ACCOUNTING FOR CONCENTRATED AND AREA SOURCES OF IMIDACLOPRID IN GROUNDWATER, SUFFOLK COUNTY, LONG ISLAND, NY

A Thesis

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Master of Science

by

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ABSTRACT

The groundwater in Suffolk County, New York provides drinking water for over one million people and is especially sensitive to contamination from the land surface. The area's suburban and agricultural landscapes are among New York's heaviest users of pesticides. Thus Suffolk County has become the critical test case for New York's regulation of pesticides in groundwater. Imidacloprid —-1-(6-chloro-3-pyridinylmethyl)-N-nitroimidazolidin-2-ylidenamine—- is a systemic chloronicotinyl insecticide and neonicotinoid-class insect neurotoxin and is the most widely used insecticide in the world. It treats a broad variety of crops and ornamentals and is permitted for use on most of Suffolk County's land area. Imidacloprid provides a useful case study of New York's and Suffolk County's ground water protection approach. Existing literature contains numerous examples of contamination of surface waters from uses of imidacloprid in agricultural fields. (US EPA, 2008; Starner & Goh, 2012; Main, et al., 2014; Nemeth-Konda, 2002; Lamers, et al., 2011; Bortoluzzi, et al., 2007). The impact of most agricultural products used in greenhouses -- a very important part of Suffolk County's agriculture -- has not been thoroughly considered, and represents a potential source of groundwater pollution (Kreuger, et al., 2010). This study evaluates results from about 2000 samples from pesticide-targeted monitoring wells in Suffolk County's from 2001 -2010. These data were integrated with applications of root zone and vadose zone transport and fate models, covering both field uses and concentrated uses such as greenhouses with fugitive emissions..

Data from monitor wells show that, in general, imidacloprid concentrations stay far below the State's 50 µg/L standard for unspecified organics in drinking water (NYS DEC, Bureau of Pest Management, 2015). The few exceptions are outlying cases where spills or misuse may have occurred. The root zone and vadose zone models help to account for why widespread imidacloprid use does not translate into widespread ground water contamination in Suffolk County. The deep water table and imidacloprid's degradation rate in the near surface soil are well-documented factors. Degradation within the deeper vadose zone, and unquantified emission pathways from greenhouses are the least understood potential contributors to groundwater quality.

BIOGRAPHICAL SKETCH

The author was born in Ithaca, NY in 1978. In 2003, she graduated from St. Lawrence University (Canton, NY) with a Bachelors of Science in Biology and Physics. After more than ten years of exploring careers ranging from cancer research to animal rescue, she found inspiration in an agricultural soil testing and science lab. She then resumed her graduate studies in the Biological and Environmental Engineering graduate program at Cornell University in 2013, and completed the requirements for a Master of Science Degree there in January 2017.

To my Family

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I would like to thank Prof. Tammo Steenhuis for believing me, giving me this opportunity and supporting me throughout this endeavor. I would also like to thank Prof. Jean-Yves Parlange and Dr. Brian Richards for serving as committee members and for their insights.

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Finally, I extend deepest gratitude and thanks to Robert Schindelbeck, in Cornell Crop and Soil Sciences for all his help in this project, and his friendship. Last but not least, I give endless thanks to my family for their love, encouragement and support in everything throughout my whole life. I am very grateful to you all.

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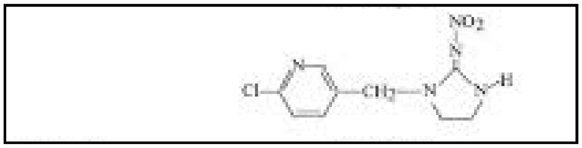
1. Introduction and Background

Imidacloprid-- 1-(6-chloro-3-pyridinylmethyl)-N-nitroimidazolidin-2-ylideneamine -- is the most widely used insecticide in the world (Yamamoto, 1999) and is sold in numerous different forms, formulations, and under hundreds of different product names. Bayer CropScience (Bayer AG) patented it (now expired) and is the primary chemical manufacturer (US EPA, 2008). It is used extensively in agriculture, arboriculture, for turf and gardening, on domestic animals, and on lumber and in homes to prevent and control the presence of, and the damage caused by biting and chewing ectoparasites, insects and larvae (Federoff, et al., 2008). It is most commonly used on rice, cereal, corn and maize, sunflowers, potatoes, fruits, vegetables, lawns and pets (Bajeer, et al, 2012). In agricultural usages, it can be applied by: soil and tree injection; as seed-coat pretreatment; as liquid or granular, surface or trench soil, injection and ground applications, as broadcast foliar application, tree injection, seed pretreatment, and direct plant skin application (National Pesticide Information Center, 2010). It is used extensively in Suffolk County, Long Island, NY, a region with well-known high hydrological sensitivity to chemicals having properties like imidacloprid's.

Since groundwater monitoring for imidacloprid began in Suffolk County, NY in 1995, it has been detected frequently in numerous monitoring wells and some drinking water wells. Imidacloprid is a systemic chloronicotinyl (Canadian Council of Ministers of the Environment, 2007) insecticide and insect neurotoxin belonging to the neonicotinoid chemical class. These chemicals act on the central nervous system by blocking the nicotinergic neuronal pathway, resulting in the accumulation of the neurotransmitter acetylcholine, causing insect paralysis and death on contact (Extoxnet, 1996). Because nicotinergic neuronal pathways are much more abundant in insects than mammals, Imidacloprid is selectively more toxic to insects than mammals (Gervais, et al., 2010). Though imidacloprid's toxicity to humans is minimal, it is highly toxic to honeybees and birds, moderately toxic to lesser mammals and earthworms, and is non-toxic to fish. It is highly soluble, non-volatile, moderately mobile and persistent in soil and water. Its risk of bioaccumulation is minimal. (University of Hertfordshire, 2016). US.EPA's human drinking water guideline of 399 µg/L is higher than New York's State's applicable default 50 µg/L (NYS DEC, Bureau of Pest Management, 2015). The hundreds of detections in local area groundwater monitoring wells have triggered extra regulatory attention.

Table 1: Imidacloprid properties



Molecular weight:	255.7
Water solubility:	514 mg/L (20^{o}C at pH 7)
Vapor pressure:	1.00 x 10-7 mmHg (20^{o}C)
Hydrolysis half-life:	>30 days (25^{o}C at pH 7)
Aqueous photolysis half-life:	<1 hour (24^{o}C at pH 7)
Anaerobic half-life:	27.1 days
Aerobic half-life:	997 days
Soil photolysis half-life:	38.9 days
Field dissipation half-life:	26.5 – 229 days
Henry's constant:	6.5 x 10-11 atm m^3/mole (20^{o}C)
Octanol-water coefficient (K_{ow}):	3.7
Soil adsorption coefficient:	
K_d:	0.956–4.18
K_{oc}:	132–310

Sources: (González-Pradas E, 2002; Fossen, 2006)

Table 1 source: All data were submitted in approved studies and obtained from the Pesticide Chemistry Database (California Department of Pesticide Regulation, internal database).

Because of its widespread use and environmental fate properties (and in particular, due to its persistence over time, mobility and water solubility), potential for the transport from agricultural fields, greenhouses and domestic usages, into surface and groundwater resources is of great concern. Several studies and publications have demonstrated the contamination of surface waters from uses of imidacloprid in agricultural fields (US EPA, 2008; Starner & Goh, 2012; Main, et al.,2014; Bortoluzzi et al., 2007; Nemeth-Konda, et al., 2002; Lamers, et.al., 2011). These studies, among many others, have led to changes in the allowed uses of the product, in order to minimize the contamination of fresh water resources. Nevertheless, continued detection of imidacloprid in groundwater monitoring wells in Suffolk County indicates that contamination is still ongoing. Due to its combined persistence and mobility, further investigation is necessary to determine if routine usages of the product are causing this phenomenon, and whether Imidacloprid based products should be banned from regular use, or if their labeled allowed application rates need to be adjusted for use in this area,

The objective of this assessment is to quantify how both routine use and non-routine misuse of imidacloprid in Suffolk County has caused continued detections in groundwater. In particular, with this and other agricultural chemicals, routine uses in greenhouses have not been extensively or thoroughly considered elsewhere, and represent potential point sources for groundwater pollution (Kreuger, et al., 2010).

Chapter 1 of this report outlined the problem and objective. Chapter 2 provides background on Suffolk County's terrain, water balance, and hydrogeology then describes the data and interpretive methods employed to interpret ground water monitoring results. Chapter 3 presents observed data for a variety of case studies. Chapter 4 focuses on modeling the concentrated use case studies, most notably greenhouses; Chapter 5 focuses on modeling the effects of diffuse outdoor imidacloprid uses (such as agricultural fields, lawns and vineyards) on groundwater. Chapter 6 draws together conclusions about the effects of concentrated and area-wide uses.

2. Data and Methods

This chapter provides background about the Long Island hydrogeological setting, imidacloprid usage on Long Island, imidacloprid occurrence in Long Island ground water, and certain technical tools that help to quantify how usage contributes to occurrence in groundwater. This paves the way toward detailed site case studies covered in Chapters 3, 4, and 5.

2.1 Imidacloprid Use

In order to understand the presence of imidacloprid in monitoring wells an understanding of its use in the region is necessary, especially in light of the potentially very broad use of imidacloprid-based products. The range of applications implies that there are many routes that could contribute to its presence in the region's essential freshwater aquifer system. The main usages can be considered in terms of four subsets: Agricultural (i.e. farmers); commercial (i.e. large scale greenhouse operations); other/urban (i.e. lawn care and pet treatments etc.); and non-users. These are summarized in Table 2 below.

Table 2: Land Use groups

Greenhouses	Field crops and Vineyards	Recreational Land	Urban Uses	Non-Input Sources
*Field and container grown plants *All ornamental plants	*Potatoes *All greenhouse veggies (especially tomatoes and cucumbers)	*All lawns and grassy areas *Landscape trees, shrubs, flowers and ground covers	*Private lawn, tree and landscape application	* Rainwater
*All glasshouse, hoop house and hothouse plants	*Leafy greens *Hops *Herbs	*Multi-family residential complexes	*Lumber and structural material pre-treatments *Industrial uses	* Storm runoff
* All indoor plants in flats, benches, bedding and potting arrays	*Fruits (including fruit bearing trees) *Soy beans and other legumes	*Golf Courses *Shopping complexes *Air ports	*Bedbug, cockroach and termite home treatments	*Snow melt
*All veggie replants intended for resale	*Trees: All Christmas tree varieties, poplar, ash, cottonwood and others	*Turf and sod farms *Cemeteries *Athletic fields	*Home gardens and private orchards	*Recharge basins
*All nut Trees and bushes *All non-fruit bearing trees *All field and forest nurseries	*Field and forest nurseries *Grassy areas, cover crops and between row plantings	*Private, municipal, city, state and national wooded forests and national parks	*Veterinary uses	

Table 2 source: *(Gilrein, 2015)* Adapted from material by Dan Gilrein, Cornell Cooperative Extension of Suffolk County, as used in NYS DEC pesticide strategy.

The primary land uses and agricultural types in Suffolk County were determined with data from: the CropScape crop mapping program of the US Department of Agriculture (USDA) (USDA National Agricultural Statistics Service, 2016), the Suffolk County GIS (Suffolk County, 2016), and the NYS Department of Environmental Conservation's (DEC's) 2015 imidacloprid data package (NYS DEC, Bureau of Pest Management, 2015).

The land areas used by the major agricultural groups are displayed in Figure 1 below. In 2012, of the 14558 Ha of farmland: 2887 Ha of land were dedicated to grapes and vineyards; 1125 Ha to devoted to commercial Sod and Turf production; 1054 Ha to Potatoes (NYS DEC, Bureau of Pest Management, 2015).

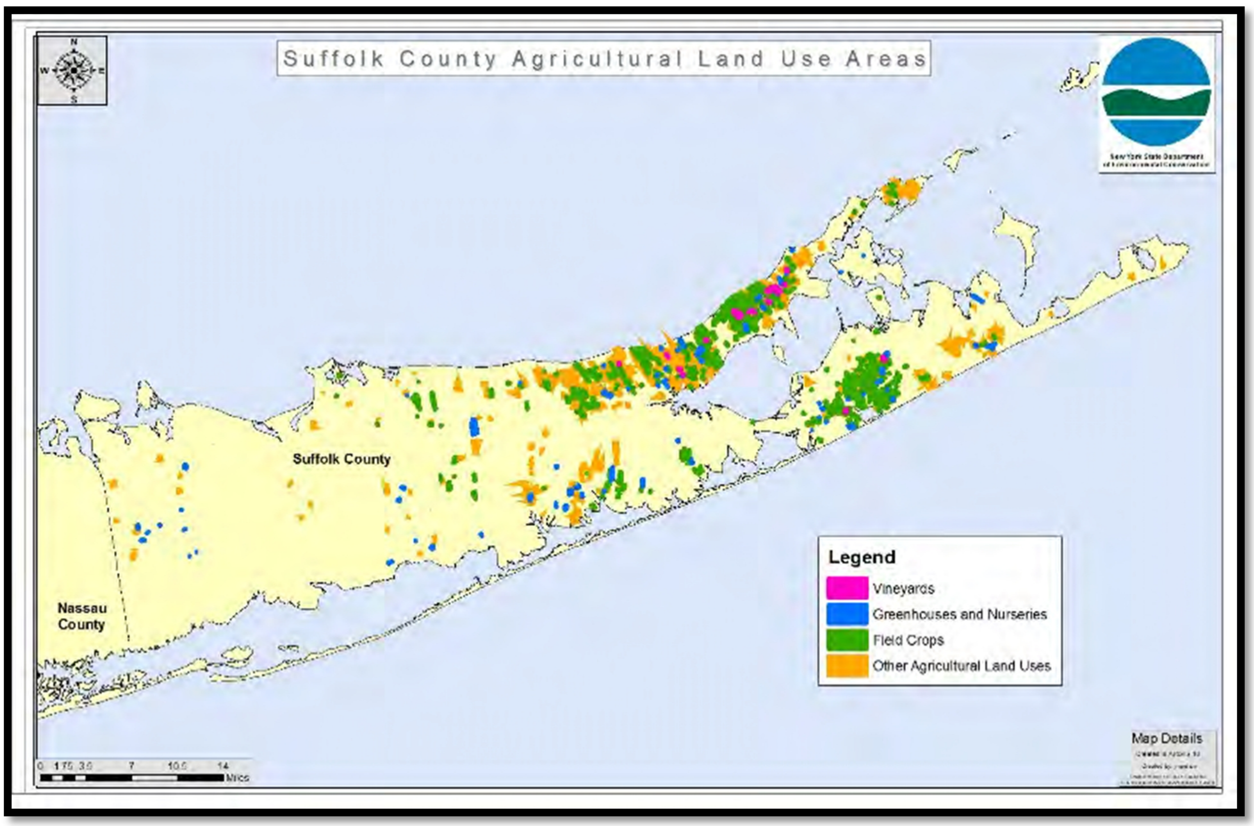


Figure 1: Agricultural Lands potentially using Imidacloprid in Suffolk County

Figure 1 Caption: The locations of vineyards (shown in purple), greenhouses and nurseries, (shown in blue), field crops (shown in green), and other agricultural land uses (shown in yellow) in Suffolk County are represented in this figure. Note that the North Fork has a much larger relative proportion of the county's agricultural lands and vineyards than the South Fork. Greenhouses and nurseries are located throughout Suffolk County, and do not appear to be concentrated in any specific area. Map source: *(NYS DEC, Bureau of Pest Management, 2015)*

In New York State, Long Island is the top region for the sale of nursery, greenhouse, floriculture and sod production (Durst, et al., 2000). Estimates for 2012 indicate that there were 222 businesses listed as Nursery/Greenhouse/Floriculture Farms at that time, though specifics on the land area occupied by this group was not readily available (Ruckdeschel, 2013). In addition to greenhouse, horticultural areas and agricultural lands, a notable expanse of land is devoted to golf courses, and private residences with well-manicured lawns. In Suffolk County, approximately 3870 hectares are used for golf course purposes alone (NYS DEC, Bureau of Pest Management, 2015) .

