

Imidacloprid Residues in Willapa Bay (Washington State) Water and Sediment Following Application for Control of Burrowing Shrimp

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Pesticides have been used in the Willapa Bay estuary in western Washington State to control the exotic invasive plant species *Spartina alterniflora* (cordgrass) and the native species of burrowing shrimp (*Callinassa* sp.; *Upogebia* sp.) that affect oyster production. Carbaryl, the only registered insecticide for control of burrowing shrimp, has not been extensively studied in the Willapa Bay. However, carbaryl use has been severely restricted, and alternatives likely to have less severe environmental impacts are being sought. Imidacloprid applied directly to exposed sediments when the tide is out is efficacious for burrowing shrimp control but lacks studies of its behavior in the estuary. For this study, imidacloprid dissipation was monitored as the tide was rising in Willapa Bay. Over 99% of applied material dissipated from small plots within 24 h, but residues near the analytical detection limit were found in sediments 28 days later. At a distance of 152 m along a transect from the plot in the direction of tidal flow, imidacloprid residues in water peaked within 10 min after initiation of tidal flow. Within 30 min, imidacloprid residues were not detected, nor were residues detected in the water any time over the next month after application. Carbaryl residues in water were also monitored, and they exhibited the same rise and fall at the 152 m distance from the experimental plot as did the imidacloprid residues. However, carbaryl levels significantly above the detection limit were still present in water over the next month after application. The rapid dissipation of imidacloprid from water was hypothesized to be due to extensive dilution by the tide. The hypothesis was tested in batch equilibration sorption studies with radiolabeled imidacloprid and Willapa Bay sediment. Sorption distribution coefficients were <1 mL/g, and hysteresis was not observed during two desorption cycles, suggesting that imidacloprid was widely dispersed to extremely low levels soon after application.

KEYWORDS: Imidacloprid; carbaryl; residues; environmental behavior; sorption; water; estuary; burrowing shrimp; oyster

Willapa Bay is an especially productive estuary located on the western coast of southern Washington (**Figure 1**). It is home to a national wildlife refuge and contributes significantly to regional income as a resource for oyster cultivation and fishing. Both exotic and native pests, however, threaten the continued productivity of Willapa Bay. The estuarine plant *Spartina alterniflora* is native to East Coast marshes, but it has become established in Willapa Bay; its invasiveness threatens habitat losses for valuable marine resources (1). Two native crustacean species, the ghost shrimp, *Callinassa* sp., and the mud shrimp, *Upogebia* sp., burrow into the bay sediment, significantly disturbing oyster habitat. Estimated annual economic losses from marine burrowing shrimp range to the millions of dollars (2).

Although estuaries are occasionally sprayed with pesticides to control mosquitoes, they are not typically treated to control pests that directly affect their productivity. Willapa Bay is an

exception to this generalization, which has generated controversy among the competing interests of stakeholders living in the region.

Spartina is being controlled with only limited success by a combination of mowing and application of Rodeo (glyphosate; *N*-phosphonomethylglycine). Marine burrowing shrimp are controlled by applications of Sevin (carbaryl; 1-naphthyl *N*-methylcarbamate). Applications of either pesticide must receive permits from the Washington State Department of Ecology and are strictly limited in permissible treated acreage during any one season.

In the permit process, the applicant must ensure that nontarget effects from the use of an approved pesticide will be very limited. Several studies of glyphosate fate and effects in Willapa Bay and other Washington State wetlands have strongly suggested that this compound can be used with a reasonable certainty of no adverse effects on the estuary (1, 3–5). A recent comprehensive ecological hazard assessment of glyphosate supports this view (6).

