

Detections of the Neonicotinoid Insecticide Imidacloprid in Surface Waters of Three Agricultural Regions of California, USA, 2010–2011

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Abstract Seventy-five surface water samples were collected from three agricultural regions of California and analyzed for the neonicotinoid insecticide imidacloprid. Samples were collected during California's relatively dry-weather irrigation seasons in 2010 and 2011. Imidacloprid was detected in 67 samples (89%); concentrations exceeded the United States Environmental Protection Agency's chronic invertebrate Aquatic Life Benchmark of 1.05 µg/L in 14 samples (19%). Concentrations were also frequently greater than similar toxicity guidelines developed for use in Europe and Canada. The results indicate that imidacloprid commonly moves offsite and contaminates surface waters at concentrations that could harm aquatic organisms following use under irrigated agriculture conditions in California.

Keywords Imidacloprid · Surface water · Pesticide mixtures · Agriculture

Imidacloprid is a systemic, neonicotinoid insecticide used in urban and agricultural environments worldwide to control termites, turf insects, ectoparasites, and agricultural pests (CCME 2007, Jeschke et al. 2011). Use in agricultural areas is high; in California, over 90,000 kg of imidacloprid active ingredient (AI) was applied to agricultural crops in 2010 (CDPR 2011). Environmental fate data for imidacloprid indicate that it has the potential to contaminate surface water (Table 1); the US EPA has classified imidacloprid as very highly toxic to aquatic invertebrates

(US EPA 2008). Based its widespread use, persistence, and aquatic toxicity, the potential for transport from agricultural fields to surface water is a concern (US EPA 2008). However, very few surface water monitoring results for imidacloprid in agricultural areas have been reported (Lamers et al. 2011, Kreuger et al. 2010, van Dijk 2010); no reports of imidacloprid detections in agricultural areas of California are available.

The California Department of Pesticide Regulation (CDPR) conducted surface water monitoring for imidacloprid during the dry irrigation seasons of 2010 and 2011 in three agricultural areas of California. The objective of this analysis is to document the occurrence and distribution of imidacloprid in these agricultural areas and to assess the potential for aquatic toxicity by comparison of detected concentrations to aquatic toxicity benchmarks.

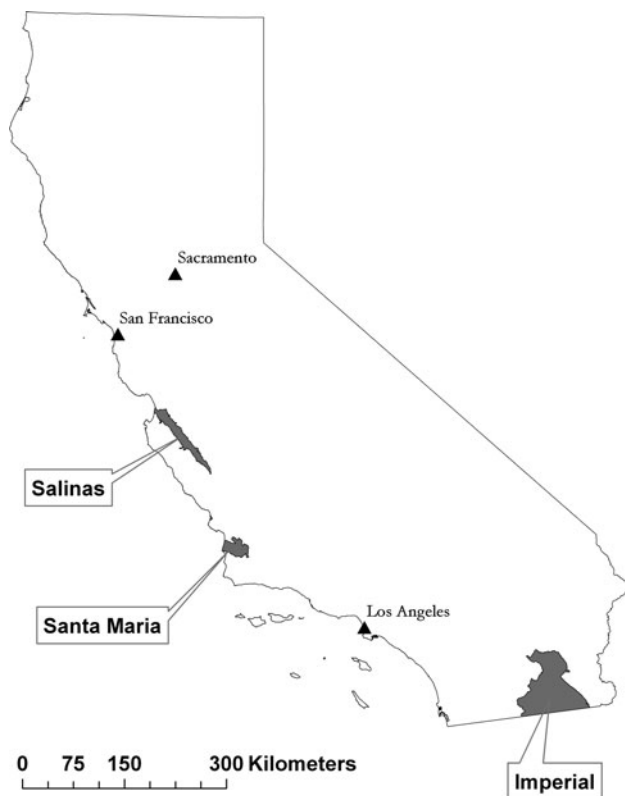
Materials and Methods

Monitoring was conducted in three regions with historically high agricultural use of imidacloprid: Salinas Valley, Santa Maria Valley and Imperial Valley (Fig. 1). Monitoring sites were previously selected as part of CDPR's on-going agricultural surface water monitoring program (Starner et al. 2011). Samples were collected from a total of 23 monitoring sites. Seven sites were rivers; the remaining sites were small creeks or drains. The water bodies sampled receive input primarily from agricultural lands. Samples were collected during California's relatively dry-weather irrigation seasons between March and October; over 90% of all agricultural use takes place during this period (CDPR 2011). In 2010, samples were collected in May, June, and October; in 2011, samples were collected in April, May, June, July, August and October.