Private residences, public areas and institutions with well-manicured lawn areas are also important for imidacloprid assessment, but recent data are not available due to the difficulty of mapping many discrete, small turfed areas. Much of the pervious fractions of residential land, commercial properties, and institutional properties contain expanses of professionally maintained turf grass that might be treated with imidacloprid.

Using zip code based sales and use records, provided by New York State's Pesticide Sales and Use Reporting system (PSUR), primary application patterns for imidacloprid products were determined. Figure 2 below provides a geographic summary of the first ten years of PSUR data covering imidacloprid.

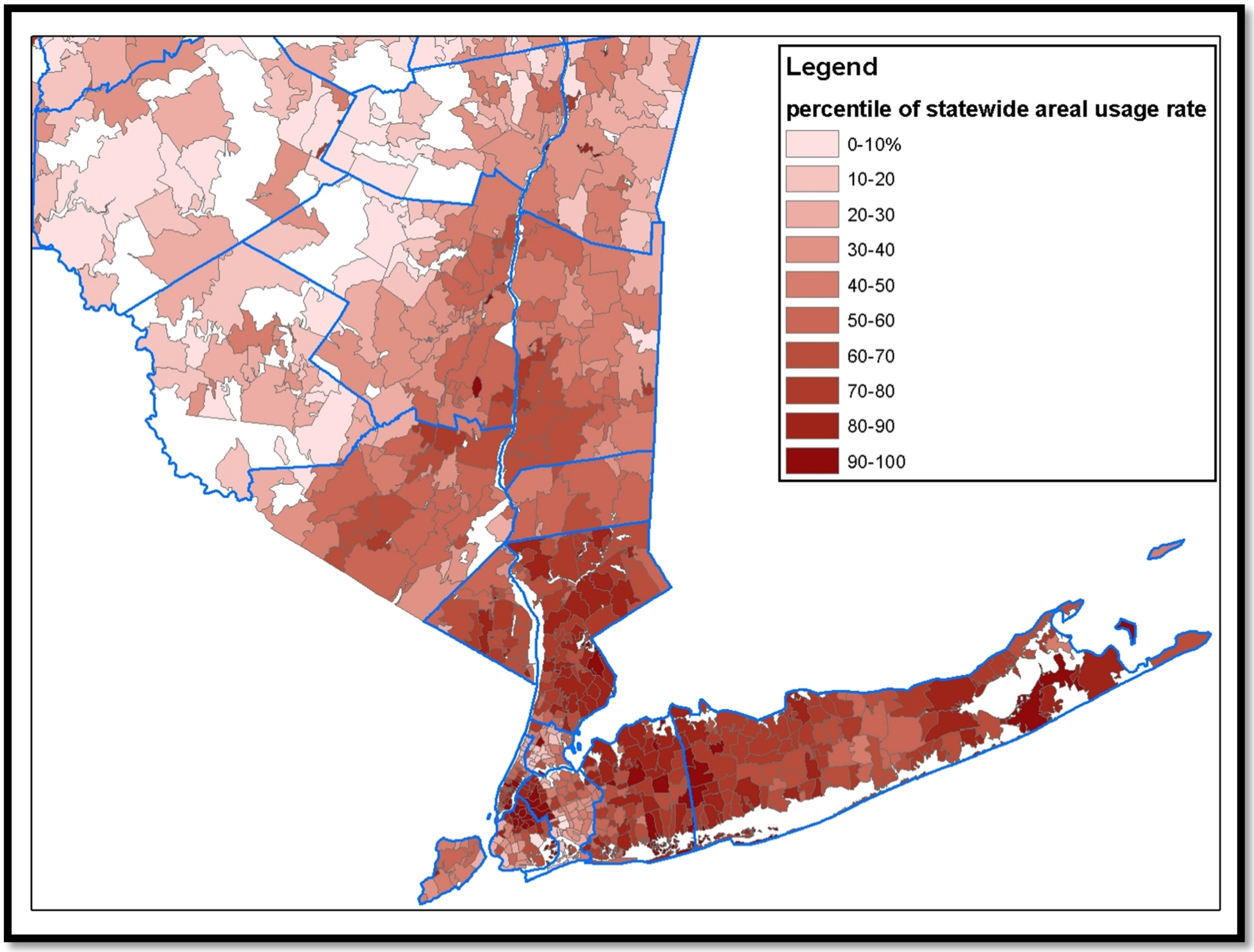


Figure 2: Relative areal intensity of imidacloprid use and sales, as reported to New York State, 2000-2009

Figure 2 Caption: This map is based on 2000-2009 imidacloprid sales (to farmers) plus use (non-farmers) data. The ten differently shaded intervals represent the percentile of reported statewide areal usage rates (in kg active ingredient/km^2) in New York State during that time. The areas that are entirely white denote regions in which no use or sales were reported, the darkest regions are those with the highest reported use rates; the 90th percentile is about 0.4 kg/ha over that time period. In this context, imidacloprid usage rates on Long Island and Westchester County north of New York City are among the highest in the State. This map is a slight underestimate because it excludes data that misreport liquid or solid product forms.

From the most detailed public PSUR product-level data by zip code, discussions with Suffolk County Cornell Cooperative Extension (CCE) associates, and several local users, applicators, and stakeholders, the products most frequently used in Suffolk County were determined, and their product labels reviewed for each crop type. Pesticide labels are very important, and the information and instructions summarized on them resulted from many years of monitoring, testing and research. The label, unique to each formulation and product, provides users with regulatory guidelines, and health and safety information. Maximum yearly allowed, appropriate application rates, concentrations, and schedules for each specific crop are detailed, so that applicators, consumers, wildlife and the environment as a whole are not harmed by the use of the product (Cornell PMEP, 2016).

For the purpose of this assessment, it was assumed that, unless specifically stated, all reported users of imidacloprid-based products followed the specific directions on the product labels. Product labels were used to reconstruct the most likely and realistic application scenarios for each major use group and crop type since imidacloprid became available; this information was applied in case studies in later chapters of this report.

2.2 Soils, Hydrogeology, and Climate

Hydrogeologic Background

Eastern Long Island's uppermost geological structure developed mostly from Pleistocene era glaciation events. Unconsolidated deposits, constituting the Upper Glacial aquifer, lie atop the eastern coastal sedimentary Magothy formation, in some areas divided by the confining Raritan clay. Minor aquifers and confining layers beneath the thick Magothy lie atop Precambrian bedrock, which slopes southward at slightly less than one degree. Unconsolidated material above the bedrock reaches a thickness of 610 meters in South Central Suffolk County, thinning to zero under Long Island Sound.

This Upper Glacial aquifer is most often contaminated and most often monitored since it is nearest the surface and the most convenient source for water supply. The two advances of the Wisconsin ice sheets covered the island with till, ice-contact stratified drift, outwash deposits and deposits comprised of clay, silt, sand, gravel and boulders. Two terminal moraines and the north shore are composed primarily of stratified drift with some till. Central and south Long Island, the areas between the moraines, and to the south of the moraines are made up of mostly of glaciofluvial outwash deposits. Table 3 and Figure 3 characterize the various layers.

Table 3: Long Island's vertical hydrogeologic strata

Hydrogeologic Unit	**Approximate Max Thickness**	**Water-Bearing Character**
Upper glacial aquifer	122m	Mainly sand and gravel of moderate to high permeability; also includes clayey deposits of low permeability.
Gardiners Clay	46m	Clay, silty clay, and a little fine sand of low to very low permeability.
Jameco aquifer	61m	Mainly medium to coarse sand of moderate to high permeability.
Magothy aquifer	305m	Coarse to fine sand of moderate permeability; locally contains highly permeable gravel, and abundant silt and clay of low to very low permeability.
Raritan Clay	91m	Clay of very low permeability; some silt and fine sand of low permeability.
Lloyd aquifer	91m	Sand and gravel of moderate permeability; some clayey material of low permeability.

Table 3 Source: (Cohen, et al., 1968)

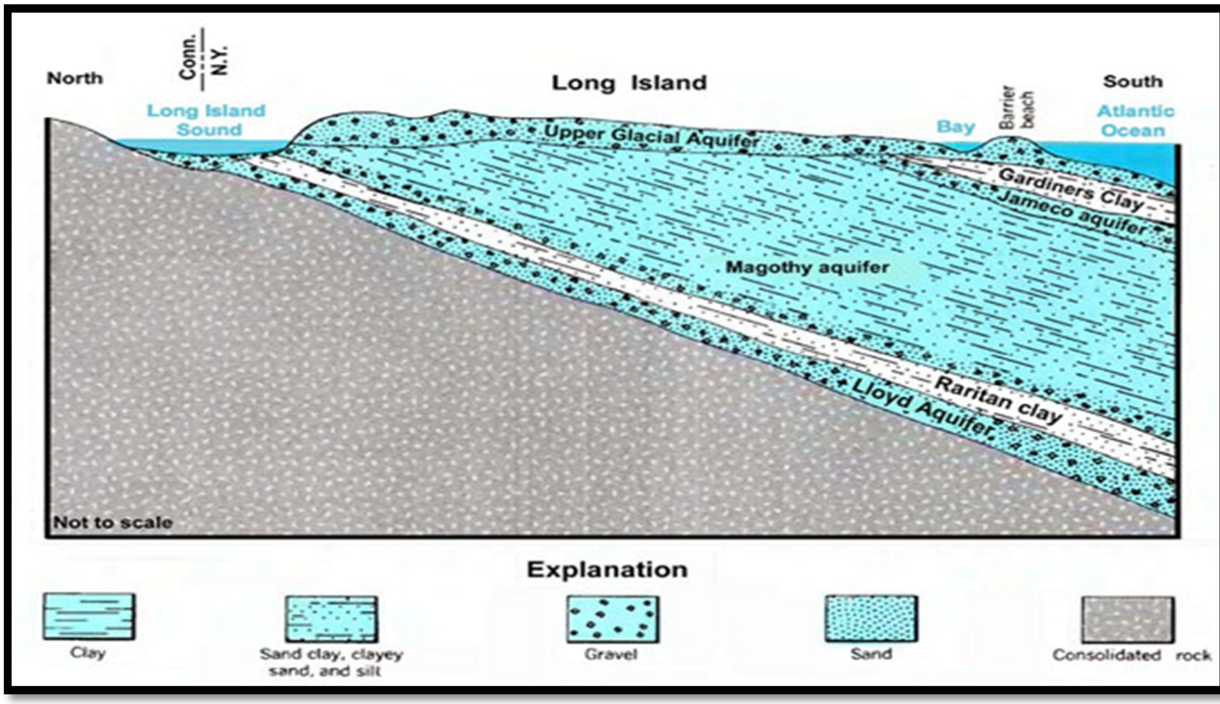


Figure 3: Hydrogeologic cross section of central Long Island

Figure 3 Caption: The two major confining units in the Long Island aquifer system are shown in this figure. The Pleistocene Gardiners Clay, found mainly in the island's southern regions, provides some flow limitations between the Upper Glacial and Magothy aquifers; the relatively thick Raritan confining unit, restricts flow between the Lloyd and the Magothy aquifers (Franke & Cohen, 1972).

Both the Magothy and Upper Glacial aquifers are mainly unconfined, and hydraulically, the two aquifers can be considered to function as one. Since the Upper Glacial aquifer's potentiometric surface is slightly higher than that of the Magothy aquifer below it, the gradient is downward vertically, and recharge water moves from the land surface, into the aquifers (Isbister, 1966).

Western and central Long Island's areal ground water divide follows the long, east-northeasterly axis of Long Island. In east-Central Suffolk, the divide splits in two, with one divide continuing along the Island's north fork, and the other along the Island's south fork. The vertical gradient reverses along the coasts where groundwater ultimately flows upwards to discharge into marine bays, Long Island Sound, or the Atlantic Ocean. Both the vertical and horizontal gradients drive the flow, with hydraulic conductivities reaching 80 meters/day horizontally. Since most of the soil surface material was deposited by flowing water, it is anisotropic and exhibits vertical conductivities on the order of 10-fold smaller than horizontal conductivities. (Franke & Cohen, 1972).

Figure 4 displays the 2006 water table contours atop shading that represents unsaturated thickness above the water table, paler shadings represent thicker and darker shading represent thinner regions, respectively. Unsaturated thickness ranges from zero at the coasts (not significant for water supply) to over 270 feet (90 meters) near the heights of land at the moraines.

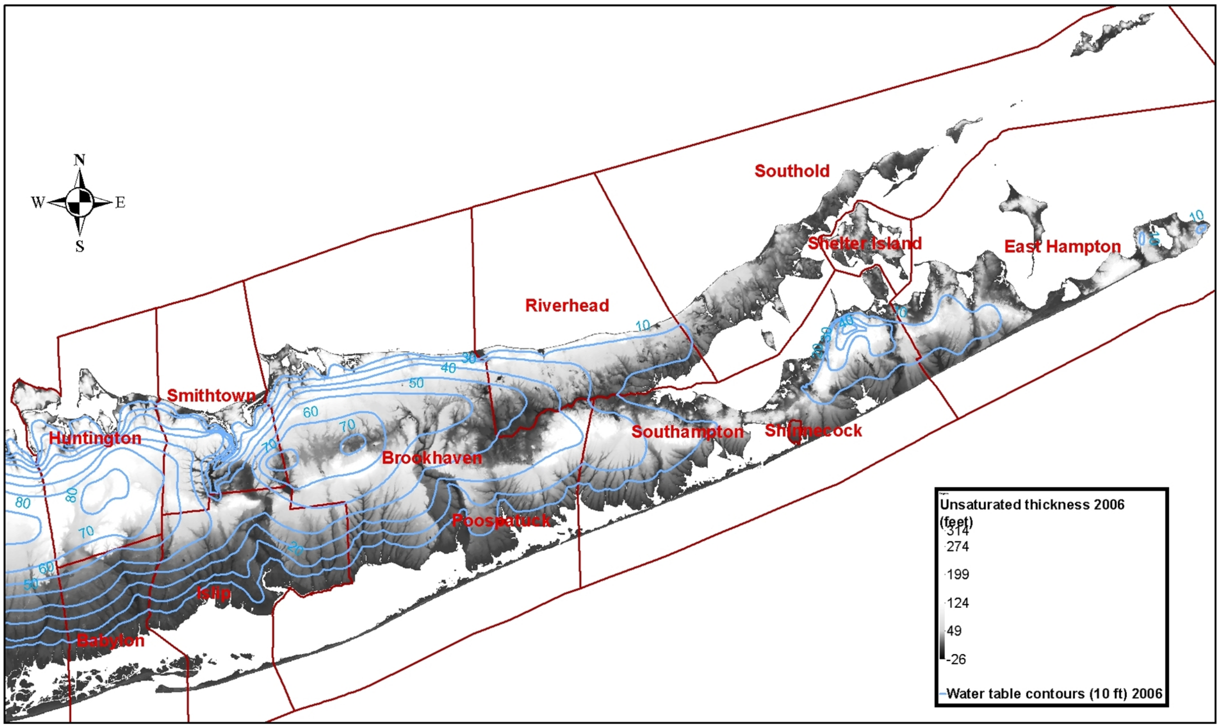


Figure 4: 2006 Water table contours and unsaturated thickness

Figure 4 Caption: Map rendered from USGS GIS files (Monti & Busciolano, 2009). The contours indicate that horizontal ground-water flow directions are generally toward the bay, sound, and ocean shorelines or the rare inland waterways (Olcott, 1995).