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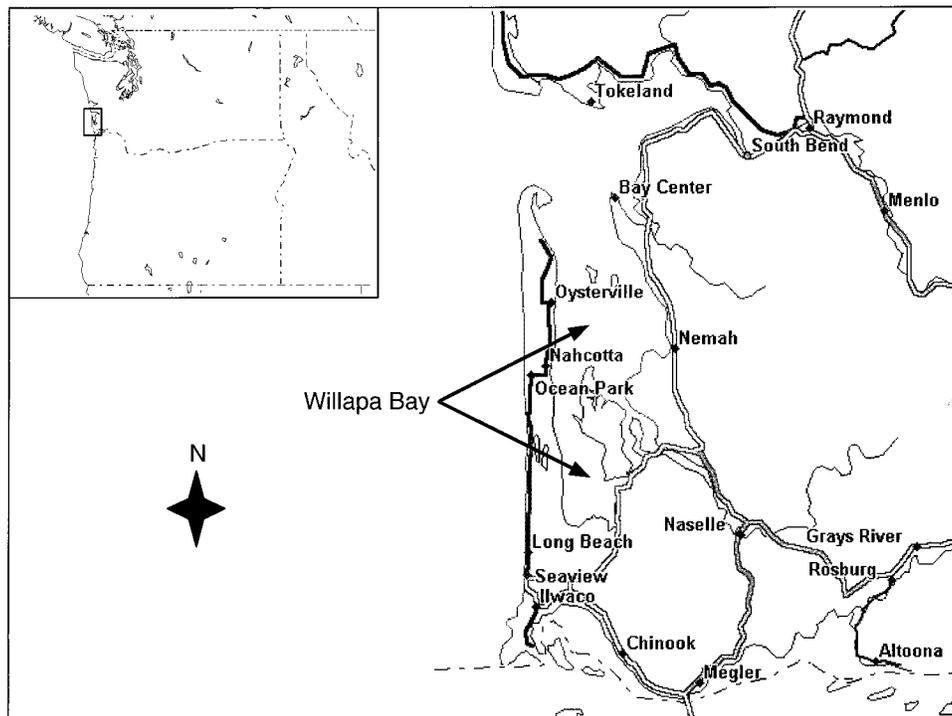


Figure 1. Location of study area in Willapa Bay near Ocean Park in coastal Washington State.

In contrast to the information available about glyphosate, little study of carbaryl's fate and effects in estuaries or wetlands has been undertaken to support its safety to nontarget marine organisms. Being an insecticide with reversible acetylcholinesterase activity, carbaryl could adversely affect other nontarget invertebrates. In contrast to glyphosate, which would be sprayed directly on patches of *Spartina*, carbaryl is sprayed by helicopter on the surface of exposed mudflats during low tide. Tidal changes in Willapa Bay may exceed 3 m (1), so extensive dispersal from the application site may occur with concomitant exposure to nontarget organisms.

Owing to the potential effects of conventional neurotoxic insecticides in aquatic habitats, continued use of carbaryl in oyster production is threatened. Furthermore, severe restrictions have been placed on the use of carbaryl. The infestation of oyster beds with burrowing shrimp has been estimated to exceed 2500 acres, but only 800 acres per year are permitted for treatment (2).

In an effort to find a compound with less potential impact on nontarget organisms, other insecticides have been screened for efficacy in controlling burrowing shrimp. The neonicotinoid insecticide imidacloprid [1-[(6-chloro-3-pyridinyl)methyl]-*N*-nitro-2-imidazolidinimine] is one compound that seems to be effective on burrowing shrimp, but nothing is known about its fate in Willapa Bay. Imidacloprid has comparatively high water solubility (500 mg/L), low vapor pressure (0.13 μ Pa), and moderate persistence in soil ($t_{1/2}$, 48–190 days) (7). It is known to have strong systemic properties, and its mobility may be an advantage in trying to control burrowing organisms after a single surface spray. Although neonicotinoids are acetylcholine receptor agonists, and therefore properly classified as neurotoxins, imidacloprid is generally considered of low toxicity to fish and aquatic invertebrates in comparison to organophosphate, carbamate, and pyrethroid insecticides (8).

To aid possible registration of imidacloprid for burrowing shrimp control, we monitored imidacloprid residues after application to mudflats in Willapa Bay. We also conducted

sorption studies on Willapa Bay sediments to test the hypothesis that the huge fluctuations in water volumes associated with tidal changes dispersed residues to levels below analytical detection limits.

MATERIALS AND METHODS

Experimental Design. The study location was near Ocean Park, WA, in an area of compact sandy sediment in Willapa Bay (Figure 1). The residue study was part of an efficacy study intended to compare imidacloprid with carbaryl after spraying at different application rates and volumes of water. Three application rates of imidacloprid [0.28, 0.56, and 1.12 kg of active ingredient (ai)/ha] were compared to carbaryl (4.48 and 8.96 kg of ai/ha). Two application volumes were used for each insecticide treatment—93.5 and 468 L/ha. Only the highest treatment rate of imidacloprid (1.12 kg/ha) sprayed in 468 L/ha of water was sampled for residue analysis. This volume of water simulated application by a typical ground sprayer, although the plots were treated by a hand-boom pressurized with CO₂. The highest rate of carbaryl treatment was also monitored for comparison to imidacloprid.

The basic experimental design was a stratified random block with four replications. The 10 possible insecticide treatments and 1 untreated control were randomly assigned to one of 11 6.1-m \times 6.1-m plots in each of four blocks. Adjacent plots within a block were separated from one another by an untreated 6.1-m buffer. Treatments were randomized within a block with the caveat that imidacloprid treatments had to be interspersed with carbaryl treatments or the untreated check.