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Table 1 Environmental fate parameters for imidacloprid (US EPA 2008)

Parameter	Value
Solubility (ppm)	580
Hydrolysis half-life (days)	Stable
Aerobic soil half-life (days)	520
Aerobic aquatic half-life (days)	1,040
Photolysis half-life in water (days)	0.2–39
Organic carbon partition coeff. (mL/g)	178

**Fig. 1** Three imidacloprid monitoring regions in California, USA

Samples for imidacloprid analysis were collected into 1-L amber glass bottles using a grab pole. Bottles were sealed with Teflon-lined lids, transported on wet ice and stored at 4°C until extraction for chemical analysis. Chemical analyses were performed by the California Department of Food and Agriculture's Center for Analytical Chemistry. Surface water samples were passed through two Varian Focus solid phase extraction Cartridges (Agilent Technologies, Santa Clara, CA, USA) connected in tandem. The cartridges were then reconnected in reverse order and eluted using 10 mL of methanol/acetonitrile/2% formic acid in water (60/30/10) (v/v/v). Sample extracts were concentrated, reconstituted in 1:1 methanol/water (v/v) and analyzed using a Finnegan Surveyor HPLC system with a

Finnigan TSQ Quantum mass spectrometer (Finnigan/ThermoQuest, San Jose, CA, USA). The method detection limit (MDL) for imidacloprid was 0.010 µg/L; the reporting limit (RL) was 0.050 µg/L. Additional analytical method detail is available (CDFA 2008). Quality Control (QC) for this study was conducted in accordance with CDPH Standard Operating Procedure QAQC001.00 (Segawa 1995). Reagent blank samples were run with each extraction set to monitor for laboratory contamination. No contamination was detected. Blank-matrix spike samples were analyzed with each extraction set. Blank-matrix spikes are blank water samples fortified with an analyte at a known concentration and extracted and analyzed with an extraction set. For the data presented here, blank-matrix spike recovery performances were 83%–114%. Blind spike samples were also added to some analytical sets. A blind spike is a blank-matrix sample which has been spiked and submitted to the lab disguised as a field sample. Blind spike recoveries for the data presented here ranged from 88%–99%.

Analytical results were compared to the US EPA Office of Pesticide Programs' Aquatic Life Benchmark ("toxicity benchmark") for aquatic invertebrates. Each Aquatic Life Benchmark is based on the most sensitive, scientifically acceptable toxicity endpoint available to the US EPA (US EPA 2011). The aquatic invertebrate chronic exposure benchmark of 1.05 µg/L was used for the analysis.

Recent agricultural use of imidacloprid in the three regions was determined using data from CDPH's Pesticide Use Reporting Database (PUR) (CDPH 2011). Use data from 2010 was the most recent data available and was used in this analysis.

Results and Discussion

Seventy-five samples were collected for imidacloprid analysis. Results are summarized in Table 2. Samples were collected from rivers, small creeks and agricultural drains. A total of 23 different monitoring sites were sampled on a total of 15 different sampling dates (Tables 3 and 4). Imidacloprid was frequently detected in all three regions (Salinas 85%, Santa Maria 100% and Imperial 93%). Overall, imidacloprid was detected in 67 samples (89%), and the US EPA Benchmark was exceeded in 14 samples (19%) (Table 2).

In Imperial Valley, imidacloprid use occurs mainly in the fall (September through November). In 2010, about 50% of fall applications (by amount of AI applied) were to lettuce, with use on broccoli, cauliflower and sugarbeets accounting for an additional 40%. A total of 14 samples were collected from 9 monitoring sites in Imperial Valley during the fall use season (5 samples in 2010 and 9 in 2011). Imidacloprid was detected in 13 samples (93%); the

toxicity benchmark was exceeded in one sample (7%). This sample had the highest concentration detected during the study (3.29 $\mu\text{g/L}$) (Tables 2 and 4).