Figure 5 shows typical flow directions in the vertical plane along a horizontal flow path in the mainland areas.

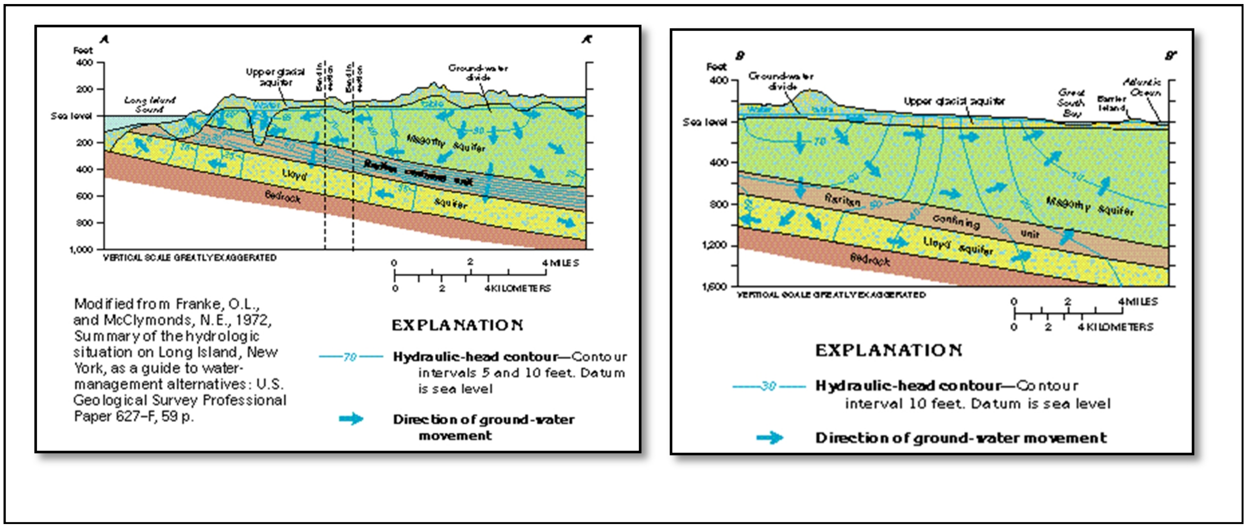


Figure 5: Ground water flow in vertical section across long axis of Long Island

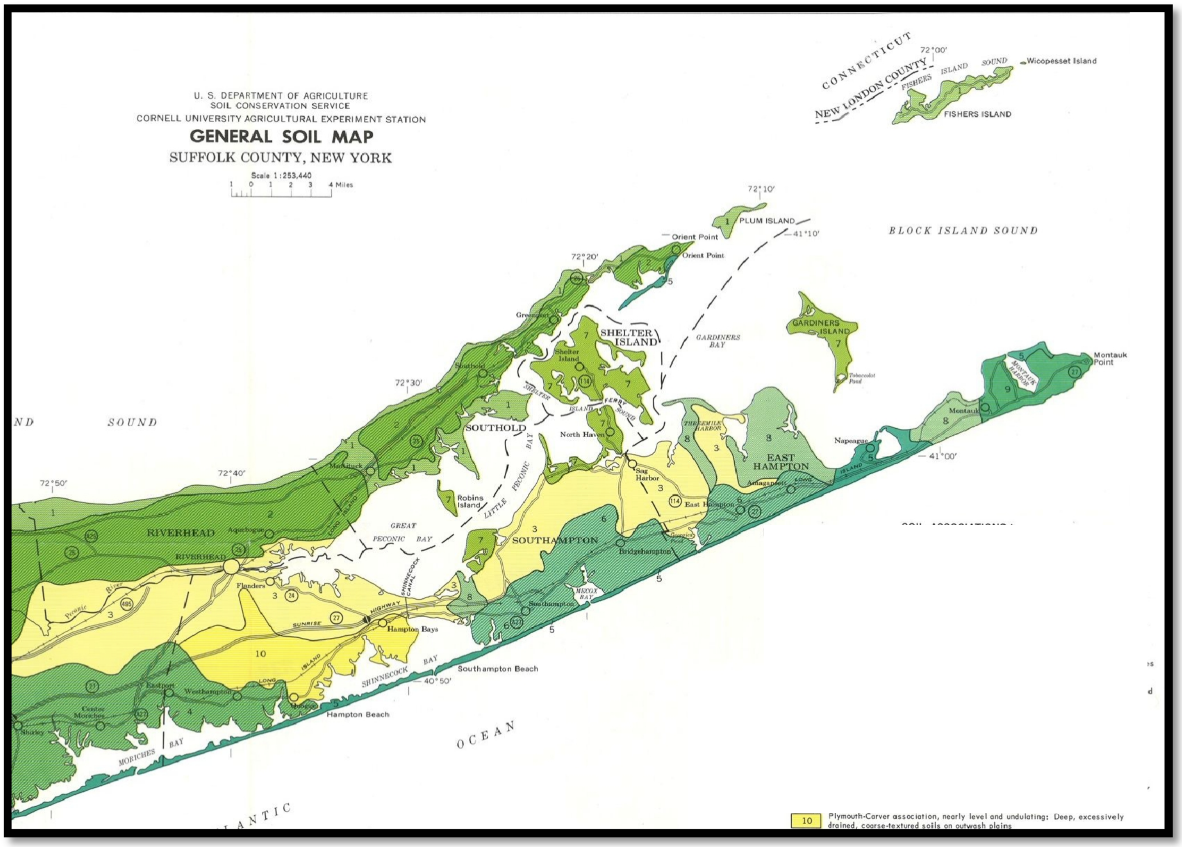
Figure 5 Caption: Flow is vertically downward at the ground water divides, nearly vertically upward at the discharge areas under coastal waters, and dominantly horizontal in between. (Olcott, 1995)

The ground water is discharged from the aquifers by three primary processes: seepage to streams and springs, subsurface outflow, and groundwater evapotranspiration. As indicated in Table 6 below, the evapotranspiration component is relatively small; most ground water discharges through subsurface outflow into a stream, or coastal waters.

Under natural conditions, virtually all groundwater recharge on Long Island results from the infiltration of precipitation into first the vadose zone, followed by the subsequent downward percolation though the water table into the saturated zone. Hence, a discussion of the nature and composition of the unsaturated surface soil material is necessary.

Soils

A general soil map of Eastern Suffolk County is depicted in Figure 6. In the study regions, the predominant soil series found are Riverhead, Haven, Plymouth, and Bridgehampton; these are all very deep soils, and have relatively uninhibited downward drainage, sometimes at very high rates. (This is partly responsible for the minimal run off and surface discharge in Long Island's water budget, as discussed above).



SOIL ASSOCIATIONS*

1 — Carver-Plymouth-Riverhead association: Deep, rolling, excessively drained and well-drained, coarse textured and moderately coarse textured soils on moraines

2 — Haven-Riverhead association: Deep, nearly level to gently sloping, well-drained, medium-textured and moderately coarse textured soils on outwash plains

3 — Plymouth-Carver association, rolling and hilly: Deep, excessively drained, coarse-textured soils on moraines Ronkonkoma Moraine

4 — Riverhead-Plymouth-Carver association: Deep, nearly level to gently sloping, well-drained and excessively drained, moderately coarse textured and coarse textured soils on the southern outwash plain

5 — Dune land-Tidal marsh-Beaches association: Sand dunes, tidal marshes, and beaches of the barrier beach and south shore

6 — Bridgehampton-Haven association: Deep, nearly level to gently sloping, well drained to moderately well drained, medium-textured soils on outwash plains

7 — Montauk-Haven-Riverhead association: Deep, nearly level to strongly sloping, well drained to moderately well drained, moderately coarse textured and medium-textured soils on moraines

8 — Montauk, sandy variant-Plymouth association: Deep, rolling and hilly, excessively drained, coarse-textured soils on moraines

9 — Montauk-Montauk, sandy variant-Bridgehampton association: Deep, rolling and hilly, excessively drained and moderately well drained to well drained, medium-textured to coarse-textured soils on moraines

10 — Plymouth-Carver association, nearly level and undulating: Deep, excessively drained, coarse-textured soils on outwash plains

* Texture refers to surface layer in major soils of each association.

Figure 6: General soil map of eastern Suffolk County

Figure 6 Caption: Each area shown in this map represents more than one kind of soil and soil profile. This map depicts only the most prevalent soil series in each region, and does so in a generalized, non-specific manner. Source: Suffolk County USDA Soil Survey *(USDA Soil Conservation Service and the Cornell University Agricultural Experiment Station, 1972)*

Table 4 describes the dominant soil series at sites analyzed later in this report.

Table 4: Characteristics of selected soils

Series	**Parent Material**	**Upper soil hydraulic conductivity**	**Subsoil hydraulic conductivity**
Riverhead	Glacial outwash	High.	Very high.
Haven	Sandy and gravelly glacial outwash	Moderately high to high	Very high.
Plymouth	Glaciofluvial or deltaic deposits	High or very high.	Very high.
Bridgehampton	Outwash plans and summits (thick silty)	Moderate.	Moderate in subsoil. Moderate to very in substratum.

Table 4 Source: (Soil Survey Staff, Natural Resources Conservation Service, USDA, 2013)

Climate and Hydrologic Budget

Long Island's climate is moderated by the nearby coastal waters, which limit the average duration of snow cover and create the longest growing season conditions in New York. Except in large paved lots, or other areas of extensive connected impervious surfaces, the relatively flat terrain and very high soil infiltration rates yield the simple surficial hydrologic regime: precipitation = recharge + actual evapotranspiration. In inland urban areas, the runoff from impervious surfaces is collected and infiltrated into the highly permeable subsoil via recharge basins (Alley, et al. 1999)

Precipitation does not have any pronounced seasonal patterns, but it does vary considerably from year to year in response to regional drought and storm patterns. This report focuses on the period from the beginning of imidacloprid use on Long Island, the mid 1990's, through 2010. Table 5 lists annual total precipitations at four weather stations from eastern to western Long Island for the 11 years to illustrate time and geographic variability. The stations are ordered from east to west.

Table 5: 1994-2005 Annual precipitation (mm) at four representative Long Island stations

YEAR	Bridgehampton	Riverhead	Islip	Mineola
1995	1219	958	*	897
1996	1029	1461	*	*
1997	1715	975	1120	1107
1998	1207	*	1466	1083
1999	1417	1234	1204	1103
2000	1118	1097	1148	1161
2001	1100	1184	909	*
2002	1252	1811	1100	1227
2003	1331	1461	1143	1290
2004	1676	*	996	1112
2005	1359	1346	1044	1253
* Missing one or two months of data				

Table 5 source: (National Climate Data Center, 2016)

The rates at which water moves into, through and out of the groundwater flow system in central Long Island are estimated in Franke and McClymonds' classic Long Island water budget (Table

6). It indicates that, nearly half of the precipitation falling on Long Island becomes groundwater recharge naturally; unnatural recharge sources include storm water recharge basins and ubiquitous onsite sanitary sewage systems (which return pumped ground water). Aside from highly urbanized areas, there is very little surface runoff; Because of the flat surface topography and soil composition, the accumulation of precipitation at (or near) the land surface is minimal, and the moisture is rapidly evaporated.

Steenhuis et al corroborated that Long Island's inland natural recharge is about half of annual precipitation (Steenhuis, et al., 1985).

Table 6: Average annual "natural conditions" water budget for Nassau and Western Suffolk Counties

Water movement	Water flux (mm/year over water years 1940-1965--1940 km^2 water budget area)
Surface perspective:	
Precipitation	1140
Evapotranspiration from soil	570
Direct runoff	10
Groundwater recharge	560
Fates of groundwater:	
Groundwater discharge to streams	230
Underflow to saltwater bodies	320
Evapotranspiration of groundwater	10

Table 6 source: Modified from (Franke & McClymonds,1972)

Because local recharge rates are dependent on land use, season, and storm water and sewage management, they range from 29% to 57% across Long Island (Masterson et al, 2013). Spatial differences in the mean annual recharge across Nassau and Suffolk counties, averaged over 2005-2009, are shown in Figure 7.

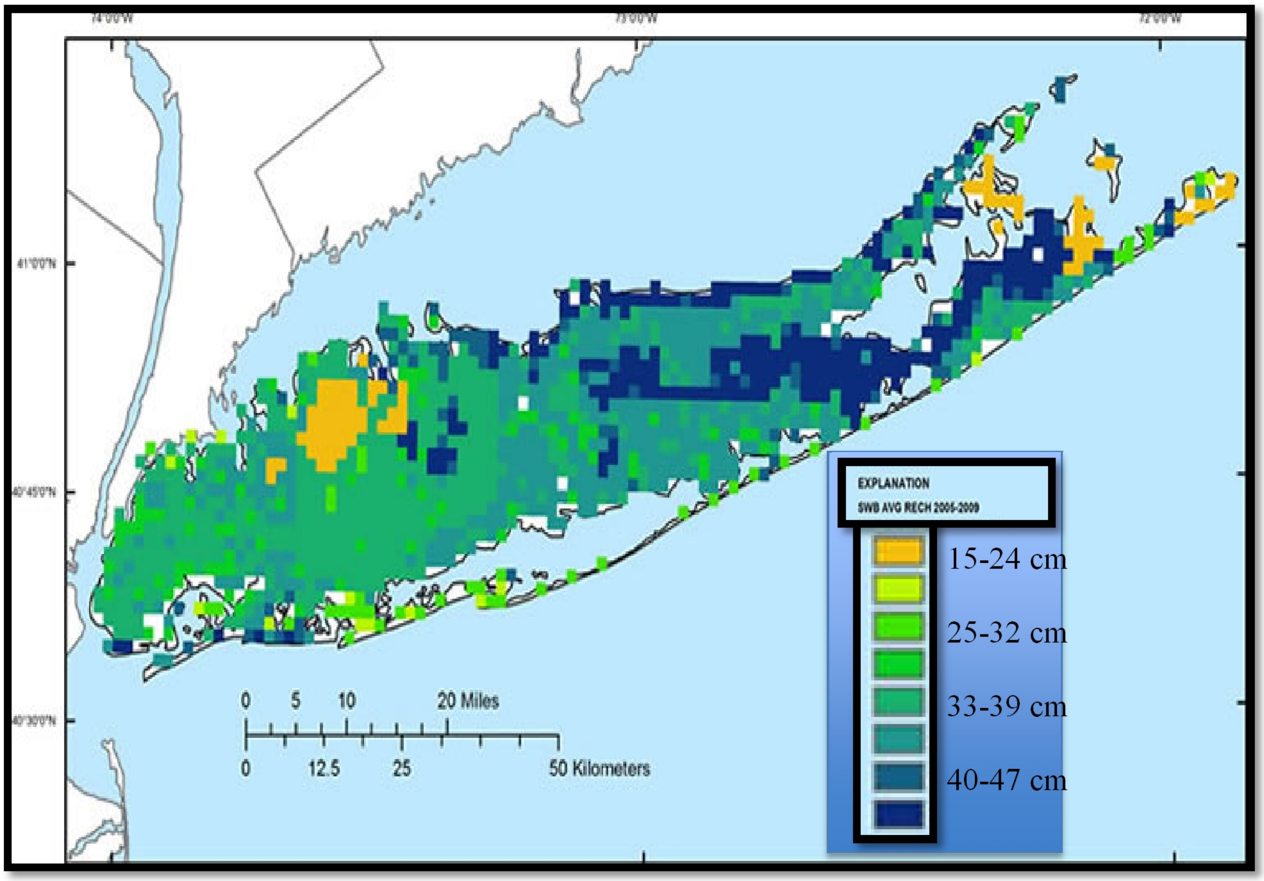


Figure 7: Spatial variation in simulated recharge from Soil-Water-Balance Code (SWB) across Long Island, 2005-2009

Figure 7 Caption: Source: (Masterson, et al., 2013). Legend modified to use SI units instead of inches.