The four experimental blocks were arranged in a line that ran parallel to the shoreline \sim 427 m off-shore. The orientation was north–south, and the tidal flow was approximately perpendicular to the long axis of the blocks with a deflection toward the northwest.

Sediment and Water Sampling. Water and sediment were collected directly in the treated plots or at various distances along a westerly transect from the plots (Figure 2). To establish transects, the center of each plot was located and personnel walked to assigned distances in the direction of tidal flow by following the flow lines left in the sandy sediment at low tide. Water samples were collected as the tide was coming in, and sediment samples were collected during low tide after the sediment was exposed.

At distances along the transect of 0 (i.e., within the treated plot), 30, 61, 122, and 244 m (Figure 2), sediment was collected using a

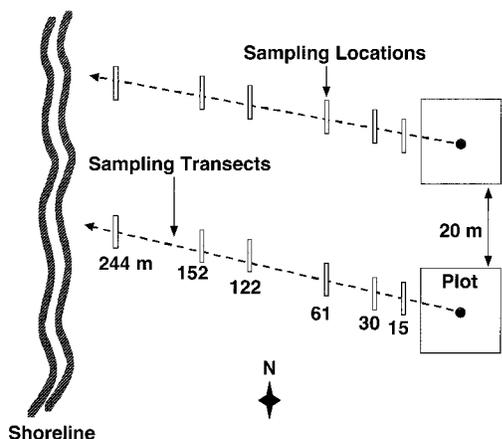


Figure 2. Schematic of typical 6.1-m \times 6.1-m plots within an experimental block. Sampling transects emanated from the center of each plot following the direction of tidal flow.

tube soil corer 2 cm in diameter and 25 cm long. At each location, six cores were collected and composited. Samples were collected prior to application, immediately after application, and 14 and 28 days later.

The day before the application of pesticides, water was collected from the plot areas as the tide was receding. After the insecticide applications, water was collected as the tide was rising at distances along the transect of 15.2 and 152 m. The first samples were collected when the depth of water was \sim 2 cm. This sample was termed the "post-flow initiation sample." An uncapped 1-L Nalgene bottle was held against the substrate with the mouth pointing in the direction of tidal flow. As the water deepened, the bottle was moved up and down to collect a sample representative of the water column. At the 152-m distance from the plots, samples were collected at 5-min intervals following the post-flow initiation sample. After 20 min, two more samples were collected at 10-min intervals. By this time, the water depth was \sim 80 cm, and extensive sampling was not practical. For the timed interval samples, only three of the four transects corresponding to the treatment plots were sampled owing to a deep channel that passed through one of the blocks, making it incomparable to the other blocks.

One day after pesticide application, water samples were collected above the treatment plots and at distances of 15.2 and 152 m as the incoming tide reached a 2-cm depth. Four weeks after application, additional water samples were collected directly above the treated plots.

Analytical Methods. Samples were kept on ice immediately after application and then frozen for \sim 24 h. Thereafter, samples were transported on ice to the Washington State University Food and Environmental Quality Laboratory and stored at -20°C until analysis.

Imidacloprid was extracted from thawed moist sediments (20 g) in a Nalgene 250-mL centrifuge bottle by reciprocal shaking for 1 h with 50 mL of 9:1 acetonitrile/water (9). After the mixture had settled for 10 min, the solvent was vacuum-filtered through a glass microfibre filter (Whatman 934AH). The sediment was re-extracted for 10 min with an additional 20 mL of acetonitrile/water, and the entire mixture was filtered as before. Acetonitrile was removed by vacuum rotary evaporation at 60°C . The remaining aqueous phase was transferred to a 250-mL separatory funnel, 70 mL of deionized water was added, and the aqueous phase was then partitioned twice with 30-mL aliquots of methylene chloride. The methylene chloride extract was drained through anhydrous sodium sulfate and then evaporated dry under nitrogen using a Turbovap (Zymark Corp., Hopkinton, MA) set at 0.7 bar and 45°C . The residue was dissolved in 1 mL of acetonitrile/water (1:1) and filtered through a $0.45\text{-}\mu\text{m}$ syringe into vials for analysis by HPLC.

Carbaryl was extracted from sediment using a modified AOAC procedure (10). Sediments (10 g) collected from the plots on the day of application were rotary shaken with 40 mL of methanol for 1 h. One milliliter of extract solution was diluted to a volume of 2 mL with water and then filtered through a $0.45\text{-}\mu\text{m}$ filter into vials for analysis by HPLC. All other sediment samples (10 g) were rotary shaken in 40 mL of acetonitrile for 1 h. The samples were filtered (Whatman No. 4

paper) and partitioned twice against 15 mL of 30% (w/v) NaCl in water. The aqueous phase was discarded, and the acetonitrile was then partitioned once with 50 mL of hexane. The acetonitrile phase was saved, and then the hexane phase was partitioned with a fresh 25-mL aliquot of acetonitrile. The combined acetonitrile fractions were partitioned three times with methylene chloride (50, 15, and 15 mL) following addition of 150 mL of water and 15 mL of 30% NaCl. The methylene chloride fraction was passed through anhydrous sodium sulfate and then rotary evaporated to dryness. The residue was taken up in 2 mL of methanol/water (1:1) that was filtered into vials through a $0.45\text{-}\mu\text{m}$ filter.

