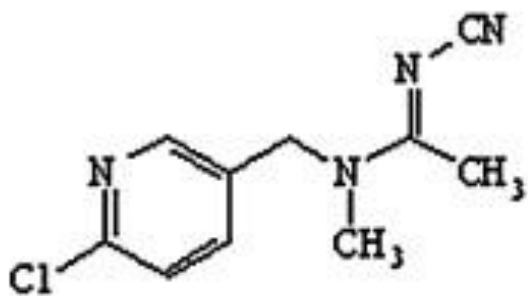
Imidacloprid



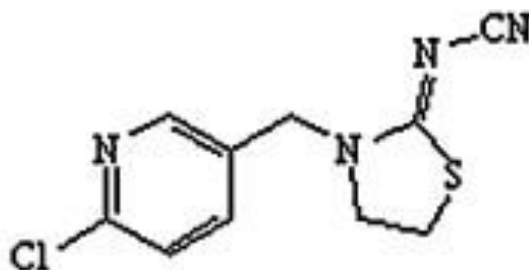
Nicotine (55 mg/kg)



Imidacloprid (424-475 mg/kg)



Acetamiprid



Thiacloprid

Major Uses of Neonicotinoids

- Seed treatments for corn and soybeans (clothianidin/Poncho and thiamethoxam/Cruiser) for flea beetle, cutworm, and bean leaf beetle control; some rootworm control
- Soil applications for grub control in lawns and systemic control of Japanese beetle adults (and other insects) on ornamental plants (imidacloprid/Bayer Advanced Insect Control and several others)
- Seed treatments for cucurbits (pumpkins, squash, cucumbers, melons) for cucumber beetle control (thiamethoxam/ Farmore)
- Soil/systemic applications for Colorado potato beetle control (imidacloprid/Admire)
- Foliar applications to orchard crops for plum curculio, aphid, and Lepidopteran (codling moth / oriental fruit moth) control (acetamiprid/Assail and ~~thiacloprid/Calypso~~)

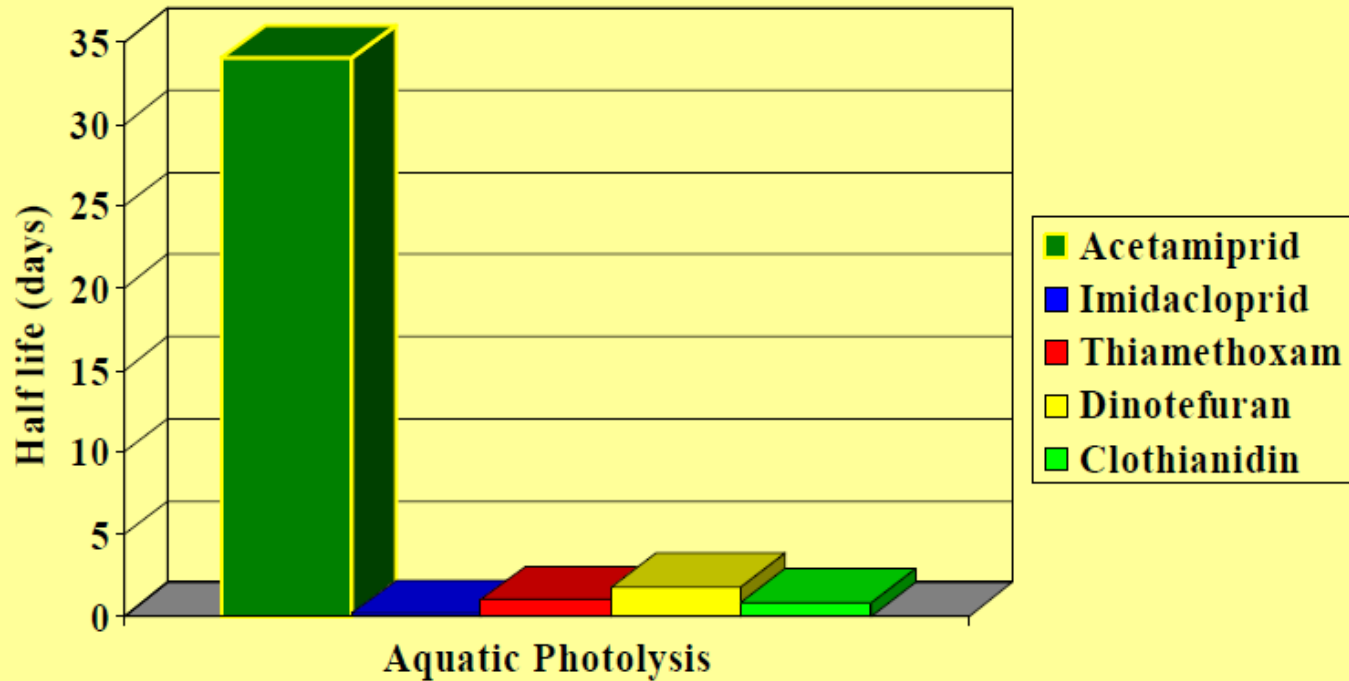
Table 3.1 Half-life in Soil of Neonicotinoids