The water budget shown in Table 6 still largely applies to eastern Long Island. It is a largely rural region, with private (non-municipal) well and septic systems. As it is a highly agricultural region, Because of its agricultural use, this is also where the greatest concerns about the effects of pesticide use on groundwater are concentrated.

2.3 Imidacloprid in SCDHS Monitor Wells 2001-2010

The Suffolk county Department of Health Services (SCDHS) provided all well sample and characteristics data used in this section. Figure 8 maps the locations of the SCDHS groundwater monitor wells from which samples were taken between 2001 and 2010 and analyzed for imidacloprid. The set consists of roughly 2000 samples; approximately half have locations validated by SCDHS; Cornell personnel match the remainder to SCDHS-located samples.

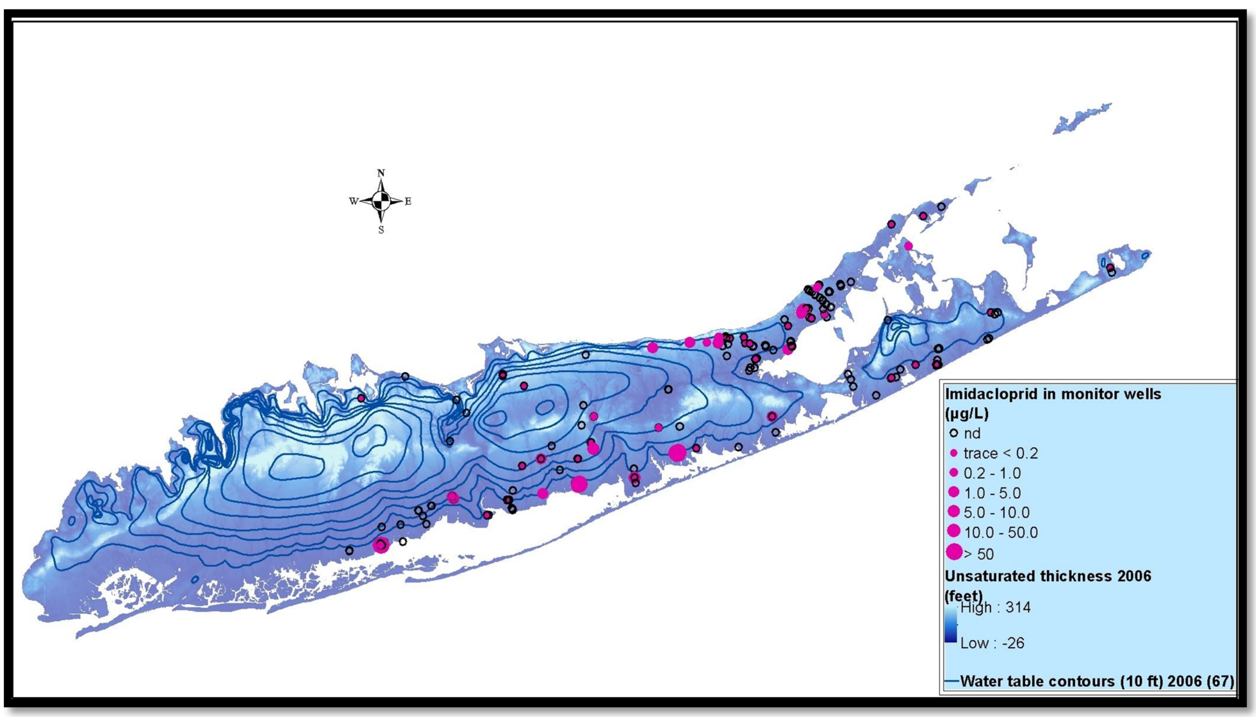


Figure 8: Imidacloprid concentrations in SCDHS monitor wells, with unsaturated thickness and water table contours

Figure 8 Caption: The map's contour lines display water table depth, and its shading exhibits the land's unsaturated thickness (same as Figure 4). The circles represent the highest concentrations (at any depth or time) of imidacloprid detects in the monitor wells sampled and are explained in detail in the figure's key: Larger diameter circles represent higher concentration; hollow circles indicate that the concentration detected was usually below 0.2 µg/L.

As a prelude to interpreting these data, it may be noted that the 0.2 µg/L quantification limit corresponds to a mere 1.2 grams/hectare loading in 60 cm/year of recharge. Thus it is not surprising to see many detections down gradient from areas where 100% of the monitor well catchment is treated. The 50 µg/L default New York State drinking water standard for organic chemicals corresponds to a loading 250 times higher, 300 g/ha/yr. Since imidacloprid application rates on labels are on the order of 100 - 1000 kg/ha/yr, routine use outdoors, absent direct soil injection (no longer allowed) and given that imidacloprid degrades in sunlight and soil, should rarely result in well concentrations above the benchmark of 50 µg/L.

In order to determine the relative contributions of each kind of imidacloprid use to groundwater, monitoring wells were sorted into three main classes: wells associated with known pesticide misuse incidents, wells in one outlier zone (with one well having oddly high concentrations), and the remaining wells representing regular or routine uses. The third group was also stratified according to SCDHS' area categorizations such as vineyards, golf courses, greenhouses or nurseries, and a final "everything else" stratum that happens to include all farmland except vineyards.

Figure 9 below presents a histogram displaying the average concentrations per category itemized by well depth, using zeroes for non-detects.

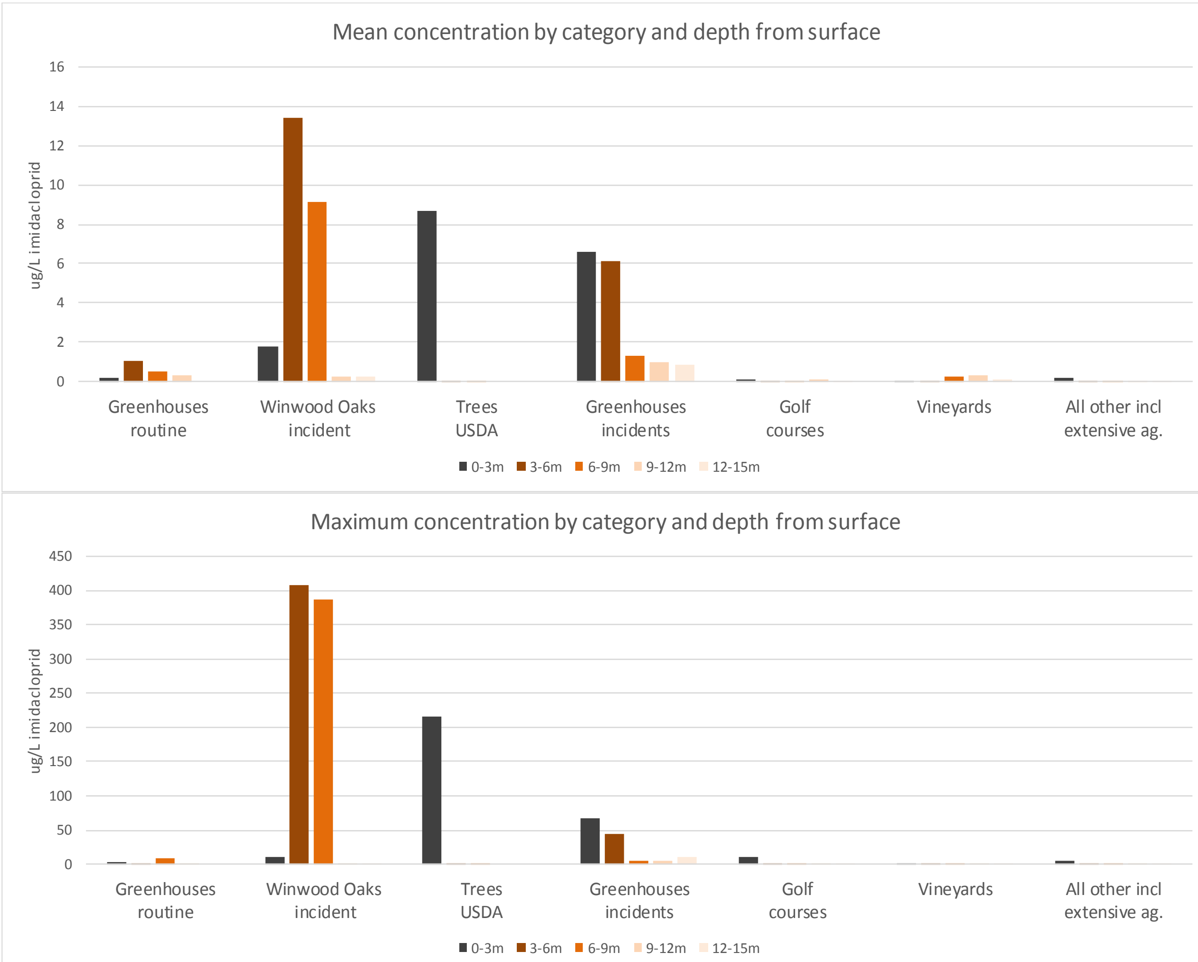


Figure 9: Mean and maximum concentrations by nearby land use

Figure 9 Caption: Each category has a depth cluster with the shallowest sampled intervals at left and darkest, and the deepest intervals at right and lightest. The depth intervals count the vadose zone thickness at 30% and saturated thickness above the sampled interval at 100%. Thus the influence across sites of the variably thick vadose zone, which can be 0 to over 80 meters, is equalized

Considering each cluster separately:

- The Greenhouse incidents category includes two locales, Moriches and Mattituck, both sampled intensively. Mean concentrations exceed 5 µg/L at several depths, indicating considerable plume spreading. The highest observed concentrations exceeded 40 µg/L in one Mattituck well.

- The Winwood Oaks superfund incident is another greenhouse-related case that involves a number of pesticides. This case has the highest average concentrations on the histogram and also the highest peaks over 400 µg/L.
- The remaining categories have mean concentrations below 1-2 µg/L and are dominated by non-detect and trace results under 0.2 µg/L.
- The outlier case labeled Trees (USDA, APHIS, 2015) includes several shallow wells near trees treated experimentally by trunk injection of imidacloprid; all wells except one had relatively low concentrations but two wells on one house lot had near correlated values, 215 and 201, perhaps indicating a spill near the tree.

These results clearly indicate that "incidents" (rather than regular uses) are the only cases that exceed the DOH 50 µg/L nonspecific drinking water standard applied to imidacloprid. The high values in the 100-400-µg/L range typically do not persist to the next sampling at the same well and depth. A non-incident setting associated with routine use rarely reaches 5 µg/L levels.

A consideration in interpreting this data set, and other well-targeted monitoring results, (of any pesticide), is that after initially finding concentrations of concern at a given well, these wells are resampled and additional wells installed and sampled. Wells with initially low detected concentrations are generally not resampled. By including focused additional resampling and new well sample data from high detect wells, and minimally resampling wells with initially low values, the discovered problems become exaggerated. More specifically, Suffolk County's environment provides SCDHS with a great deal of practice in tracking plumes of varied synthetic organics. The SCDHS' systematic sampling of the vicinities of possible problems, (such as down gradient from many greenhouses), is likely to quickly identify any actual incident-type problems. A more naïve, random sampling program would contain a much lower frequency of values above the detection limit than this non-randomly sampled data set does. It thus provides a conservatively biased "worse" view of the ambient groundwater quality, which is appropriate for public health protection. It should however be accounted for in the complex economic/environmental/health-balancing act involved in pesticide regulation.

2.4 Specific Detailed Case Studies for Modeling

Locations

To clearly form distinct associations between these various imidacloprid use categories and observed groundwater quality, representative locales with interesting monitoring data and site contexts were chosen. These isolate the impacts of the individual use types, including misuses, as much as possible. The case studies include the land surface that contributes groundwater recharge tapped by the monitor wells, to the nearby monitor wells which had to have at least two detections above the quantification limit of 0.2 μg/L. (One exception: a Bellport greenhouse area had no detections and is chosen to explore the hypothetical case of minimal detectable emissions.) Figure 10 locates the case study sites.

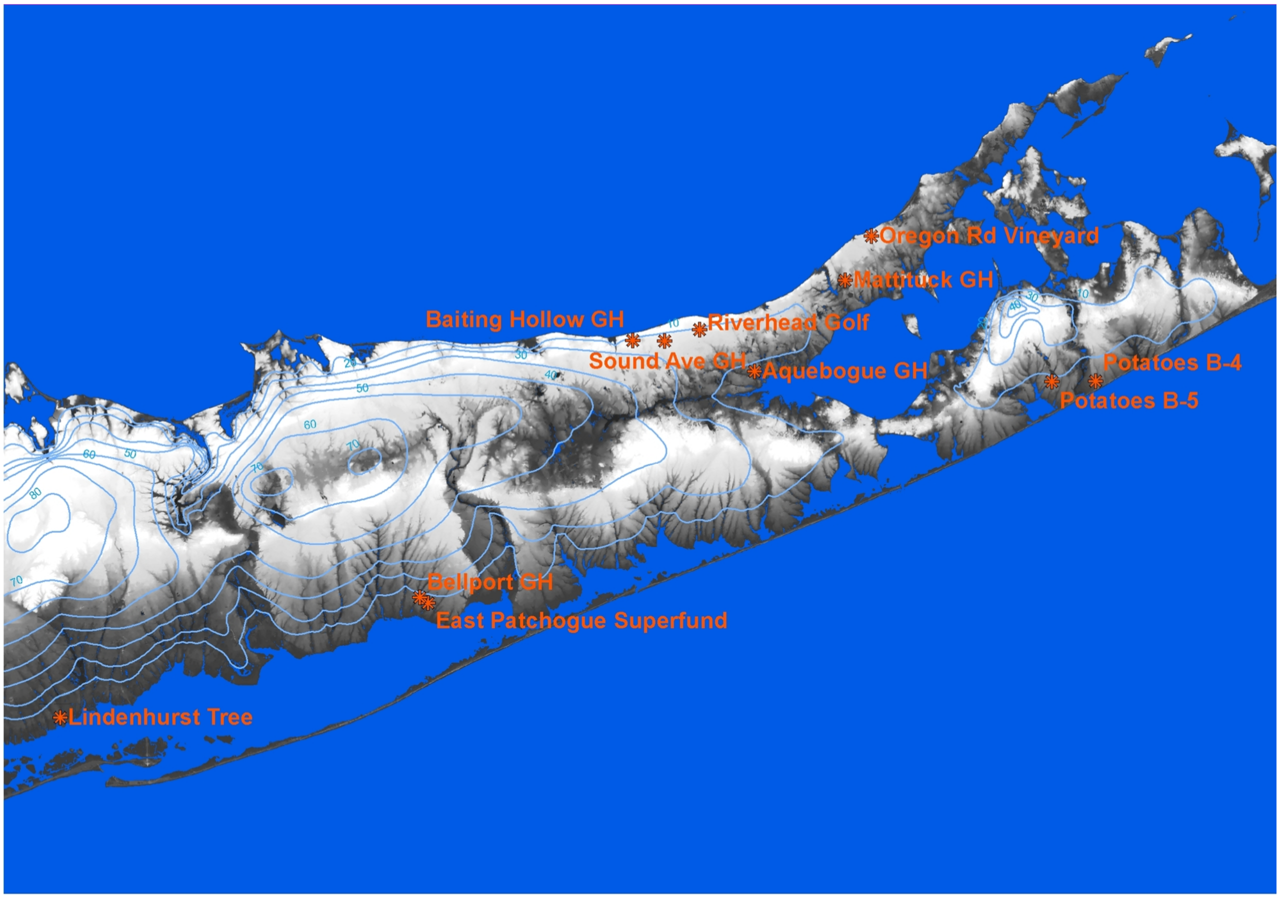


Figure 10: Locations of zoomed-in case studies

Figure 10 Caption: Locations of case study monitor wells on a base map of 2006 water table contours and unsaturated thickness, as in Figure 4. GH = greenhouse. Generic locale names to were used to obscure identities.