Both imidacloprid and carbaryl were extracted from unfiltered water samples by partitioning two and three times, respectively, with methylene chloride. Further sample concentration, solvent exchange, and filtering were identical to methods described for sediment analysis.

Imidacloprid residues were analyzed using a Varian 9012 HPLC and a Varian 9065 Polychrome photodiode array detector set to monitor absorbance at 268 nm. The column was 150 mm \times 4 mm diameter C18 reversed phase (Varian SP-18-5, Varian Instruments, Walnut Creek, CA) with a particle size of $4.5\ \mu\text{m}$. Imidacloprid was eluted at a flow rate of 1 mL/min using a mobile phase linear program of 5:95 acetonitrile/water to 95:5 acetonitrile/water over a 15-min period. Under these conditions, the retention time of imidacloprid was 7.6 min.

Carbaryl was analyzed using similar HPLC equipment, but the compound was derivatized by postcolumn reaction in a Pickering Laboratories PCX 5100 module. The resulting fluorescent moiety was detected in a Varian 9070 fluorescence detector with excitation and emission wavelengths set to 330 and 464 nm, respectively. The chromatography column was a 150 mm \times 4.6 mm diameter C18 reversed phase (YMC-Pack ODS-Aq, YMC Inc., Wilmington, NC) with a particle size of $5\ \mu\text{m}$. Carbaryl was eluted to the postcolumn reactor module at 1 mL/min in a programmed gradient of 50:50 methanol/water (1-min hold) to 80:20 methanol/water over 10 min. Under these conditions, the retention time of carbaryl was 8.2 min.

Instrumentation was calibrated using external standards. The limits of detection (LOD) for both pesticides were based on instrumental detection limits using a benchmark signal of three times the baseline noise. Given the weights of sediment and volumes of water extracted, the LODs for imidacloprid from sediment and water were $2.5\ \mu\text{g}/\text{kg}$ and $0.5\ \mu\text{g}/\text{L}$, respectively. For carbaryl, the LODs for sediment and water were, respectively, $5\text{--}6\ \mu\text{g}/\text{kg}$ and $0.06\text{--}0.09\ \mu\text{g}/\text{L}$. Concentration data for sediments were expressed on an oven-dry weight basis (minimum of 16 h at 105°C).

Extraction recovery efficiencies of imidacloprid-fortified sediment and water (from pretreated samples) were 120 ± 30 and $60 \pm 20\%$, respectively. These efficiencies were higher (sediment) and lower (water) than historical laboratory quality control data from other projects owing to an anomalous response from one of the three fortifications used for each matrix in method quality control. Carbaryl extraction recovery efficiencies from sediment and water were 100 ± 8 and $94 \pm 5\%$, respectively. Residue data were not corrected for recovery of either pesticide. For calculation of the mean residue recovered from all of the plots, samples containing concentrations lower than the LOD were considered to have a value of 50% of the LOD.

Sorption of Imidacloprid to Sediments. Because radiolabeled imidacloprid was available for use in our laboratory and the focus of this project was mainly on imidacloprid, sorption studies were conducted only with imidacloprid. The ^{14}C -methylene-labeled imidacloprid was obtained gratis from Bayer Corp., Kansas City, MO, and it had a specific activity of $1.08 \times 10^9\ \text{Bq}/\text{mM}$. All solutions used for sorption experiments were prepared by mixing a small amount of radiolabeled imidacloprid solution with an appropriate concentration of unlabeled solution.

Imidacloprid sorption to Willapa Bay sediments was determined both in simulated seawater (3.48% w/v solution of Coral Life scientific grade marine salt) and in 0.01 M CaCl_2 . Mechanical analysis of the sediments showed a composition of 84% sand, 14.8% silt, and 1.2% clay; the organic carbon content was 0.37%. Before use in the sorption experiments, sediments were oven-dried (105°C) for four consecutive days. Five imidacloprid solutions (0.01, 0.1, 1.0, 10, and $100\ \mu\text{g}/\text{mL}$) were prepared in saltwater and in calcium chloride. Ten milliliters of