Neonicotinoid	Half-life in Soil (aerobic soil metabolism)
Acetamiprid	1–8 days ¹
Clothianidin	148–1,155 days ²
Dinotefuran	138 days ³
Imidacloprid	40–997 days ⁴
Thiacloprid	1–27 days ⁵
Thiamethoxam (See note below)	25–100 days ⁶

Note: Clothianidin is a primary metabolite of thiamethoxam.

Sources: 1. EPA 2002; 2. EPA 2003a; 3. EPA 2004; 4. NPIC 2010; 5. EPA 2003b; 6. Syngenta Group 2005

Comparison of UV Stability

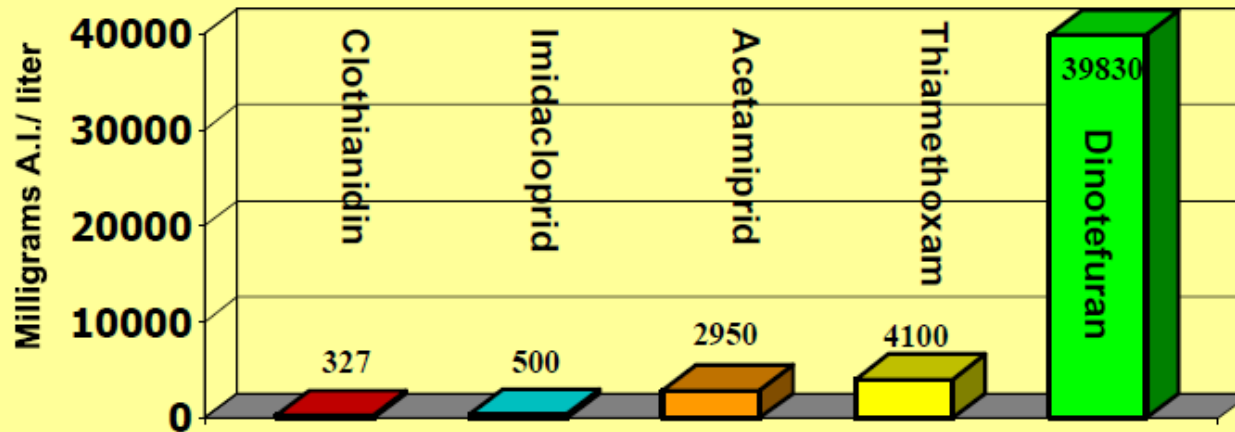


Data obtained from published EPA registration documents

Slide Credit: R. Fletcher

Relative Water Solubility of Neonicotinoids:

Water Solubility (Active Ingredient)