In both the Salinas and Santa Maria Valleys, imidacloprid use occurs primarily between April and September. Use during this period is mainly on lettuce, with additional use on broccoli, cauliflower, and wine grapes. In Salinas Valley, a total of 46 surface water samples were collected from ten monitoring sites (Table 3). Eleven of these samples were collected in 2010; 35 in 2011 (Table 4). Imidacloprid was detected in 39 samples (85%), and the US EPA benchmark was exceeded in 7 samples (15%) (Table 2). In Santa Maria Valley, a total of 15 samples were collected

from 4 monitoring sites (Table 3). Five samples each were collected in summer 2010, spring 2011, and summer 2011. Imidacloprid was detected in all 15 samples and the toxicity benchmark was exceeded in 6 samples. Of the five samples collected in spring 2011, all 5 exceeded the toxicity benchmark (Table 4). These samples were all collected from one sample site over a period of 3.5 h. Rain had occurred in the subbasin within the previous 24 h (approximately 1.5 cm) and storm runoff likely affected the results of this monitoring event, resulting in higher concentrations of imidacloprid. Ten summer samples were collected (5 each in 2010 and 2011). Imidacloprid was detected in all 10 samples, with one sample exceeding the toxicity benchmark (Table 4).

Overall, the US EPA toxicity benchmark of 1.05 $\mu\text{g/L}$ was exceeded in 19% of all samples. In comparison, the Canadian Council of Ministers of the Environment (CCME) has developed an Interim Water Quality Guideline for Freshwater Aquatic Life of 0.23 $\mu\text{g/L}$ for imidacloprid, for use in regulating imidacloprid in Canada (CCME 2007); 71% of all samples from this study exceeded that guideline. In Europe, the National Institute for Public Health and the Environment (NIPHE) in the Netherlands has developed Environmental Risk Limits (ERLs) for imidacloprid in water surface water. These ERLs “are scientifically derived values, based on (eco)

Table 2 Summary of imidacloprid monitoring results from three agricultural regions of California, 2010–2011

Region	Unique sample sites	Samples	Detection freq. (%)	Exceedance freq. (%)	Maximum conc. ($\mu\text{g/L}$)
Imperial	9	14	92.9	7.1	3.29
Salinas	10	46	84.8	15.2	3.05
Santa Maria	4	15	100	40.0	1.38
All	23	75	89.3	18.7	3.29

Exceedance concentration above 1.05 $\mu\text{g/L}$

Table 3 Imidacloprid monitoring sites, California, 2010–2011

Code	Type	Description	Samples	Latitude	Longitude
13-10	R	Alamo River at Garst	2	33.1992	-115.5962
13-22	T	Holtville Main Drn/115	2	32.9307	-115.4052
13-25	T	Verde Drn/Bonds Crnr	2	32.7555	-115.3368
13-56	R	Alamo R at Rutherford	2	33.0445	-115.4874
13-69	T	Rice Drain 3	2	32.8689	-115.6509
13-71	R	New R at Keystone	1	32.9132	-115.6055
13-73	T	Pine Drain nr HWY 115	1	32.8617	-115.4149
13-23	T	Malva Drain	1	33.0518	-115.4785
13-24	T	Vail Drain nr Young	1	33.1328	-115.6651
27-10	T	Alisal Crk/De Le Torre	6	36.6612	-121.6192
27-11	R	Old Salinas R/Potrero	4	36.7908	-121.7897
27-13	R	Salinas R/Davis	1	36.6471	-121.7013
27-14	R	Salinas R/Del Monte	6	36.7319	-121.7809
27-50	R	Old Salinas R/MDW	1	36.7716	-121.7887
27-66	T	Tembladero SI/Haro	8	36.7596	-121.7535
27-7	T	Quail Crk/HWY 101	5	36.6092	-121.5623
27-70	T	Alisal Crk/Hartnell	7	36.6436	-121.5774
27-8	T	Chualar Crk	7	36.5586	-121.5289
27-9	T	Blanco Drn/Cooper	1	36.6988	-121.7341
40-13	T	Oso Flaco Crk	2	35.0164	-120.5866
42-48	T	Orcutt-Solomon/HWY 1	2	34.9415	-120.5733
42-49	T	Main St Ditch	1	34.9549	-120.4841
42-50	T	Orcutt Crk/Main	10	34.9576	-120.6315