To explore each of the main groups of imidacloprid uses and the associated fate patterns, two mathematical modeling programs were employed, namely LEACHP (Hutson & Wagenet, 1992) and the "Sinkevich" model (Sinkevich, et al., 2005). NYS DEC uses Hutson and Wagenent's LEACHP model to forecast the environmental fate of pesticides within the root zone before they are approved for use. The Sinkevich model is a simpler steady-flow model of the vadose zone that employs a minimal parameter set needed to trace the fate of introduced solutes through convection as influenced by sorption, dispersion, and first order degradation (Sinkevich, et al., 2005).

Table 7: Case studies

Case ID	Locale	Report Section	Role (model)	Monitoring extent
USDA	Lindenhurst	3.3, 4.4	Probable spill (Sinkevich)	Short term during USDA demonstration project.
OR	North Fork, Cutchogue Oregon Rd.	3.6, 5.5	Routine use on vineyard, deep water table (Sinkevich)	Several wells, one at center monitored for several years.
B-4, B-5	South Fork	3.4, 5.3	Explore routine use on potatoes, shallow water table (LEACHP)	One well installed by Bayer and monitored afterward by SCDHS for several years.
LL	Western Riverhead	3.1, 4.3	Low-level escapes from greenhouse, deep water table (Sinkevich)	One well monitored for several years.
SA	Western Riverhead	3.1, 4.3	Low-level escapes from greenhouse, deep water table (Sinkevich)	One well monitored for several years.
HA-2, B-1	Aquebogue	3.1, 4.3	Low-level escapes from greenhouse and nursery, shallow water table (Sinkevich)	Two wells, Bayer and SCDHS respectively.
ML	North Fork	3.2, 4.5	Incident of misuse inside greenhouses (no model)	Multiple wells, including up gradient and side gradient, several years.
CC	Riverhead	3.5, 5.4	Explore routine outdoor use on ornamentals (golf course) (LEACHP)	One well, several years
SCR-2A	Bellport	4.3	Explore maximum fugitive loading that would escape detection at 0.1 µg/L.	One well, several years

LEACHP root zone model

LEACHP is a well-established model that calculates one-dimensional vertical water and solute fluxes (Durst, et al., 2000) and is used in NY, as well as several other states, to estimate the persistence of pesticides in the environment. This model uses local soil and meteorological data, as well as the specific environmental fate and transport properties of the given pesticide. It simulates how it will behave after its application in a vertical one-meter profile, in mostly unsaturated and transiently saturated soil. LEACHP simulates water movement, pesticide displacement, and pesticide degradation by providing the numerical solutions to Richards' equation and the convection-dispersion equation. It incorporates the influences of sorption, plant uptake, and first order degradation, with parameters possibly differing by depth layer. The pesticide may be incorporated at the surface or in any depth layer, at any time.

Figure 11 summarizes LEACHP, and displays a vertical cross section with a snapshot of a vertical concentration pattern superimposed on it. A second snapshot of a time series concentration pattern is displayed in the same figure below the modeled profile. The latter, time-series type LEACHP output, is displayed many times in the case studies discussed in Chapter 4, and is the basis for NYS DEC's regulatory use of this model. LEACHP also outputs mass balance summaries of the fate of introduced water and pesticide for each scenario simulated.

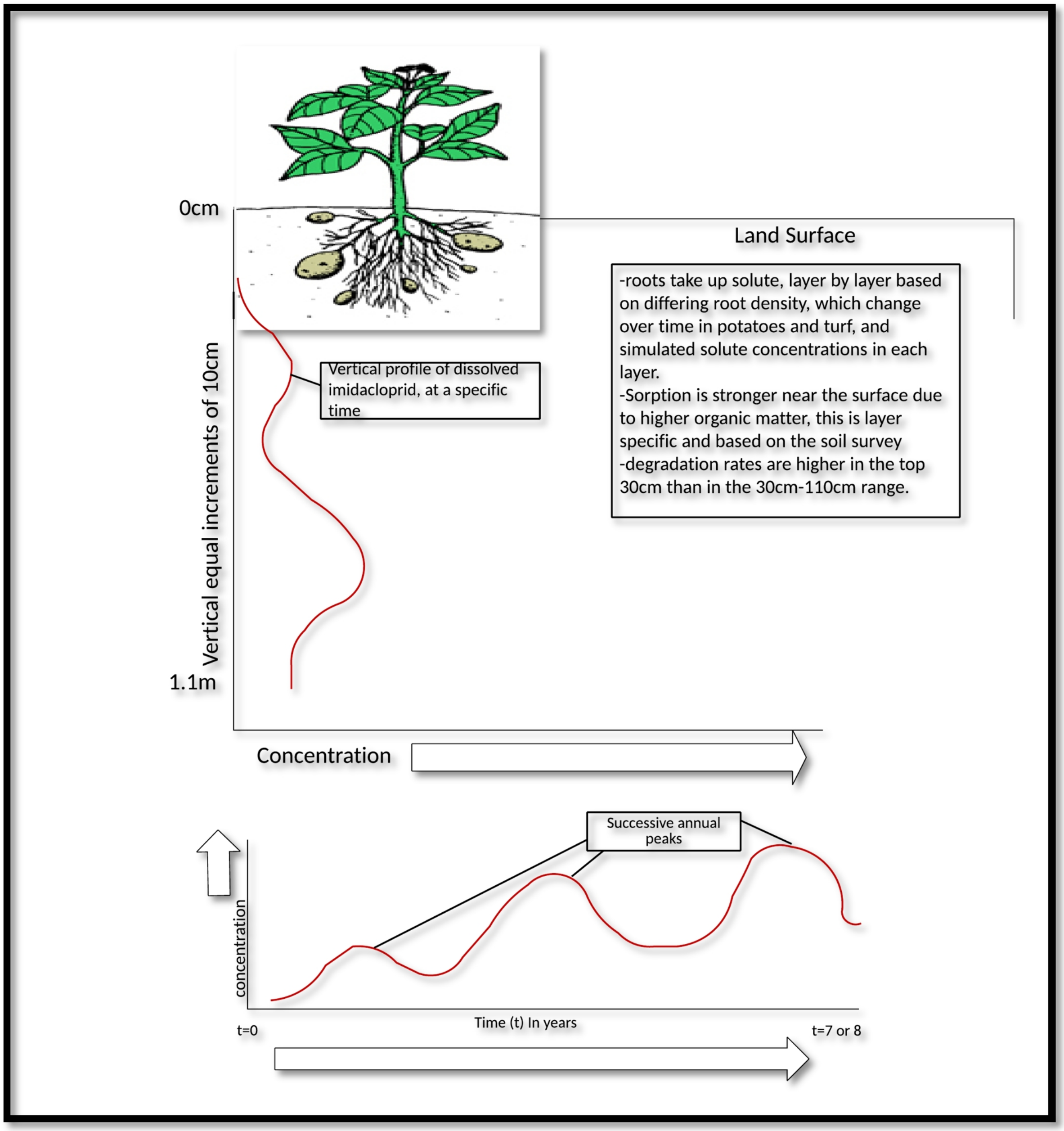


Figure 11: Definition sketch for LEACHP model

Figure 11 Caption: The upper diagram explains the central concept of the model, and has a vertical concentration profile (at one instant) superimposed on it. The lower diagram illustrates the time dimension of LEACHP results, at a fixed depth below the surface.

LEACHP was heavily motivated by the insecticide aldicarb's migration into Suffolk County's ground water in the 1970's, contaminating hundreds of wells after five years of use (Zaki, et al., 1982). Figure 12 indicates that LEACHP would have simulated aldicarb concentrations in shallow recharge in the hundreds of micrograms per liter, when realistic seasonal timings, rates, and depths of incorporation from actual aldicarb use are simulated. This is the same magnitude as aldicarb (total toxic residues) concentrations observed in the shallowest wells from the late 1970's, the origin of the aldicarb problem. (Unfortunately unpublished, but alluded to in one paper based on extensive interviewing (Wartenberg, 1988).) The time period in the figure is different from aldicarb's actual use period 1975-1979. 1965-1972 is the design time period that DEC asks registrants to use when simulating new active ingredients or new uses of existing ingredients.

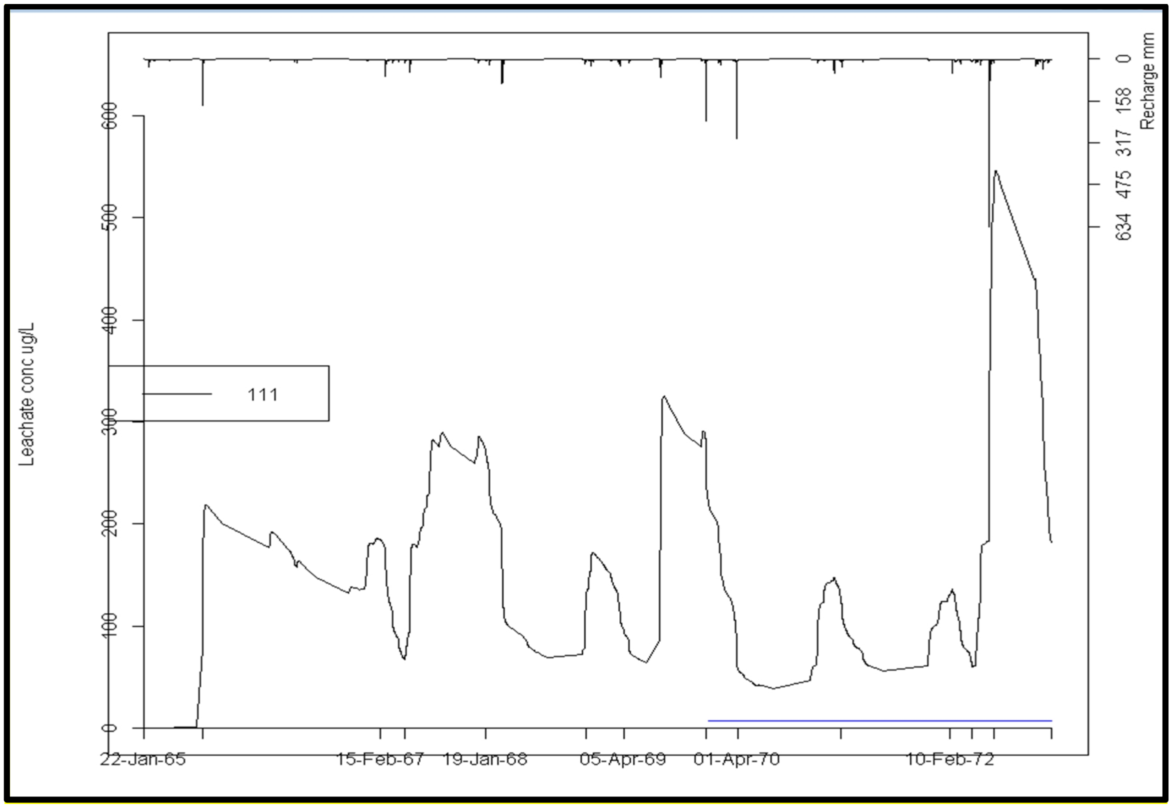


Figure 12: LEACHP simulation results at 1.0m for aldicarb on Long Island potatoes

Figure 12 Caption: The top part of the chart shows ground water recharge events, hanging downward, in millimeters. The lower part shows the daily time series of simulated aldicarb concentrations (modeled as total toxic residues including the original plus two metabolites). Simulated concentrations peaked at over 500 micrograms per liter.

There are two major implications of this simulated result:

1. With typical weather and soil data, usage specifications from labels, and literature data about aldicarb sorption and degradation in sandy soil, LEACHP gets to the right order of magnitude. It does this with zero curve fitting calibration. (Given LEACHP's origin and the strong database for aldicarb, it may be at its best for aldicarb and less good for more sorbing chemicals.)

2. Were a tool like this available in the early 1970's, it would have red-flagged aldicarb because of this result. When applied today, it red flags new chemicals that should not be used on Long Island. It does not red flag imidacloprid, as will be examined in Chapter 5.

The focus on accounting for monitor well data of this report is subject to LECHP's primary weakness: it focuses on the near surface; it was not intended to deliver residues to a deeper water table. The peak and average concentrations it predicts at the bottom of its modeled domain arrive earlier, at higher average concentrations, and at higher peak concentrations than what would arrive at a water table several meters deep. Figure 4 early in this chapter, recapped in Figure 10 nearby, indicated that Suffolk water tables are only as shallow as 1 meter along streams and coastlines, i.e. ground water discharge areas. The areas of depths 5-30 meters are much more extensive. These exhibit one or more years of solute lag time, greater attenuation of peak concentrations due to dispersion, and a drop in average concentrations due to cumulative degradation.

Sinkevich Vadose Zone Model

The Sinkevich model was adopted to complement LEACHP. It is a one-dimensional, preferential flow transport model, which describes solute transport between the land surface and the water table (Sinkevich, et al., 2005). The Sinkevich model splits the unsaturated zone into two layers:

(1) A near surface "distribution zone" completely mixes the introduced solute. The solute may decays via a first order process, and it may lag the movement of water due to sorption. Ultimately the model releases the undegraded remainder of the solute downward via an exponential form.

(2) A "transmission zone" underneath moves water and solutes following a convective and dispersive path downward. Water travels steadily at the annual average recharge rate, adjusted for the flow through only the liquid part of the unsaturated medium's volume. Solute movement lags water movement due to sorption. The solute may disappear via first order decay, generally a slower process than in the distribution zone

The "preferential" aspect is that the downward movement occurs in a fraction of the cross section instead of all soil pores, i.e. there is a more rapid delivery to the water table than the ratio of recharge to porosity, because of less than 100% saturation and because water may flow preferentially through less than 100% of the average saturated part of the cross section (i.e. something less than a 1/3 bar moisture content). The one dimensionality implies that this model does not account for sideways dispersion, thus is not suitable for very small point sources.

The model's classic convection-dispersion equation was solved analytically using Laplace transforms. For the current work, it was extended by superposition of several solutions representing different solute inputs at different times. All inputs to the distribution zone occur instantaneously; they are then released slowly from the distribution zone into the transmission zone.