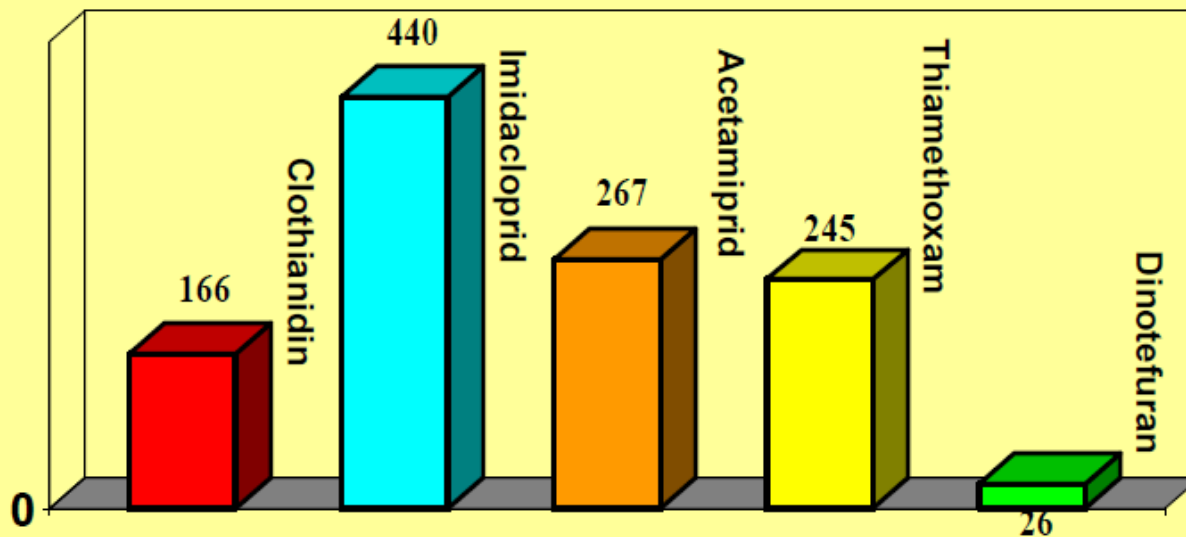
Information sources

*Clothianidin (Celero), Acetamiprid (Tristar), Dinotefuran (Safari) – EPA Pesticide Fact Sheet
Imidacloprid (Marathon), thiamethoxam (Flagship) – MSDS for Products*

Slide information courtesy J. Chamberlin

Solubility of permethrin (Pounce) is 0.4 ppm; solubility of chlorpyrifos (Lorsban) is 1 ppm ... in comparison with most other insecticides, the neonicotinoids are more soluble in water than most.

K_{oc} Values of Neonicotinoids:



Source Data: EPA Pesticide Fact Sheets

These soil sorption indices are low to moderate.

Table 1. Neonicotinoid pesticide mammalian toxicities (mg/kg of body weight).

Common name	Rat oral LD₅₀	Rabbit dermal LD₅₀
Acetamiprid	450	>2,000 (Tristar®)
Clothianidin	>5,000	>2,000 (Acceleron®)
Imidacloprid	4,870 (Gaucho®)	>2,000 (Admire®)
Thiamethoxam	>5,000	>2,000

Table 2. Neonicotinoid pesticide wildlife toxicity ranges.

Common name	Bird acute oral LD₅₀ (mg/kg)*	Fish LC₅₀ (ppm)**	Bee LD₅₀[†]
Acetamiprid	PNT	PNT	MT
Clothianidin	PNT	PNT	HT
Imidacloprid	MT	MT	HT
Thiamethoxam	ST	PNT	HT

Table 5.1 Toxicity of Neonicotinoids

Neonicotinoid	Known Toxicity to Honey Bees ¹		
		Contact LD ₅₀	Oral LD ₅₀
Acetamiprid	M	7.1 µg/bee ² –8.09 µg/bee ³	8.85–14.52 µg/bee ³
Clothianidin	H	0.022 µg/bee ² –0.044 µg/bee ⁴	0.00379 µg/bee ⁵
Dinotefuran	H	0.024 µg/bee ² –0.061 µg/bee ⁶	0.0076–0.023 µg/bee ⁶
Imidacloprid	H	0.0179 µg/bee ⁴ –0.243 µg/bee ⁷	0.0037 µg/bee ⁷ –0.081 µg/bee ⁸
Thiacloprid	M	14.6 µg/bee ² –38.83 µg/bee ⁹	8.51–17.3 µg/bee ⁹
Thiamethoxam	H	0.024 µg/bee ¹⁰ –0.029 µg/bee ²	0.005 µg/bee ¹⁰

H = highly toxic; M = moderately toxic

Toxicity: Highly toxic: LD₅₀ < 2 µg/bee; Moderately toxic: LD₅₀ 2–10.99 µg/bee; Slightly toxic: LD₅₀ 11–100 µg/bee; Practically non-toxic: LD₅₀ >100 µg/bee.

Sources: 1. WSDA 2010; 2. Iwasa et al. 2004; 3. EC 2004b; 4. EPA 2003a; 5. EC 2005; 6. EPA 2004; 7. Schmuck et al. 2001; 8. Nauen et al. 2001 ; 9. EC 2004a; 10. Syngenta Group 2005.