Table 4 Imidacloprid monitoring results, California, 2010–2011

Region	Season	Date	Code	Time	Conc. (µg/L)
Imperial	Fall 2010	10/5/2010	13-10	13:00	0.353
		10/5/2010	13-22	11:30	0.133
		10/5/2010	13-25	10:45	0.080
		10/5/2010	13-56	12:20	0.276
		10/5/2010	13-69	9:45	0.602
Imperial	Fall 2011	10/11/2011	13-71	9:40	0.559
		10/11/2011	13-69	10:25	0.789
		10/11/2011	13-25	11:15	0.114
		10/11/2011	13-73	12:00	ND
		10/11/2011	13-22	12:45	0.262
		10/11/2011	13-23	13:30	3.29
		10/11/2011	13-56	14:15	0.269
		10/11/2011	13-10	15:00	0.301
Salinas	Spring 2010	5/17/2010	27-10	13:50	1.03
		5/17/2010	27-14	15:50	ND
		5/17/2010	27-66	14:45	0.223
		5/17/2010	27-7	11:45	1.02
		5/17/2010	27-70	13:00	0.489
		5/17/2010	27-8	12:30	0.443
Salinas	Summer 2010	6/7/2010	27-10	13:45	1.24
		6/7/2010	27-66	14:30	0.647
		6/7/2010	27-7	11:45	0.544
		6/7/2010	27-70	13:00	0.924
		6/7/2010	27-8	12:30	0.626
Salinas	Spring 2011	4/25/2011	27-10	13:45	3.05
		4/25/2011	27-14	15:30	ND
		4/25/2011	27-66	14:30	0.418
		4/25/2011	27-7	11:45	0.581
		4/25/2011	27-70	13:00	2.09
		4/25/2011	27-8	12:15	0.372
		4/26/2011	27-11	12:15	0.272
		4/26/2011	27-13	14:00	ND
		4/26/2011	27-9	13:30	ND
		5/16/2011	27-10	13:30	2.06
Salinas	Summer 2011	6/13/2011	27-10	14:00	0.570
		6/13/2011	27-14	15:45	ND
		6/13/2011	27-66	15:00	0.334
		6/13/2011	27-7	12:00	2.09
		6/13/2011	27-70	13:20	0.480
		6/13/2011	27-8	12:45	0.440
		6/14/2011	27-11	7:30	0.200
		6/14/2011	27-50	10:40	0.167

Table 4 continued

Region	Season	Date	Code	Time	Conc. (µg/L)
Imperial	Fall 2010	6/14/2011	27-66	13:15	0.203
		7/18/2011	27-66	12:20	0.178
		7/19/2011	27-11	8:20	0.114
		7/19/2011	27-14	14:20	ND
		7/19/2011	27-7	10:15	0.157
		7/19/2011	27-70	11:55	1.03
		7/19/2011	27-8	11:00	0.635
		7/19/2011	27-10	13:15	1.30
Salinas	Summer 2011	8/30/2011	27-11	14:15	0.130
		8/30/2011	27-14	15:45	ND
		8/30/2011	27-66	15:15	0.162
		8/30/2011	27-70	12:30	0.450
Santa Maria	Summer 2010	6/8/2010	40-13	15:15	0.544
		6/8/2010	42-48	13:00	0.723
		6/8/2010	42-49	13:40	0.168
		6/8/2010	42-50	12:15	0.938
		6/8/2010	42-50	14:15	0.876
Santa Maria	Spring 2011	5/17/2011	42-50	10:45	1.11
		5/17/2011	42-50	11:45	1.18
		5/17/2011	42-50	12:45	1.38
		5/17/2011	42-50	13:45	1.26
Santa Maria	Summer 2011	8/31/2011	40-13	13:45	0.578
		8/31/2011	42-48	12:00	1.24
		8/31/2011	42-50	11:10	0.984
		8/31/2011	42-50	12:30	0.842
		8/31/2011	42-50	14:20	0.878

ND nondetection

toxicological, fate and physico-chemical data” (NIPHE 2008). Both acute (Maximum Acceptable Concentration = 0.20 µg/L) and chronic (Maximum Permissible Concentration = 0.067 µg/L) exposure values were developed. These values were exceeded in 73% and 88%, respectively, of the samples in this study.

No reports of imidacloprid detections in agricultural areas of the United States (US) were available in the peer-reviewed literature. However, the United States Geological Survey (USGS) reports their surface water monitoring results in an on-line database (USGS 2011); about 2% of samples collected from agricultural areas of the US had detections of imidacloprid, with one detection greater than 1 µg/L. Of the 35 samples collected from one California agricultural area, there were no detections of imidacloprid. Outside of the US, imidacloprid detections have been reported in agricultural areas in the Netherlands (van Djik 2010), Sweden (Kreuger et al. 2010), and Vietnam (Lamers et al. 2011). In the Netherlands,

concentrations were reported as high as 200 µg/L. Other maximum concentrations reported were 15 µg/L (Sweden), 2.59 µg/L (Brazil) and 0.48 µg/L (Vietnam). The concentrations reported in the current study (maximum 3.29 µg/L) are higher than those reported previously in the US, but at the lower end of concentrations reported outside the US.