The parameters required to apply the Sinkevich model to a given scenario are:

- Pesticide application rates and timings;
- Organic carbon partition coefficient (K_{oc}) for the solute;
- Organic matter contents of both zones;
- First order solute degradation rates of both zones;
- Bulk densities of both zones (used in deriving saturation moisture content);
- Thicknesses of both zones;
- Active water content (fraction of cross-section actively flowing) of the transmission zone; and
- Average recharge rate.

Figure 13 portrays the Sinkevich model. Like LEACHP, it produces either a single-time vertical concentration profile or a time series of concentrations at a fixed depth below the land surface, and both are displayed in this figure.

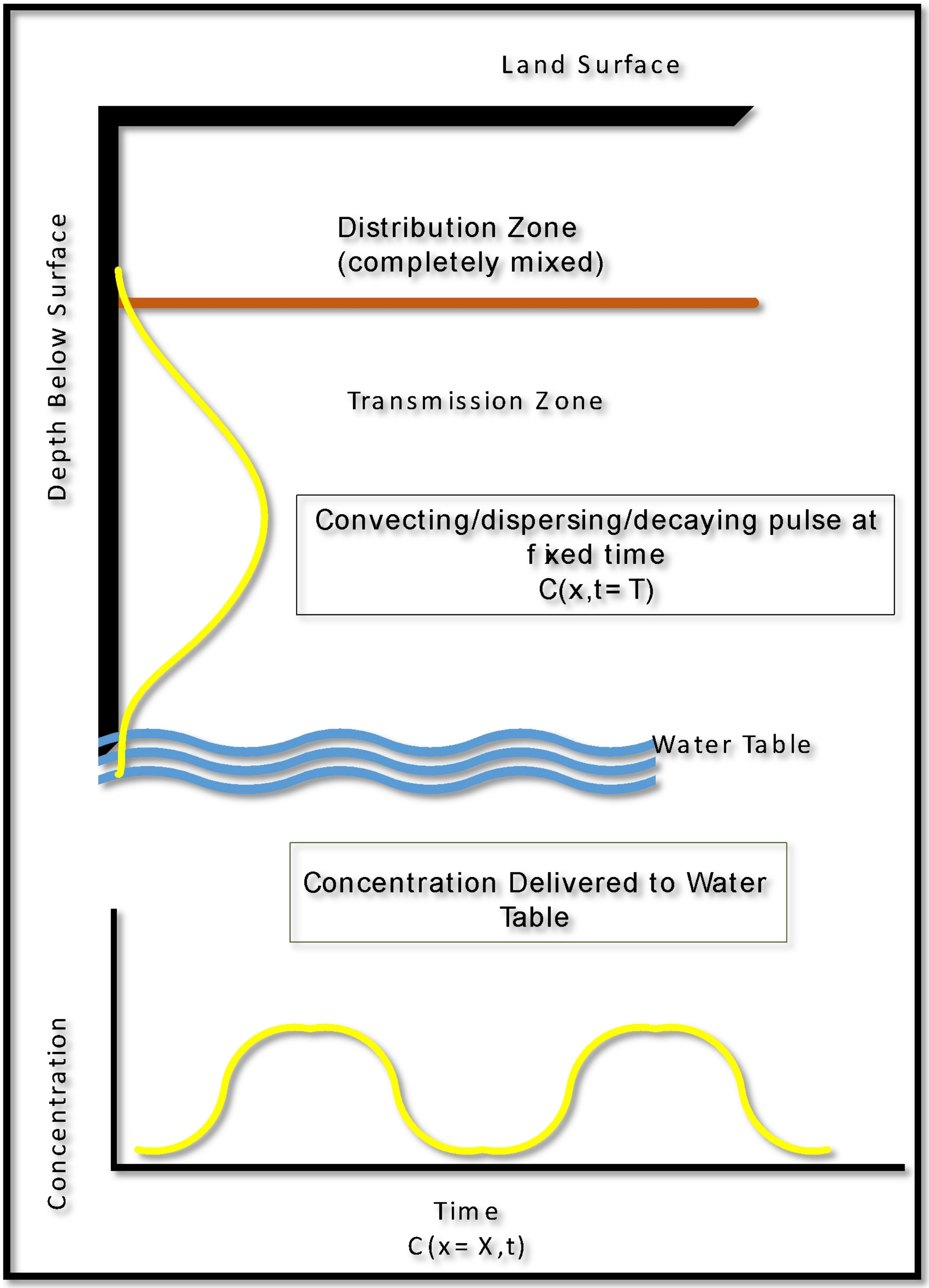


Figure 13: Definition sketch for Sinkevich model

Figure 13 Caption: The single-time vertical concentration from the Sinkevich model is shown above; the time series at a fixed depth below the land surface is shown below.

For the purposes of this work, the Sinkevich model was expressed as a function in the R-Project's scripting language that was cross-compared with an evolved version of the original author Mike Sinkevich's spreadsheet as has been used for prior county reports to DEC.

This model was applied using input data representing the aldicarb case illustrated in the previous subsection about LEACHP -- most importantly application rates, sorption, and degradation. Figure 14 demonstrates that it simulates aldicarb to reach the same order of magnitude of a few hundred µg/L as LEACHP did (in this case at 5m depth), consistent with unpublished late 1970's findings in shallow monitor wells.

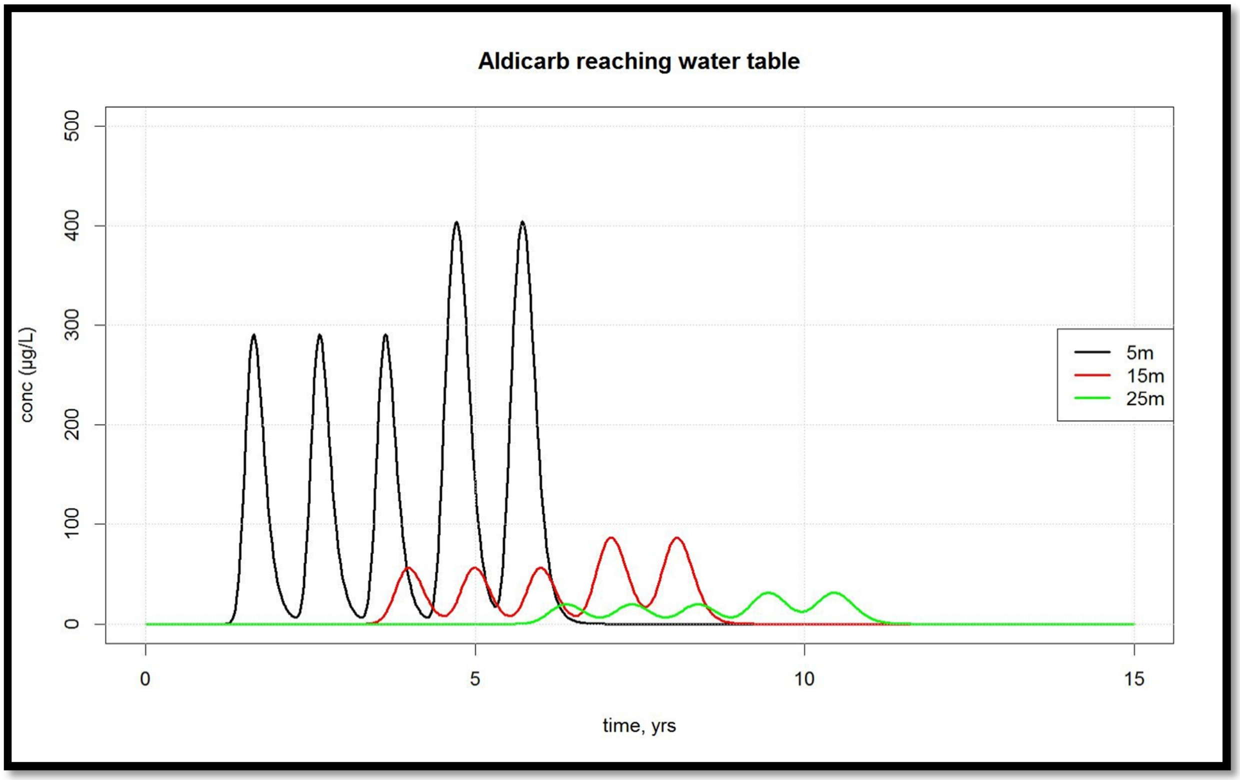


Figure 14: Aldicarb simulated to reach water table at 5-25m, Sinkevich model

Figure 14 Caption: Three colors track the time series of simulated concentrations at different depths below the surface. The black line represents shallowest, red intermediate, and green deepest.

Model execution with the code in R language:

```
slineit2S( x=c(500,1500,2500), M=c(3,3,3,3,2,3,2),
tv=c(0.33,1.33,2.33,3.33,3.5,4.33,4.5), cmax=500,
decaystar=c(0.7,0.6,0.5), decay=c(4.4,4.4,4.4), tmax=15, R=48,
rho=1.31, rhoT=1.66, Af=0.3, dthick=20, koc=10, fom=0.03,
fomT=c(0.0025,0.001,0.001), tinc=0.02, main="Aldicarb reaching
water table", cap=c("5m","15m","25m"), domassbals=FALSE,
legendPos="right"  )
```

Figure 14 demonstrates the ability of the Sinkevich model to reach a deep water table. Aldicarb at 5 meters has much higher peak and average concentrations than at 15-25 meters, due primarily to ongoing chemically mediated degradation in the subsoil. This example also demonstrates that the deeper and deeper levels have later initial breakthrough (first concentrations visible above zero), and the latest trailing effects after cutoff of the inputs after five years.

Applying the Sinkevich model to five years of triple inputs summing to 1 kg/ha total (still representing potato management), Figure 15 shows that imidacloprid's lower input rates (1 kg/ha/year versus 3-5 kg/ha for aldicarb) and stronger sorption to organic matter (220 versus 10 for the organic carbon partition coefficient for aldicarb) translate into concentrations more than 10x below aldicarb's. These factors more than offset imidacloprid's slower environmental degradation 1.5/year (0.004/day) versus 4.4/year (0.014/day) for aldicarb in the upper layer. Imidacloprid's higher sorption keeps the chemical in the upper zone for longer thus compensating for the difference in degradation.

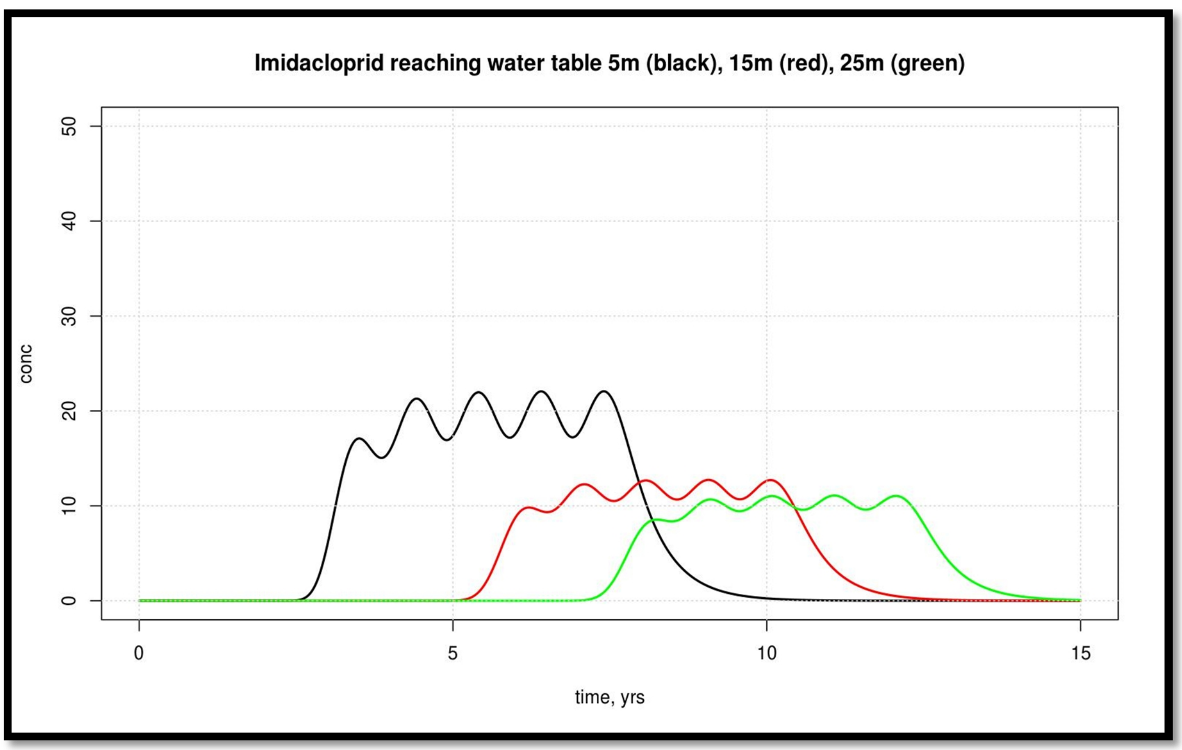


Figure 15: Imidacloprid reaching water table at 5-25m, Sinkevich model

Figure 15 Caption: Model code:

```
slineit2S( x=c(500,1500,2500), M=c(0.6,0.2,0.2, 0.6,0.2,0.2,
0.6,0.2,0.2, 0.6,0.2,0.2,0.6,0.2,0.2), tv=c(0.33,0.50,0.65,
1.33,1.50,1.65, 2.33,2.50,2.65, 3.33,3.5,3.65, 4.33,4.5,4.65),
cmax=50, decaystar=c(0.4,0.3,0.2), decay=c(1.5,1.5,1.5),
tmax=15, R=48, rho=1.31, rhoT=1.66, Af=0.3, dthick=20,
koc=220, fom=0.03, fomT=c(0.0025,0.001,0.0005), tinc=0.02,
main="Imidacloprid reaching water table",
cap=c("5m","15m","25m"), legendPos="right" )
```

Because sorption is more important to imidacloprid than aldicarb, the imidacloprid illustration and later applications to real sites pay extra attention to organic matter content in the subsoil. The four Long Island prototypical soils used in this report have organic matter 0.25% at 1 meter depth. This will fall off much farther by 15m or 25m, thus the green and red traces in Figure 15 include lower and lower transmission zone organic matter percentages.

Table 8 summarizes the geometry, time scale and applicability of each model.

Table 8: Applicability of different models

Model	Geometry	Time	Applicability
LEACHP	• Unsaturated zone, top ~1M, vertical detail. • Uniform (to infinity) laterally. • Solute added at surface or in profile.	• Daily time steps for 7-8 years. • Multiple brief solute inputs, any time.	• Comparing crops, management regimes, soils, weather. • Determining mass balances representing different environmental fates of applied chemical.
Sinkevich	• Unsaturated zone to water table, vertical detail, 1-dimensional advection and dispersion. • Uniform (to infinity) laterally. Solute added to completely mixed layer near surface.	• Steady flow. • Multiple brief solute inputs by superposition. • Any simulation length.	• Estimating influence of unsaturated zone on time lag and concentration reduction.

3. Detailed Case Study Monitor Well Data

This chapter presents Suffolk Health's monitoring data at each case study site. The following two chapters apply the respective Sinkevich and LEACHP models to extend the interpretations of such data, linking to label rates or inferring unintentional (fugitive) emissions.