Neonicotinoids and Bees

The image shows a screenshot of a PLOS ONE research article page. The page has a blue header with the PLOS ONE logo and the text 'A peer-reviewed, open access journal'. Below the header is a navigation bar with links for 'Home', 'Browse Articles', 'About', 'For Readers', and 'For Authors and Reviewers'. The article title is 'Multiple Routes of Pesticide Exposure for Honey Bees Living Near Agricultural Fields'. The authors listed are Christian H. Krupke^{1*}, Greg J. Hunt¹, Brian D. Eitzer², Gladys Andino¹, and Krispn Given¹. The article is marked as 'RESEARCH ARTICLE' and 'OPEN ACCESS'. There are buttons for 'Article', 'Metrics', 'Related Content', and 'Comments: 2'. The abstract text begins with 'Populations of honey bees and other pollinators have declined worldwide in recent years. A variety of stressors have been implicated as potential causes, including agricultural pesticides. Neonicotinoid insecticides, which are widely used and highly toxic to honey bees, have been found in previous analyses of honey bee pollen and comb material. However, the routes of exposure have remained largely undefined. We used LC/MS-MS to analyze samples of honey bees, pollen stored in the hive and several potential exposure routes associated with plantings of neonicotinoid treated maize. Our results'.

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RESEARCH ARTICLE OPEN ACCESS

Multiple Routes of Pesticide Exposure for Honey Bees Living Near Agricultural Fields

Article Metrics Related Content Comments: 2

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Abstract [Top](#)

Populations of honey bees and other pollinators have declined worldwide in recent years. A variety of stressors have been implicated as potential causes, including agricultural pesticides. Neonicotinoid insecticides, which are widely used and highly toxic to honey bees, have been found in previous analyses of honey bee pollen and comb material. However, the routes of exposure have remained largely undefined. We used LC/MS-MS to analyze samples of honey bees, pollen stored in the hive and several potential exposure routes associated with plantings of neonicotinoid treated maize. Our results

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Abstract

... Neonicotinoid insecticides, which are widely used and highly toxic to honey bees, have been found in previous analyses of honey bee pollen and comb material. However, the routes of exposure have remained largely undefined. We used LC/MS-MS to analyze samples of honey bees, pollen stored in the hive and several potential exposure routes associated with plantings of neonicotinoid treated maize. Our results demonstrate that bees are exposed to these compounds and several other agricultural pesticides in several ways throughout the foraging period. **During spring, extremely high levels of clothianidin and thiamethoxam were found in planter exhaust material produced during the planting of treated maize seed. We also found neonicotinoids in the soil of each field we sampled, including unplanted fields. Plants visited by foraging bees (dandelions) growing near these fields were found to contain neonicotinoids as well. This indicates deposition of neonicotinoids on the flowers, uptake by the root system, or both.** Dead bees collected near hive entrances during the spring sampling period were found to contain clothianidin as well, although whether exposure was oral (consuming pollen) or by contact (soil/planter dust) is unclear. We also detected the insecticide clothianidin in pollen collected by bees and stored in the hive. **When maize plants in our field reached anthesis, maize pollen from treated seed was found to contain clothianidin and other pesticides; and honey bees in our study readily collected maize pollen.** These findings clarify some of the mechanisms by which honey bees may be exposed to agricultural pesticides throughout the growing season. These results have implications for a wide range of large-scale annual cropping systems that utilize neonicotinoid seed treatments.

Insecticide Residues in Pollen and Nectar of a Cucurbit Crop and Their Potential Exposure to Pollinators

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This article is part of the [Florida Pesticide Residue Workshop 2011](#) special issue.

ACS Section: **Toxicology**

Abstract

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Neonicotinoids are systemic insecticides widely used on many pollinated agricultural crops, and increasing evidence indicates that they move to some extent into pollen and nectar. This study measured levels of neonicotinoid residues in pollen and nectar from a pumpkin crop treated with formulated products containing imidacloprid, dinotefuran, and thiamethoxam using different timings and application methods. Environmental conditions have a significant effect on overall residue levels; nectar residues were 73.5-88.8% less than pollen residues, and metabolites accounted for 15.5-27.2% of the total residue amounts. Foliar-applied treatments and chemigated insecticides applied through drip irrigation during flowering resulted in the highest residues of parent insecticide and metabolites, which may reach average levels up to 122 ng/g in pollen and 17.6 ng/g in nectar. The lowest levels of residues were detected in treatment regimens involving applications of insecticides at planting, as either seed dressing, bedding tray drench, or transplant water treatment.