Table 1. Imidacloprid and Carbaryl Residues (Micrograms per Kilogram) Recovered from Sediments of Sprayed Plots

sampling day	imidacloprid		carbaryl	
	mean	range	mean	range
preapplication	<2.5 ^a		<6.0 ^b	
0	461	330–593	2773	1290–4360
1	16.4	c	71.6	25.7–205
14	2.67	<2.50–6.94	6.2	<6.0–9.3
28	4.72	3.86–6.33	<6.0	<6.0

^a Limit of detection (LOD) = 2.5 $\mu\text{g}/\text{kg}$. ^b LOD = 6.0 $\mu\text{g}/\text{kg}$. ^c Only one sample was analyzed.

imidacloprid-containing solution was shaken with replicate 2-g samples of dried sediment (no. 10 sieve, 2-mm particle size) for at least 2 h in 25-mL Corex centrifuge tubes. Preliminary laboratory studies with agricultural field soils indicated equilibrium was achieved within 2 h. The tubes were centrifuged for 15 min at 12500g. After removal of two 2-mL aliquots for analysis by liquid scintillation counting (Packard TriCarb 1900), 4 mL of fresh unfortified saltwater or calcium chloride was added to the tubes and the process of desorption started. Tubes were shaken for 3 h and then centrifuged. Another 4 mL of supernatant was removed. Sediments were then subjected to a final desorption by addition of another 4 mL of unfortified solution and shaking overnight (~15 h). Tubes were weighed prior to each removal of supernatant and after addition of fresh solution.

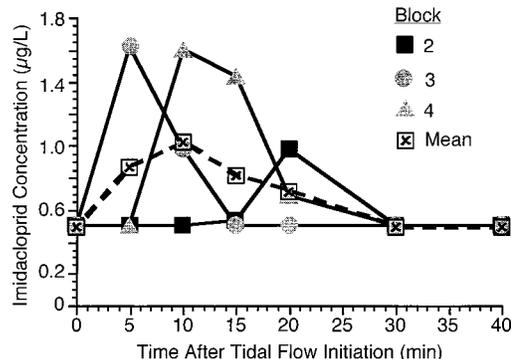
Because preliminary results indicated an extremely low sorption potential of imidacloprid on sediments, an experiment was designed to determine if carbon would increase sorption potential. Batch equilibrium experiments with one desorption cycle were conducted as described above using the aforementioned five concentrations of imidacloprid in simulated seawater. Oven-dried sediments were mixed in a 2:1 ratio with crushed Filtrasorb 300 activated carbon (no. 30 sieve, 600- μm particle size) prior to the start of the sorption experiments.

Data were transformed to micrograms per milliliter of imidacloprid present in supernatants, and the magnitudes of adsorption and desorption were determined by difference from recoveries in tubes containing imidacloprid solutions without sediment. The sediment partition coefficients (K_d) for adsorption and desorption were calculated as the ratio of sorbed imidacloprid (micrograms per gram) to imidacloprid present in solution (micrograms per milliliter). Data were also log transformed for estimation of the Freundlich adsorption coefficient (K_f) and slope ($1/n$) as given by the equation $\log x/m = 1/n \log C + K_f$, where x/m is the sorbed concentration of imidacloprid ($\mu\text{g}/\text{g}$), and C is the solution concentration ($\mu\text{g}/\text{mL}$) (11).

RESULTS AND DISCUSSION

Pesticide Residues in Sediments. The highest per hectare rates and volumes of pesticide application were chosen for study to maximize residue detection in a limited sampling plan. The expected concentrations of carbaryl and imidacloprid in a 25-cm-deep soil core, assuming a bulk density of 1.3 g/cm^3 , are 2846 and 356 $\mu\text{g}/\text{kg}$, respectively. Initial recoveries of carbaryl averaged 2771 $\mu\text{g}/\text{kg}$ (range = 1290–4360 $\mu\text{g}/\text{kg}$). Initial recoveries of imidacloprid averaged 461 $\mu\text{g}/\text{kg}$ (range = 330–593 $\mu\text{g}/\text{kg}$) (Table 1). Thus, residues recovered within the application plots were representative of the theoretical application rate. Immediately after application, the residues would likely be within the top 1 cm of sediment and thus nearly 10-fold higher. Given the moderately high water solubility of imidacloprid (500 mg/L), however, a deeper core was taken because we were predicting rapid movement of chemical into the substrate as the tide came in.

One day following application, recovered pesticide residues in the treatment plots had dropped by >96% (Table 1). Within 2 weeks, both pesticides were recovered from the plots at levels close to the detection limits. Imidacloprid was still detected at

**Figure 3.** Imidacloprid residues in water following tidal flow initiation.

28 days after application, but carbaryl residues were below the detection limit. Residues of neither pesticide were detected in any sediment samples collected along the transect away from the plots in the direction of tidal flow.