3.1 Concentrated Sources: Greenhouses

Imidacloprid based products are regularly used in greenhouses as it provides nearly season-long control for long-term crops, most notably in Poinsettias, which are an important greenhouse crop on Long Island. The systemic imidacloprid replaced using repeat spray treatments of less effective products with longer re-entry intervals and worse environmental fate properties. There are only limited alternatives to media and soil applications of imidacloprid available for the management of Oriental Beetle Grubs, Root Aphids, Whiteflies, Flatheaded Borer Beetles, Boxwood Leafminers, and several others, especially in greenhouse hanging baskets and potted plants. Media applications of imidacloprid to treat greenhouse whitefly was once frequent is but has decreased due to development of imidacloprid resistance in the Sweet potato whitefly, which is a primary target species (Cornell University, Cooperative Extension, various, greenhouses).

A greenhouse will typically have several crops per year, thus there may be more than one use of imidacloprid.

Some greenhouse growers on Long Island are recycling water. These use highly mechanized systems to recycle and reuse water while growing lettuce and herbs in the middle of winter. Recycling and reusing the water allows the farmer to control the water, disease, runoff and water waste (Cornell University, Cooperative Extension, various, greenhouses).

While it may seem that pesticides used in a greenhouse are used "indoors", not in the open environment, a typical Long Island greenhouse will have a sand floor. Unless the greenhouse has deliberate water recycling, overflow and drainage from pots will spill onto the pervious floor and enter the soil. It is not unknown for a greenhouse to have a collection system for fugitive emissions from pots onto a less pervious base -- Cornell University in Ithaca was cited for what they did with the outflow from a collection system: directing it untreated to a surface watercourse which is a violation of the Federal Clean Water Act. The collected pot overflow was then routed to a wastewater treatment plant. Sanitary sewers are rare in rural areas including much of eastern Suffolk County, thus the option of collect and treatment is also rare.

In an earlier era "collect and dispose to drywell or cesspool" would have been rational for Long Island, since it gets rid of the water quickly and a cesspool is the usual method for onsite residential waste disposal. Today one can hope that the environmental literacy of Long Island's greenhouse pesticide users rules this out.

Table 9 inventories the greenhouse and other ornamentals monitoring areas in the County 2001-2010 monitor well sample database.

Table 9: Greenhouses and related sites in SCDHS database

Locale	**Wells**	**Description**	**Sampling results**
Amityville	O-1, O-2	Greenhouse and lawn care facilities	All nondetects
Bayport	KW-1	Greenhouse and lawn care facilities	Detections to 4 µg/L
Bellport	SCR-2	Greenhouse	All nondetects
Medford	Bis-1	Nursery	All nondetects
East Patchogue	WO-various	Winwood Oaks incident. Superfund site.	High detections, up to 407 µg/L
Riverhead	GG-1	Greenhouse	All nondetects (one profile sample set)
Riverhead	SA-1	Retail garden store with small greenhouse	Low detections
Baiting Hollow	LL-1	Greenhouse	Low detections
Center Moriches	KWN-various	Greenhouse incident?	Detections to 30.5 µg/L, quite a few wells, few with detections (small plume).
Mattituck	ML-various	Greenhouse incident	Many detections to 43 µg/L
Southold	BA-1	Greenhouse	All nondetects
Water Mill	WM-1	Landscaper	All nondetects
Yaphank	TC-1	Lawn, shrub, tree care company (no greenhouse apparent). Periodic spills?	Detections to 8.9 µg/L

Table 9 Sources: Comments accompanying unpublished SCDHS analytical results; aerial photos; Google Maps landmark data.

The sites having all non-detects do not have enough information to determine if the non-detects are due to careful handling or complete non-use. Non-detects could also result from the concentrations being dispersed and diluted to below the detection limit, or from the samples all being taken before or after any transient plume existed. (It is unlikely that Suffolk Health personnel misplaced the well relative to the target source site; ground water flow directions are well known and the staff have extensive experience in site investigations far beyond pesticides.)

The few "low detections" are compatible with interpretation. There must have been some imidacloprid used before or during the monitoring period (as adjusted for time lags); the wells typically skim the water table and are immediately down gradient from the potential use sites.

The WO and ML wells provide illustrations of concentrated greenhouse sources with higher detects. Most sites probably have indoor situations that could leak residues from the plant containers into an overflow collection system leading outdoors, or directly onto a sand floor within the greenhouse. In addition to indoor greenhouse use, there may be outdoor imidacloprid use on plants stored outdoors during warmer months. These facilities tend to be far from sanitary sewer systems; thus any runoff and waste are primarily disposed of onsite.

Nursery with Greenhouse in Aquebogue

A nursery with a small greenhouse on Hubbard Avenue (HA), Aquebogue, was monitored once with two vertical profile wells in the HA series and for several years using a different shallow well in the B (Bayer) series. This case was chosen for its relatively shallow 5-meter water table depth and long monitoring period. The data from the HA-2 well indicate that the property owner used imidacloprid at some time during the monitoring period. The B well series (including at other sites), installed by the Bayer Company earlier than 2001, were situated near initial imidacloprid customers, as part of the initial regulatory agreement covering its use in New York.

The nursery/greenhouse property's soil is mostly Plymouth, the "sandiest" soil of the four soil types modeled in this report. From a recent aerial photo, the site has a small building (possibly a greenhouse) and a large outdoor planting area. The HA-1 and HA-2 wells are near the building; well B-1 is unaffected by the building; it is across the road from the outdoor planting area.

Well HA-2 had one trace of 0.1 µg/L at the shallowest (1-2 m below water table) in a vertical profile taken in May 2009. Shallow Bayer well B-1 showed all non-detects 2001 through 2005.

This case provides an example of a shallow well affected by very low source emissions, modeled in section 4.3. Also covered in 4.3 is the case of a greenhouse in Bellport whose monitor well always yielded non-detects.

Greenhouse Case SA: Home and Garden Store with Small Greenhouse

This case was chosen because of consistent detections on the order of 1.0 μg/L. The well is at the down gradient edge of a home and garden store with associated greenhouse, and was sampled several times between 2005 and 2007. The predominant soil type in this locale is Haven. The water table at 28 m allows plenty of time to attenuate peak concentrations via longitudinal dispersion, and to degrade, as compared to the much briefer travel time at Aquebogue.

Figure 16 shows the pattern of detections over the sampling period. The 2005 profile sample indicated a higher concentration in the second-from-top depth increment. The samples in 2006 and afterward continued to tap water a few meters below the water table. (Note: Two non-detects from samples taken on 9/7/2005 were excluded; 9/12/2005 samples more consistent with the rest of the time series were retained.)

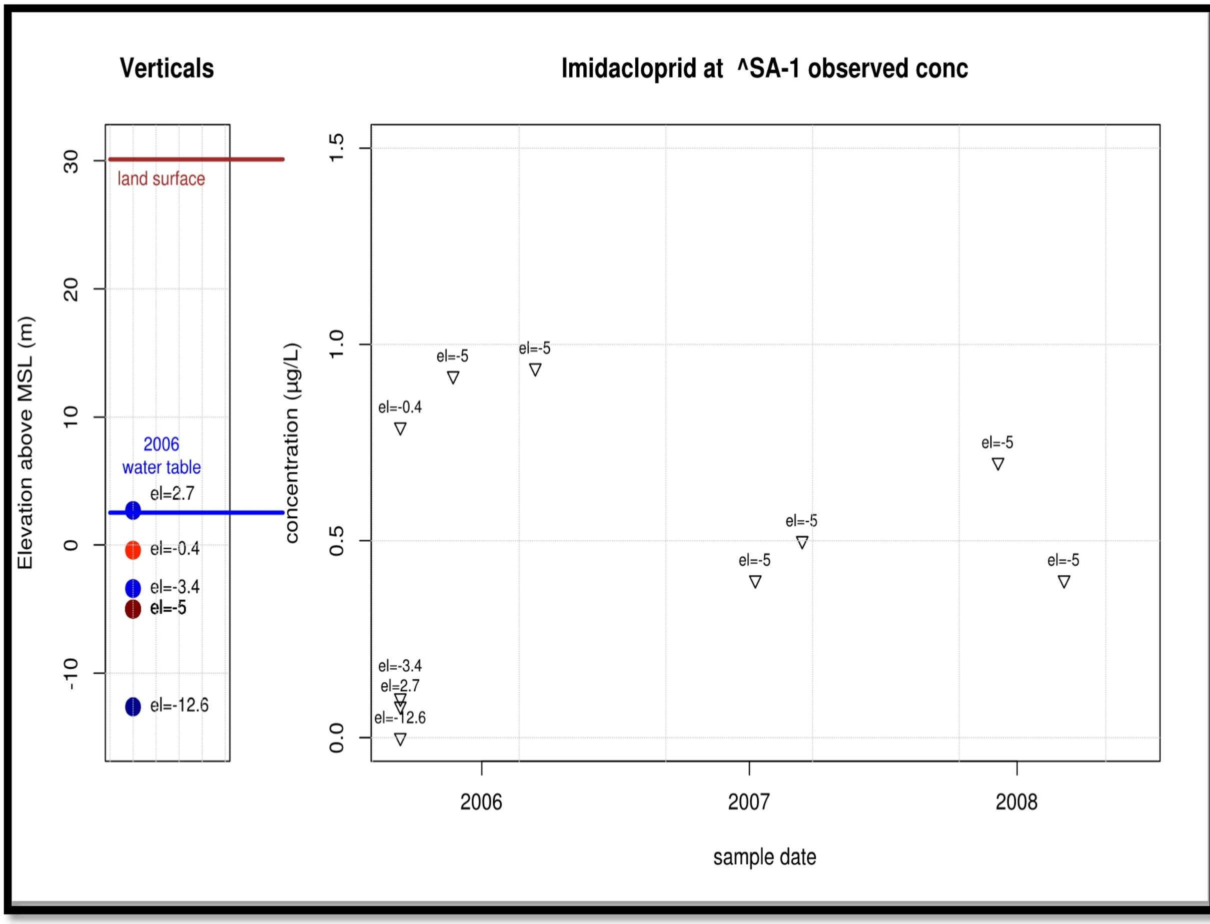


Figure 16: Imidacloprid near a small greenhouse north of Riverhead

<u>Figure 16 Caption</u>: The "verticals" subchart indicates the elevations in meters above sea level where samples were taken (top of screened interval), along with the land surface and 2006 fall water table. The right subchart traces concentrations (Y axis) versus time (X axis), labeling points with the elevation of the sample in case that more than one depth was sampled repeatedly. The same symbology applies to all of the time series plots shown in the remainder of this chapter.

The greenhouse on this site is modestly sized, as at Aquebogue. Emissions were greater than at Aquebogue due to the deeper water table and the consistent, concentration an order of magnitude higher. Based on discussions with several greenhouse owners, and on observations of other operating greenhouses, it is plausible that the emissions are routine ones from use on containers while the containers are outdoors during warmer seasons, or via leachate from container plants indoors, or from chemigation (imidacloprid applied via irrigation water) that misses containers, or from imperfect application of granular products indoors. A greenhouse may appear to be a very contained indoor environment, but if it has a sand floor (common practice in eastern Suffolk County) there is not containment for soluble chemicals. It was noted that few Suffolk greenhouses are near sanitary sewer systems, thus there is not an opportunity to collect and simply treat floor "wastewater" (an option used in some greenhouses at Cornell University in Ithaca, NY).

As noted earlier, the Suffolk Public Health Lab's analytical detection limit for imidacloprid permits finding just one gram of imidacloprid dissolved in a one's year's recharge from 10,000 meters squared (1 hectare) of land. One 0.25 liter container of Marathon II liquid imidacloprid contains 60 grams of imidacloprid (Olympic Horticultural Products, 2000). It must be assumed that some of such product will escape into a pervious floor or when used outdoors.

This case provides an example of a deep well with moderate, recurring emissions, modeled in section 4.3.

Baiting Hollow (BA) Major Greenhouse

The next site considered is a major greenhouse complex, in Baiting Hollow in northwestern Riverhead; a nearby well was monitored for several years. At 33m, it has the deepest water table of all of the greenhouse cases in this report. The well is at the upgradient edge of a residential area downgradient (north) from the greenhouses. The soil is a mix of Plymouth and Haven types; Plymouth parameters were used.

As indicated in Figure 17 an initially clean profile was observed in 2004; perhaps it was not sampled at a shallow enough depth increment, or perhaps imidacloprid had not broken through yet to the deep water table. This is followed by an increasing trend in the observed data from 0.8 μg/L to 2.0 μg/L. This could represent an initial breakthrough from recurring emissions by early 2006, perhaps tracing back to fugitive emissions that began in the late 1990's. It might also indicate increasing use or changes in handling that lead to a greater escape from the plant containers.

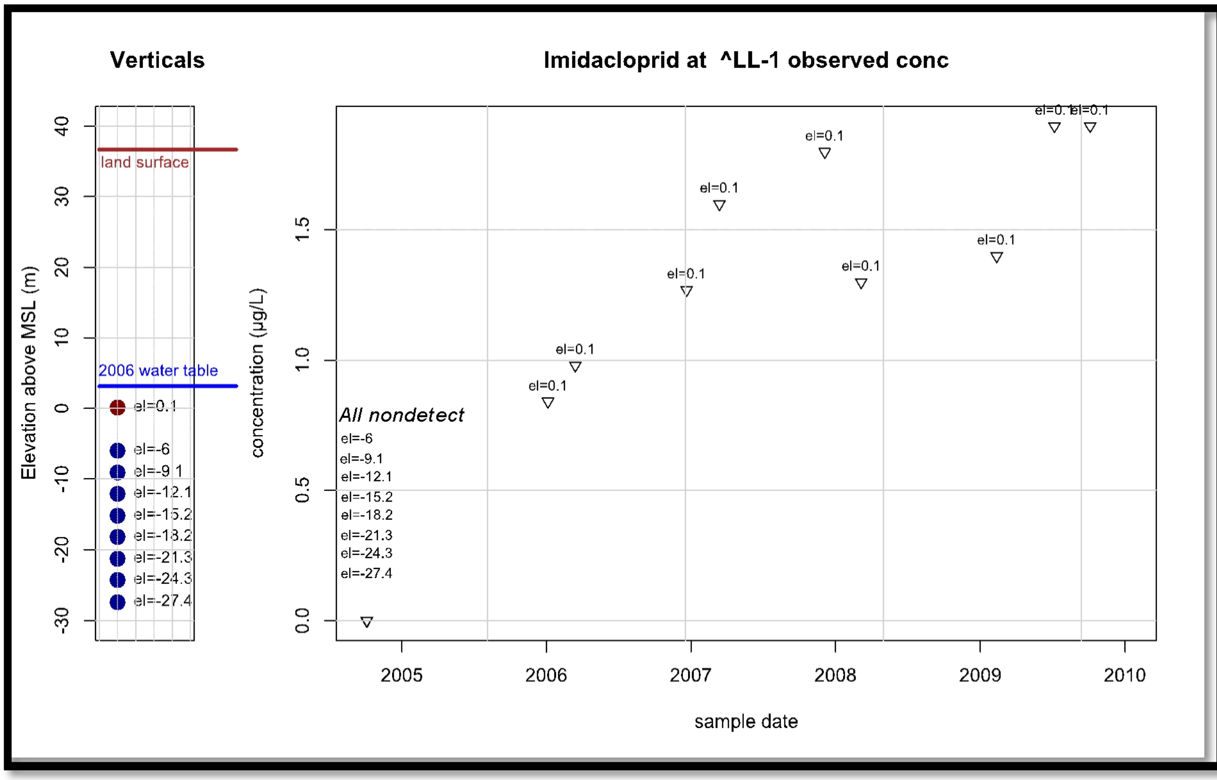


Figure 17: Imidacloprid near major Baiting Hollow greenhouse complex

Figure 17 Caption: See Figure 16 Caption.