Keywords: neonicotinoid residues; pollen; nectar; pollinators; Cucurbitaceae

- The parent neonicotinoids and several metabolites were identified and quantified in 92.1, 88.2, and >98% of the pollen, nectar, and leaf samples from the treated plots, respectively.
- The bedding tray drench resulted in the lowest residue levels of imidacloprid, ranging from 0.1 to 6.7 ng/g in pollen and from ND to 0.5 ng/g in nectar.
- Applications of the low label rate of imidacloprid in transplant water resulted in significantly higher ($p < 0.05$) residue amounts in pollen, ranging from 13.2 to 40.1 ng/g, than in nectar, ranging from 3.8 to 7.3 ng/g.
- The highest residues of imidacloprid were found in samples from plots receiving the high label rate but as split applications in transplant water followed 3 weeks later by drip chemigation.

- We presented here evidence to support our hypothesis that **higher residues are present in pollen and nectar if systemic neonicotinoids are applied closer to flowering. Foliar treatments and chemigation through drip irrigation applied during flowering resulted in the highest residues of parent insecticide and metabolites.** The three neonicotinoids in the study showed similar residue profiles in pollen and nectar with regard to the split transplant-drip treatment regimen. **The lowest levels of residues were detected in treatment regimens involving applications of insecticides at planting, as either seed dressing, bedding tray drench, or transplant water treatment.** The uptake and translocation of residues from these at-planting applications clearly decreased as the growing season progressed and the crop approached flowering. **If neonicotinoids are needed for insect control on cucurbits, they should be applied at planting or shortly after to mitigate the exposure to pollinators.**

ARE NEONICOTINOIDS KILLING BEES?

A Review of Research into the Effects of Neonicotinoid Insecticides on Bees,
with Recommendations for Action



Jennifer Hopwood, Mace Vaughan, Matthew Shepherd, David Biddinger,
Eric Mader, Scott Hoffman Black, and Celeste Mazzacano

THE XERCES SOCIETY FOR INVERTEBRATE CONSERVATION

Exposure of bees to neonicotinoids

- ↪ Neonicotinoid residues found in pollen and nectar are consumed by flower-visiting insects such as bees. Concentrations of residues can reach lethal levels in some situations.
- ↪ Neonicotinoids can persist in soil for months or years after a single application. Measurable amounts of residues were found in woody plants up to six years after application.
- ↪ Untreated plants may absorb chemical residues in the soil from the previous year.
- ↪ Products approved for home and garden use may be applied to ornamental and landscape plants, as well as turf, at significantly higher rates (potentially 120 times higher) than those approved for agricultural crops.
- ↪ Direct contact with foliar neonicotinoid sprays is hazardous to pollinators, and foliar residues on plant surfaces remain toxic to bees for several days.
- ↪ Neonicotinoids applied to crops can contaminate adjacent weeds and wildflowers.

Effects on honey bees

- ⇒ Imidacloprid, clothianidin, dinotefuran, and thiamethoxam are highly toxic to honey bees.
- ⇒ Thiacloprid and acetamiprid are mildly toxic.
- ⇒ After plants absorb neonicotinoids, they slowly metabolize the compounds. Some of the resulting breakdown products are equally toxic or even more toxic to honey bees than the original compound.
- ⇒ Honey bees exposed to sublethal levels of neonicotinoids can experience problems with flying and navigation, reduced taste sensitivity, and slower learning of new tasks, which all impact foraging ability.

Exposure of bees to neonicotinoids

- ⇒ Application methods other than seed coatings (foliar sprays, soil drenches, and trunk injections) apply a higher dosage per plant and may result in much higher—even toxic—levels of neonicotinoid residues in pollen and nectar.
- ⇒ Application of neonicotinoids shortly before and during bloom may lead to higher residue levels in pollen and nectar.
- ⇒ Application by soil drench or trunk injection may result in high residue levels in blossoms of woody ornamental species more than a year after treatment.