The Washington State Department of Ecology (DOE) had investigated carbaryl in several sprayed oyster beds in Willapa Bay (12). Two days following carbaryl applications of 8.4 kg of ai/ha, sediments to a depth of 6 cm contained an average carbaryl concentration of 2933 $\mu\text{g}/\text{kg}$ (range = 2000–3400 $\mu\text{g}/\text{kg}$). Residues immediately after application were not monitored, but theoretically there should have been 10825 $\mu\text{g}/\text{kg}$. Thus, during the first 2 days after application in the DOE study, ~73% of the theoretical concentration of carbaryl may have dissipated in contrast to the >96% loss that we had observed. Carbaryl residues were still present 30 and 60 days after application, unlike in our study where we observed more rapid dissipation despite achieving lower detection limits (6 vs 60 $\mu\text{g}/\text{kg}$).

The DOE study reported detectable carbaryl residues ranging from 180 to 220 $\mu\text{g}/\text{kg}$ in cores collected 30 days after application. In cores collected 60 days after application, carbaryl residues ranged from 86 to 120 $\mu\text{g}/\text{kg}$. Although carbaryl declined more slowly in the DOE study than in our study, at least 99% of theoretically applied concentrations dissipated within 60 days. More importantly, carbaryl residues were not detected in prespray sediment samples in our study nor in the DOE study. Thus, prolonged persistence of carbaryl at a detectable level of 6 $\mu\text{g}/\text{kg}$ in sediments seems to be unlikely beyond several months after application.

Pesticide Residues in Water. The first water sample was collected at a distance of 15 m from the plot when the tidal depth was 2 cm. A wide variation in residue concentrations occurred among blocks at this distance (carbaryl, 0.77–820 $\mu\text{g}/\text{L}$; imidacloprid, <0.5–17.7 $\mu\text{g}/\text{L}$).

The pesticides were also sampled at timed intervals at a distance of 152 m from the plot. This distance was chosen because it should have represented significant potential to achieve mixing of residues as the tide was rising and, therefore, a more homogeneous representation of residues among the treatment blocks. Along the transect corresponding to block 2, imidacloprid was first detected 5 min post-flow initiation, but the first detections in blocks 3 and 4 occurred 5 and 20 min post-flow initiation (Figure 3). In contrast, carbaryl residues were first detected 10 min after flow initiation along the transects corresponding to all blocks (Figure 4). Average imidacloprid and carbaryl residues (1.0 and 13.2 $\mu\text{g}/\text{L}$, respectively) peaked 10 min post-flow initiation. Imidacloprid was not detected in the 30- and 40-min samples, but carbaryl residues ranged from 0.8 to 3.8 $\mu\text{g}/\text{L}$.

Water was sampled from above the plots 1 day after application. Only one of the three sampled blocks contained

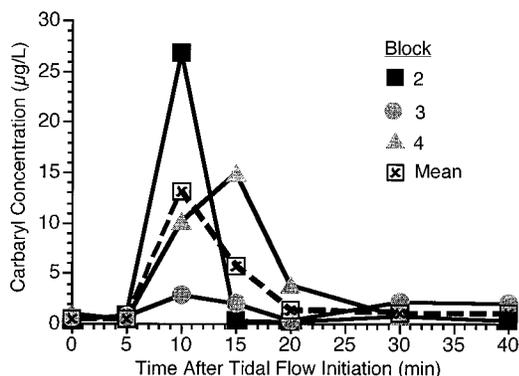


Figure 4. Carbaryl residues in water following tidal flow initiation.