Imidacloprid is also used extensively in urban areas; this study focused on agricultural areas and does not address the potential for offsite movement in urban areas. CDPR has also conducted surface water monitoring for imidacloprid in urban areas of the state (CDPR unpublished data); these results will be reported separately. Results of surface water monitoring efforts conducted in urban and agricultural areas are best considered separately due to differences between the two in application rates (often higher in urban areas), application timing, and pathways of offsite movement (more impervious surfaces in urban areas), as well as other factors (Phillips and Bode 2004).

Imidacloprid acts at the nicotinic acetylcholine receptor (nAChR) agonist site and shares a common mode of action with the other neonicotinoid insecticides, including acetamiprid, clothianidin, dinotefuran, thiacloprid and thiamethoxam (Casida 2011, Jeschke et al. 2011). As such, additive toxicity in aquatic mixtures of neonicotinoids is possible. Recent research indicates synergistic toxicity can also occur (Loureiro et al. 2010). The worldwide use of the neonicotinoids is expected to increase significantly over the next few years (Jeschke et al. 2011); research on the aquatic toxicity of neonicotinoid mixtures, as well as increased surface water monitoring, is needed for a more complete characterization of their potential impact on aquatic systems. Two additional classes of insecticides, the nereistoxin analogues and the spinosyns, target the same molecular site as the neonicotinoids. The nereistoxin analogues include the bis(thiocarbamate) proinsecticides cartap, bensultap, and thiocyclam; the spinosyns include spinosid and spinetoram (Jeschke et al. 2011). Due to the common targeted molecular site, there is the potential for additive or synergistic effects in aquatic mixtures with the neonicotinoids; additional research and monitoring data are needed.

Organophosphate and carbamate insecticides are commonly detected in surface water in agricultural areas of California; several were frequently detected simultaneously with imidacloprid in surface water samples from this study (Starner et al. 2011, CDPR unpublished data). Although they act in a different way from the neonicotinoids, these insecticides also inhibit acetylcholinesterase (AChE) (Loureiro et al. 2010). In aquatic mixtures, additive or synergistic effects are possible; additional research is needed.

Several environmental degradation products of imidacloprid have been identified. One of these degradates, imidacloprid olefin, has shown higher insecticidal properties than the parent chemical (Casida 2011). Research on

the toxicity of the imidacloprid degradates to aquatic organisms is needed. Inclusion of imidacloprid degradates in surface water monitoring efforts should be considered in areas of significant use of the parent compound.

In the three California agricultural regions in this study, imidacloprid was frequently detected, and a US EPA toxicity benchmark was exceeded, in all three regions. Overall, imidacloprid was detected in 89% of samples and the toxicity benchmark was exceeded in 19%. Aquatic toxicity guidelines developed by government regulatory agencies outside of the US were also exceeded, in as many as 88% of samples. The three agricultural regions monitored represent different California climates, soil types and agricultural practices, factors which impact the potential for offsite movement of pesticides; however, detection frequencies were high in all three regions (Table 2). These results indicate that the potential for off-site movement of imidacloprid under irrigated agriculture conditions may be substantial and warrants further research and monitoring efforts.

Imidacloprid is the most widely used insecticide in the world, registered for use on over 140 crops in more than 120 countries, and its use continues to increase (Jeschke et al. 2011). In California, agricultural use has doubled since 2005 (CDPR 2011). Worldwide, very few surface water monitoring results for imidacloprid have been reported. The results presented here show that imidacloprid can move offsite from agricultural fields and contaminate surface water at concentrations that may be harmful to aquatic organisms. As such, increased surface water monitoring for imidacloprid is recommended worldwide in areas of its use. Furthermore, there is a significant need for additional research on the aquatic toxicity of mixtures of imidacloprid with other pesticides, especially other neonicotinoids, organophosphate and carbamate insecticides, and the spinosyn insecticides such as spinosid and spinetoram. Additional research is also needed on the aquatic toxicity of the environmental degradates of imidacloprid.

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