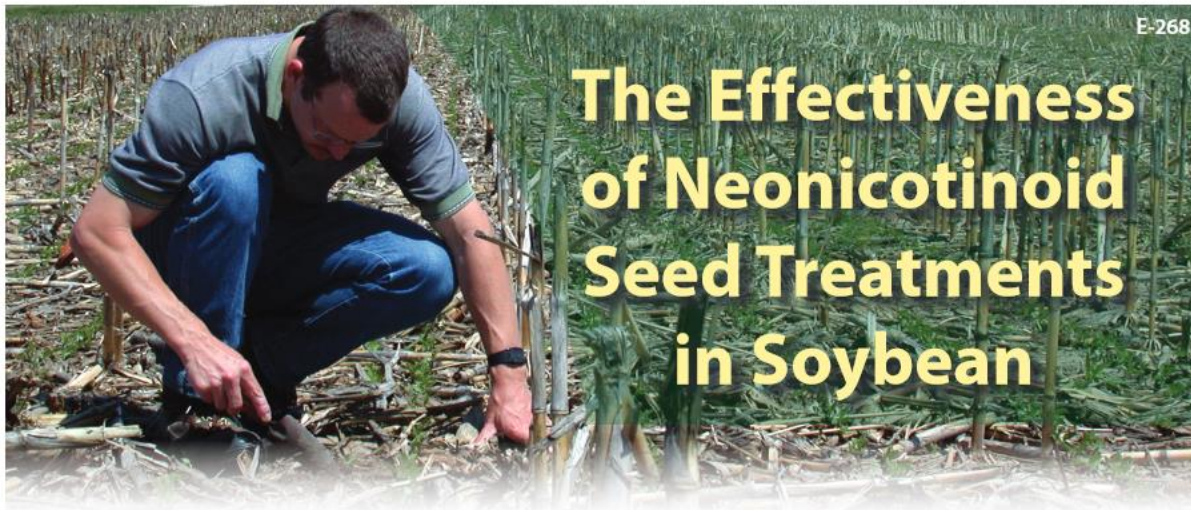
<p>Imidacloprid</p>	<p>Application as seed dressing, soil drench, granules, injection, or spray to a wide range of field and tree crops, as well as ornamental plants, trees, and turf.</p> <p>(Also, topical use on pets for flea control and application to buildings for termite control.)</p>	<p>Admire Gaucho Imicide Provado Macho Malice Sepresto Widow Wrangler</p>	<p>Bayer Advanced 3-in-1 Insect, Disease, & Mite Control Bayer Advanced 12 Month Tree & Shrub Insect Control Bayer Advanced 12 Month Tree & Shrub Protect & Feed Bayer Advanced Fruit, Citrus & Vegetable Insect Control Bayer Advanced All-in-One Rose & Flower Care concentrate DIY Tree Care Products Multi-Insect Killer Ferti-lome 2-N-1 Systemic Hi-Yield Systemic Insect Spray Hunter Knockout Ready-To-Use Grub Killer Lesco Bandit Marathon Merit Monterey Once a Year Insect Control II Ortho Bug B Gon Year-Long Tree & Shrub Insect Control Orhto MAX Tree & Shrub Insect Control Surrender Brand GrubZ Out</p>
<p>Thiacloprid</p>	<p>Application as foliar spray to cotton and pome fruit crops.</p>	<p>Calypso</p>	
<p>Thiamethoxam</p>	<p>Application as seed dressing, soil drench, injection, granules, or foliar spray to a wide range of field crops, as well as ornamental plants and turf.</p>	<p>Actara Adage Crusier Centric Platinum</p>	<p>Flagship Maxide Dual Action Insect Killer Meridian</p>

So ...

- Expect increasing regulatory action (maybe).
- Until then ... we should not use neonicotinoids that are especially toxic to bees if applications (even seed treatments) will result in bee kill. Particularly toxic neonics include ...
 - Imidacloprid (Admire Pro, many homeowner products)
 - Thiamethoxam (Actara, Platinum)
 - Clothianidin (Poncho seed treatments)
 - Dinotefuran (Scorpion, Venom)
- Use of these products (imidacloprid and thiamethoxam) as seed treatments on cucurbits presents little or no systemic risk, but later uses do result in more significant contamination of pollen and nectar.
- Seed treatments on corn and soybean seeds ... these large scale of uses presents real risks, and at least in soybeans, with no evidence of return on investment.

Effectiveness and Return on Investment ...

- The Effectiveness of Neonicotinoid Seed Treatments in Soybean
 - <https://www.extension.umn.edu/agriculture/soybean/pest/docs/effectiveness-of-neonicotinoid-seed-treatments-in-soybean.pdf>



In 2011, more than 80 percent of corn, more than 50 percent of cotton, and about 40 percent of soybean acres were planted with neonicotinoid-treated seed, a total area described as “roughly the size of California.” (Douglas and Tooker 2015).

To summarize: For typical field situations, independent research demonstrates that neonicotinoid seed treatments do not provide a consistent return on investment (Hodgson and VanNostrand 2012, 2013, 2014; Seagraves and Lundgren 2012; McCarville et al. 2014). The current use of neonicotinoid seed treatments in soybean and other crops far exceeds pest pressures.