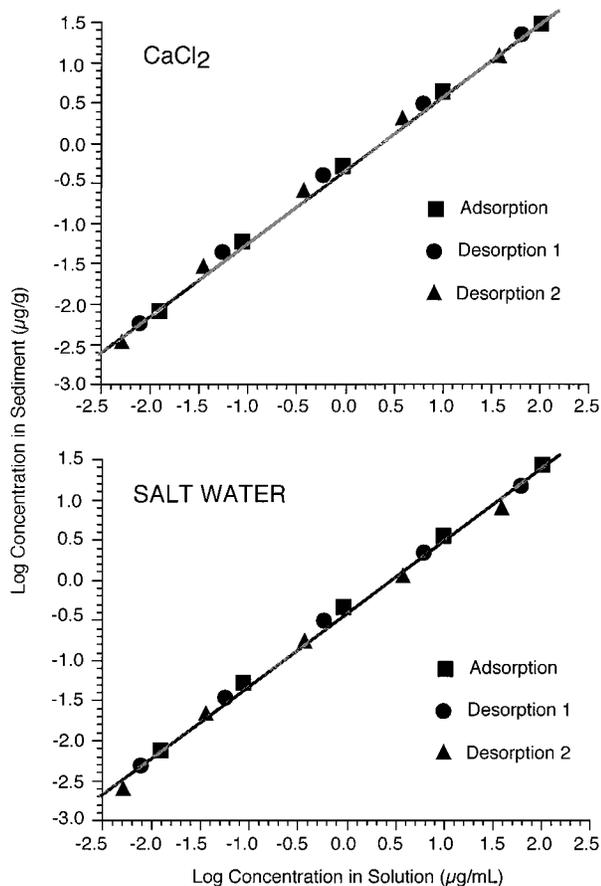


Figure 5. Sorption isotherm for imidacloprid in 0.01 M CaCl₂ and simulated seawater ("saltwater") on Willapa Bay sediment.

imidacloprid residues (block 3, 0.6 µg/L), but carbaryl residues ranged from 0.8 to 10.7 µg/L. Imidacloprid was not detected in water samples collected from above the plots 28 days after application, but carbaryl residues ranged from 0.4 to 0.7 µg/L. Similarly, imidacloprid was not detected in water samples collected 15 and 152 m from the plot the day after application, but carbaryl residues ranged from <0.09 to 1.3 µg/L.

Imidacloprid seems to have dissipated from the water column very quickly even though residues in sediments were still above detection limits 28 days after application. Carbaryl, in contrast, was not detected in sediments 28 days after application, yet it could still be detected in water. One reason for this discrepancy is that carbaryl may be present at levels below the detection limit of 6.0 µg/kg. Carbaryl was detected in prespray water samples at a level of 0.7 µg/L, suggesting persistence of very low levels from spraying in previous years. In the DOE study

Table 2. Sediment Distribution Coefficients (K_d) and Freundlich Sorption Coefficient (K_f) for Imidacloprid in Willapa Bay Sediments and Sediments Mixed with Activated Carbon

initial solution concn, mg/L	sediment distribution coefficient (K_d , mL/g)		
	CaCl ₂	saltwater	saltwater carbon/sediment (1:2)
0.01	0.59	0.52	3912
0.1	0.62	0.52	824
1	0.51	0.45	785
10	0.39	0.32	766
100	0.28	0.24	763
av K_d	0.48	0.41	1410
SD	0.14	0.13	1399
K_f	0.46	0.40	520
1/n	0.91	0.91	0.86

(12), pore water concentrations of carbaryl in 60-day postspray sediment samples reportedly ranged from 0.57 to 1.15 µg/L. However, these water residues were associated with sediment residues ranging from 86 to 120 µg/kg.

Sorption of Imidacloprid to Willapa Bay Sediment. The rapid dissipation of imidacloprid in the plot sediment and water column within 1 day after application suggested that residues were quickly diluted to levels below the detection limit. Rapid dilution would be expected for a compound that is only weakly sorbed. Indeed, published studies with agricultural soils show that imidacloprid has a very low sorption potential. For example, in a low organic carbon silt loam (0.9% OC), imidacloprid had a K_d of only 2.4 mL/g (13).

We hypothesized that imidacloprid sorption would also be low on Willapa Bay sediments, especially considering that the organic carbon content was only ~0.4%. Furthermore, the detection of imidacloprid residues 28 days after application suggested that hysteresis might be occurring over time as reported for several agricultural soils (13–15). Thus, we also measured sorption following two desorption cycles in both 0.01 M CaCl₂ and simulated seawater.

Average K_d values among five initial solution concentrations were similar for imidacloprid sorption in 0.01 M CaCl₂ and 3.8% saltwater (Table 2). Freundlich sorption coefficients (K_f) were also similar with slopes (1/n) of 0.91. However, K_d for the lower solution concentrations (0.01, 0.1, and 1 mg/L) were approximately twice that of the highest concentrations (10 and 100 mg/L). This increase in imidacloprid K_d as solution concentration decreased has been reported previously for agricultural soils (14). Despite the inverse relationship between initial solution concentration and K_d , no evidence of hysteresis in Willapa Bay sediment was observed after two desorption cycles (Figure 5). Thus, coordinates for sediment and solution concentrations following desorption did not deviate from the isotherm established during sorption.

Studies with agricultural soils have indicated that organic carbon is the most important variable influencing imidacloprid sorption. Thus, we hypothesized that very low sorption potential of imidacloprid was influenced by the very low organic carbon concentration in Willapa Bay sediment. Addition of activated carbon to the sediment in a 1:2 (carbon/sediment) ratio increased sorption by nearly 3 orders of magnitude (Table 2; Figure 6). K_d was significantly lower in sediment treated with 0.1 mg/L solutions than with 0.01 mg/mL solutions, but it was similar among the other concentrations. Ignoring the unusually large K_d for the lowest solution concentration, the average K_d was 785 mL/g, and K_f was calculated to be 748 mL/g. Despite the significant increase in sorption owing to the high level of carbon added to the sediment, the desorption and adsorption coordinates

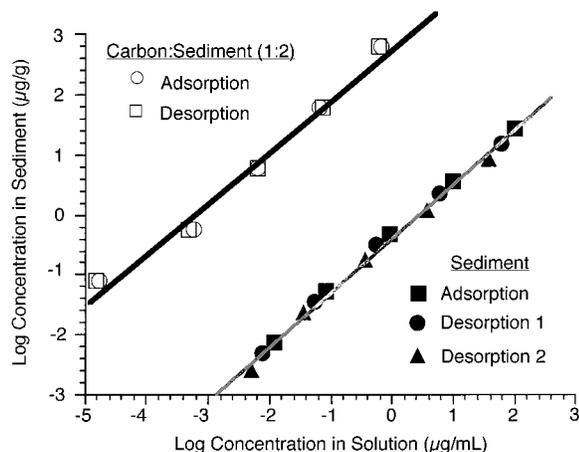


Figure 6. Sorption isotherm for imidacloprid in simulated seawater on Willapa Bay sediment mixed with activated carbon (1:2 carbon/sediment).

were essentially coincidental. Thus, hysteresis was not evident for imidacloprid sorption even in the presence of activated carbon.

In summary, the very low sorption potential of imidacloprid on Willapa Bay sediment supports the hypothesis that rapid dilution of imidacloprid residues occurred as the tide rose following application. This hypothesis is further strengthened by the lack of hysteresis following one or two desorption cycles, even in the presence of activated organic carbon.

Ecotoxicological Significance of Carbaryl and Imidacloprid Residues. A review of ecotoxicity data for carbaryl suggests that at the concentrations present in Willapa Bay, acute and chronic toxicity to estuarine organisms is possible (12). For example, the 96-h EC_{50} for Dungeness crab larvae was reported to be 10 $\mu\text{g/L}$ carbaryl, and adverse effects occurred at concentrations of 0.1 $\mu\text{g/L}$ over a 25-day exposure period (16). Estuarine organisms in an experimental system were adversely affected by levels of 11 $\mu\text{g/L}$ carbaryl over a 10-week period, but not by a level of 1 $\mu\text{g/L}$ (17). The National Academy of Science recommended a water quality criterion for carbaryl of 0.06 $\mu\text{g/L}$ (18). The criterion was developed to give a reasonable assurance of no adverse effects by applying a 100-fold uncertainty factor to the most sensitive test organism, which was *Daphnia magna* ($LC_{50} = 6 \mu\text{g/L}$).

Few ecotoxicological studies of imidacloprid have been published, largely because it has been commercialized for under 10 years. Generally, however, imidacloprid is thought to have a low potential for adverse ecological effects (19). *Mysidopsis* shrimp seems to be one of the most sensitive estuarine invertebrates, responding to imidacloprid with an LC_{50} of 37 $\mu\text{g/L}$. The LC_{50} for brine shrimp (*Artemia* sp.), however, was estimated to be > 361000 $\mu\text{g/L}$. A recent hazard assessment of imidacloprid for various aquatic invertebrates and fish showed that even computer model simulations of surface water concentrations of 17.4 $\mu\text{g/L}$ (20) resulted in risk quotients (estimated water concentration LC_{50} divided by) that were significantly below the EPA's established criteria for ecological concern (8). Given that the highest concentration of imidacloprid in the Willapa Bay experiment was transiently 1.6 $\mu\text{g/L}$, it is reasonably certain that adverse ecological effects are unlikely.

Imidacloprid dissipated rapidly and completely from the water column, but residues were found in the sediment 28 days after application at levels near the detection limit. Studies with marine worms have not been conducted, but earthworm LC_{50} ranges from 2300 to 10700 $\mu\text{g/kg}$ (8). Possible effects on sperm deformities have been observed at 200 $\mu\text{g/kg}$. Thus, even if there

were 10-fold differences in sensitivity between terrestrial and marine worms, imidacloprid residues in the sprayed plots would likely have little long-term effects.

Despite the favorable ecotoxicological profile of imidacloprid and its efficacy against burrowing shrimp, the registrant has no incentive to register it. One problem is the low acreage it would be used on, making it expensive to register relative to the potential return on investment. Another problem is the high cost of the chemical to the oyster grower; thus, it is not likely to be adopted by the growers themselves. In conclusion, the ecological concerns about pesticide residues in estuaries and the expense of developing enough data for registration of alternative compounds will continue to pose a dilemma for oyster growers in the Pacific Northwest.

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