With an even deeper water table than at the Sound Avenue greenhouse site, and higher observed concentrations, the fugitive loading would have been higher. There could also have been some outdoor imidacloprid use, as there is an open field between greenhouse and monitor well.

This case is a second example of a deep well affected by moderate emissions, modeled in section 4.3.

3.2 Concentrated Source Outlier: Mattituck Greenhouse Plume

In 2004 notable imidacloprid concentrations were observed downgradient from a greenhouse in the Mill Lane area of Mattituck on the North Fork (Figure 18). Ultimately concentrations were as high as 44 µg/L (2005) before falling to below 1 µg/L by 2009. SCDHS installed and monitored upgradient, sidegradient, and downgradient wells finding a plume that clearly originated at the greenhouse property and extended for several hundred meters downgradient. While the plume triggered monitoring, there were no concentrations above the default drinking water criterion of 50 µg/L. The owner was investigated and sanctioned by DEC for some of their practices, but not for creating the short-term plume.

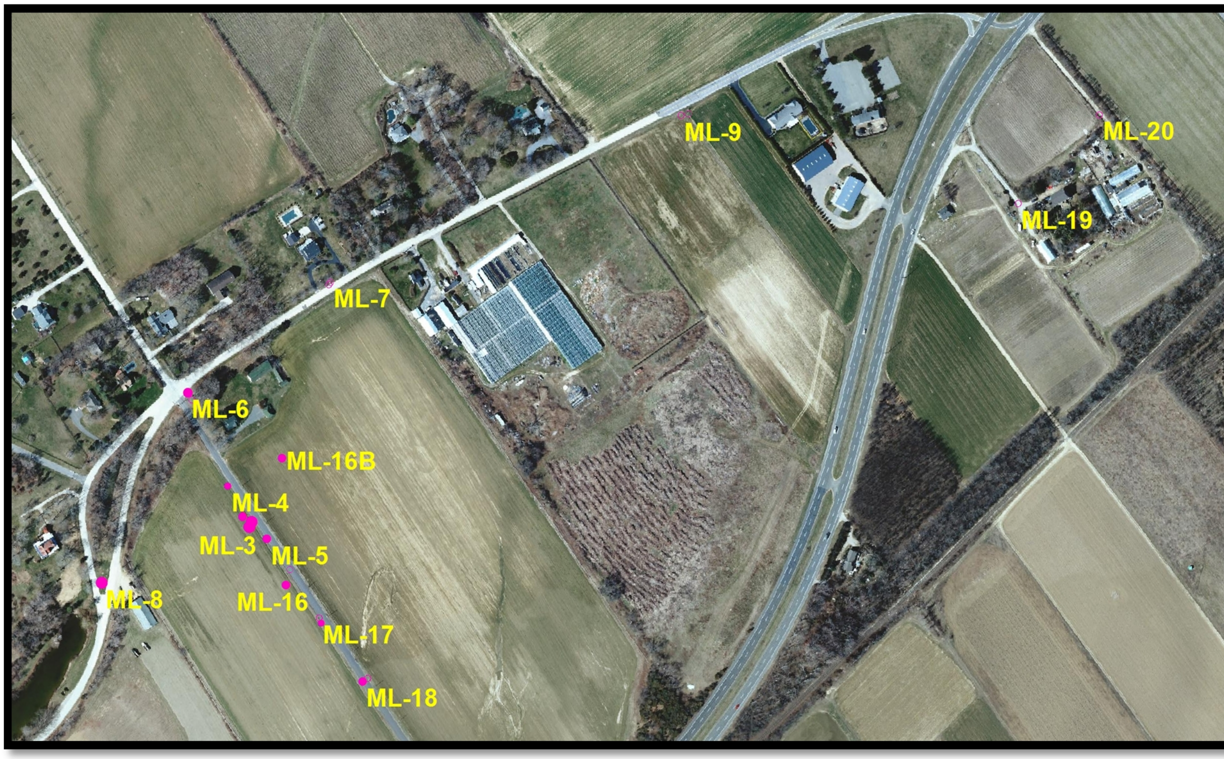


Figure 18: Mattituck greenhouse outlier case overview

Figure 18 Caption: The greenhouse array in the upper central part of the photo released a plume of imidacloprid that extended several hundred meters southwestward toward Mill Lane (road with magenta circles along it). The plume eventually discharged to Mattituck Creek to the west-southwest, just beyond the left edge of the aerial photo. Each well has a magenta circle with diameter proportional to the highest concentration found at any depth at that location. Upgradient wells ML-9, ML19, and ML-20 had non-detect results at all vertical levels - no circle at all at this scaling. Side-gradient well ML-7 just west of the greenhouse is also yielded all non-detects at all vertical levels. (Note that wells off Mill Lane are projected onto Mill Lane in later concentration plots.) Wells along Mill Lane west-southwest from the greenhouses had concentrations proportionate to

Well locations and concentrations from SCDHS unpublished database. Aerial photo base in this and other maps in this report from New York State's digital aerial photo online resource (NYS Office of Information Technology Services, 2016) accessed via ArcGIS. Aerial photos are from various dates 2010 and later.

The first samples from this vicinity in SCDHS's database were taken in 2004 (Figure 19 below).

It is notable that the entire saturated thickness below the water table (at +1m above sea level), to the deepest interval at -20m, is contaminated. Since Mill Lane is only 220 meters below the downgradient edge of the greenhouse buildings, the thick contaminated zone implies an extensive source along the flow direction. Vertical dispersion from a tiny source would be inhibited by the strong anisotropy of the aquifer that facilitates horizontal movement of water 10x to 50x faster than vertical movement (Bohn-Buxton, et. al, 1996; Schubert, et. al, 2004). The area occupied by the greenhouse buildings is approximately 100m x 100m, and is oriented along the flow direction (perpendicular to Mill Lane). Within USGS data from December 2006 (Monti & Busciolano, 2009), the water table is 9.75 m deep at the greenhouse and roughly 8m deep at Mill Lane. (Of course the water table will move lower and higher seasonally and between drier and wetter years.)

The second highest observed concentration within the 2004-2009 plume was 2004's 21.4 µg/L at -16m elevation. Also notable is that the 21.4 is deep within the profile.

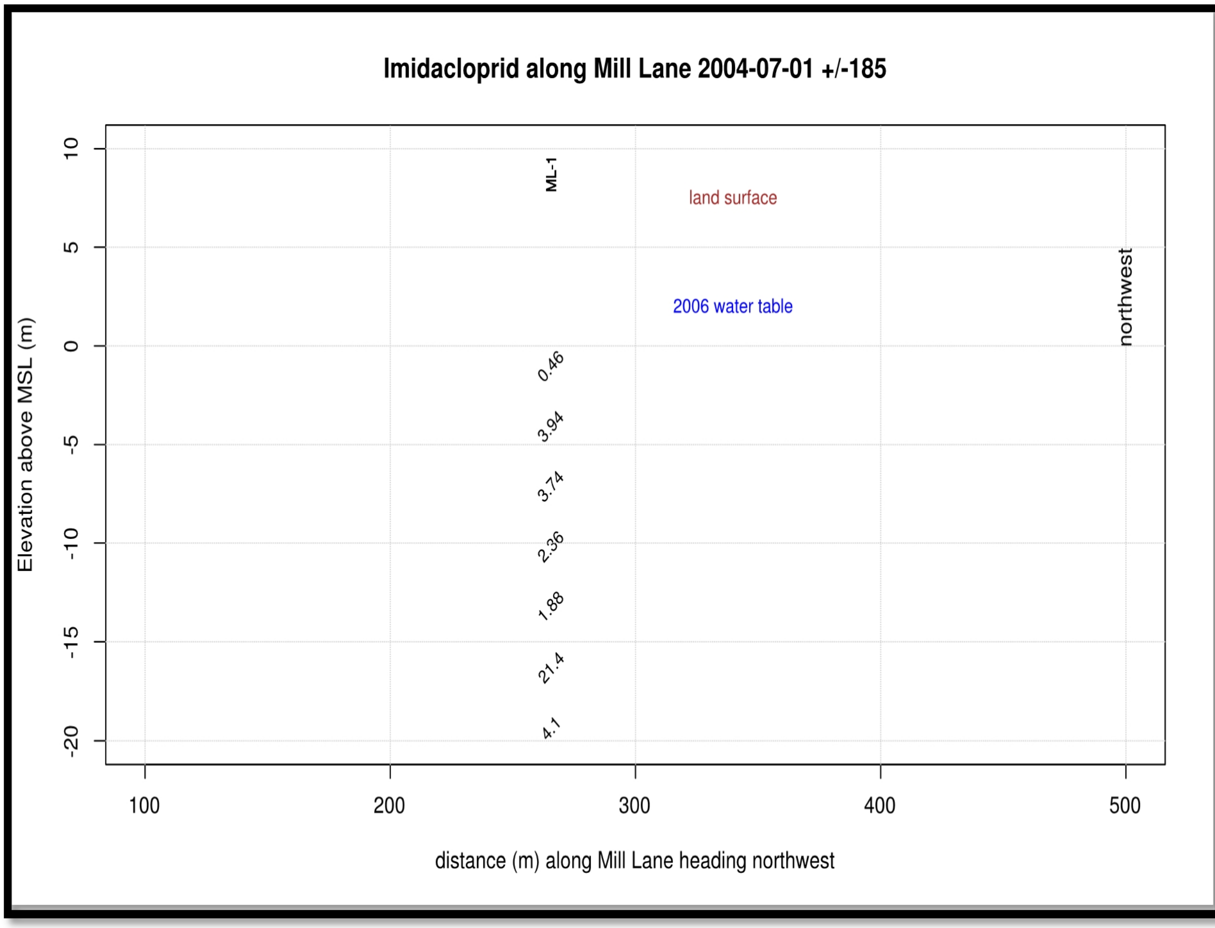


Figure 19: Imidacloprid at Mill Lane, 2004

Figure 19 Caption: This plot shows the maximum concentrations, in µg/L, per location and depth of screen as found in the year 2004. Lateral location of well is projected onto Mill Lane, which is oriented perpendicular to the local ground water flow direction. Horizontal distance is measured along the road from the direction of Mattituck (southeast), heading toward Long Island Sound (northwest). Water table and land surface plotted as single dots, obscure; see Figure 21 for a better idea of these two aspects due to inclusion of more wells.

The highest 2004-2009 concentration at Mill Lane was observed in 2005 (Figure 20) during sparse additional sampling at different wells than sampled earlier. This value was detected 6m below the water table, which is 10 m closer to the surface than the previous high in 2004.

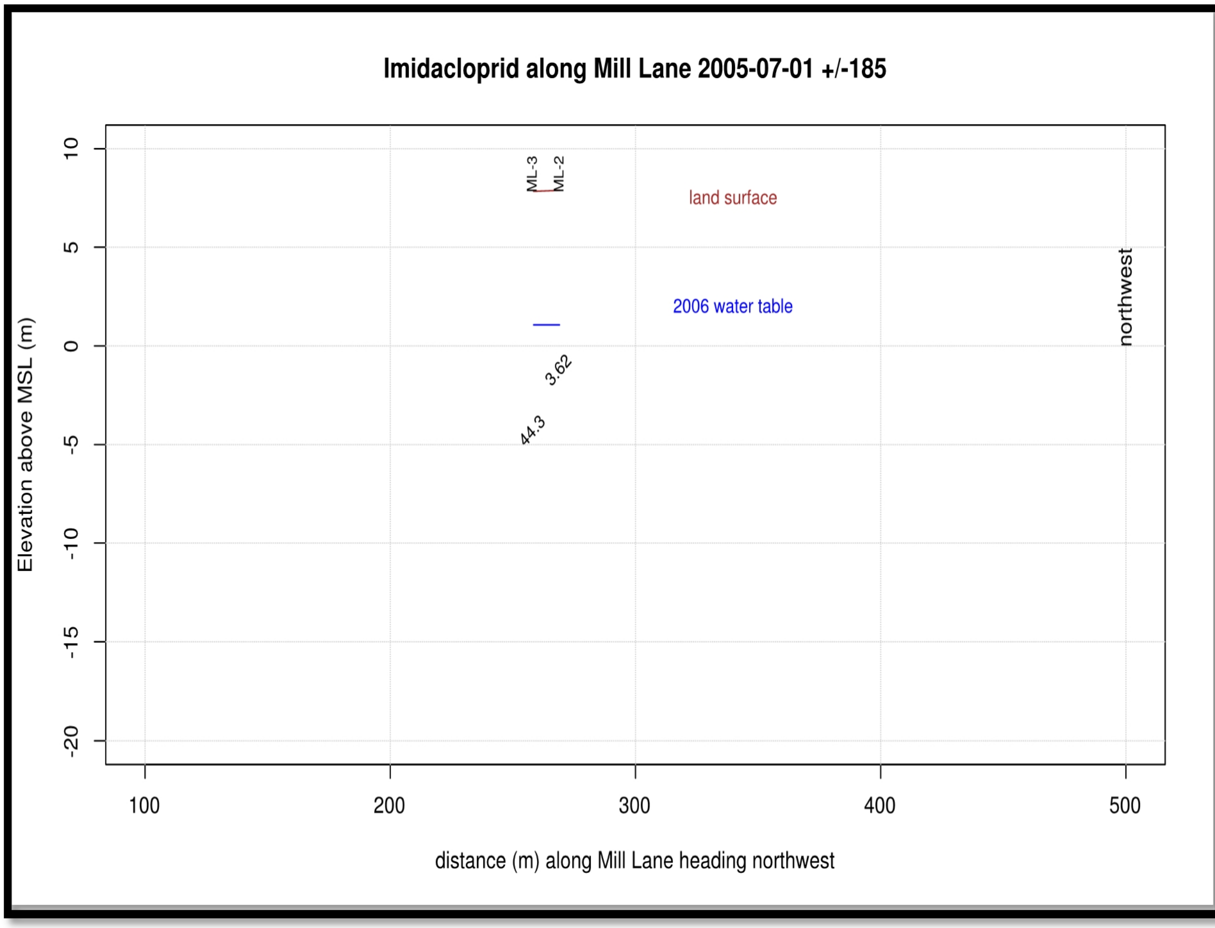


Figure 20: Imidacloprid at Mill Lane, 2005

Figure 20 Caption: See Figure 19 Caption for general explanation. Two wells were sampled in 2005, at relatively small depths below the water table which is less than 1m above sea level.

In 2006 a much more extensive sampling campaign was conducted in the Mill Lane area -- Figure 21. The plume center (highest concentration) appears at ML-3 as in 2005. The 10.9 µg/L observed at ML-3 is much lower than the highs in 2004 and 2005.

Figure 22 complements Figure 21, extending along the flow direction from left to right, with the greenhouse spanning 0-100 m at the left of the chart and the affected wells downgradient to 500

m. At ML-8, which is farthest downgradient (x=500 m) compared to Mill Lane (x=340 m), the highest concentrations were at -13 m to -19 m elevations relative to MSL, compared to higher concentrations at the wells close to Mill Lane which were at -5m. This would occur if the fields on both sides of Mill Lane were untreated or minimally-treated with imidacloprid; the fields' cleaner recharge would be on top of the more concentrated greenhouse plume and press the plume increasingly deeper until the groundwater begins to flow upward at Mattituck Creek.

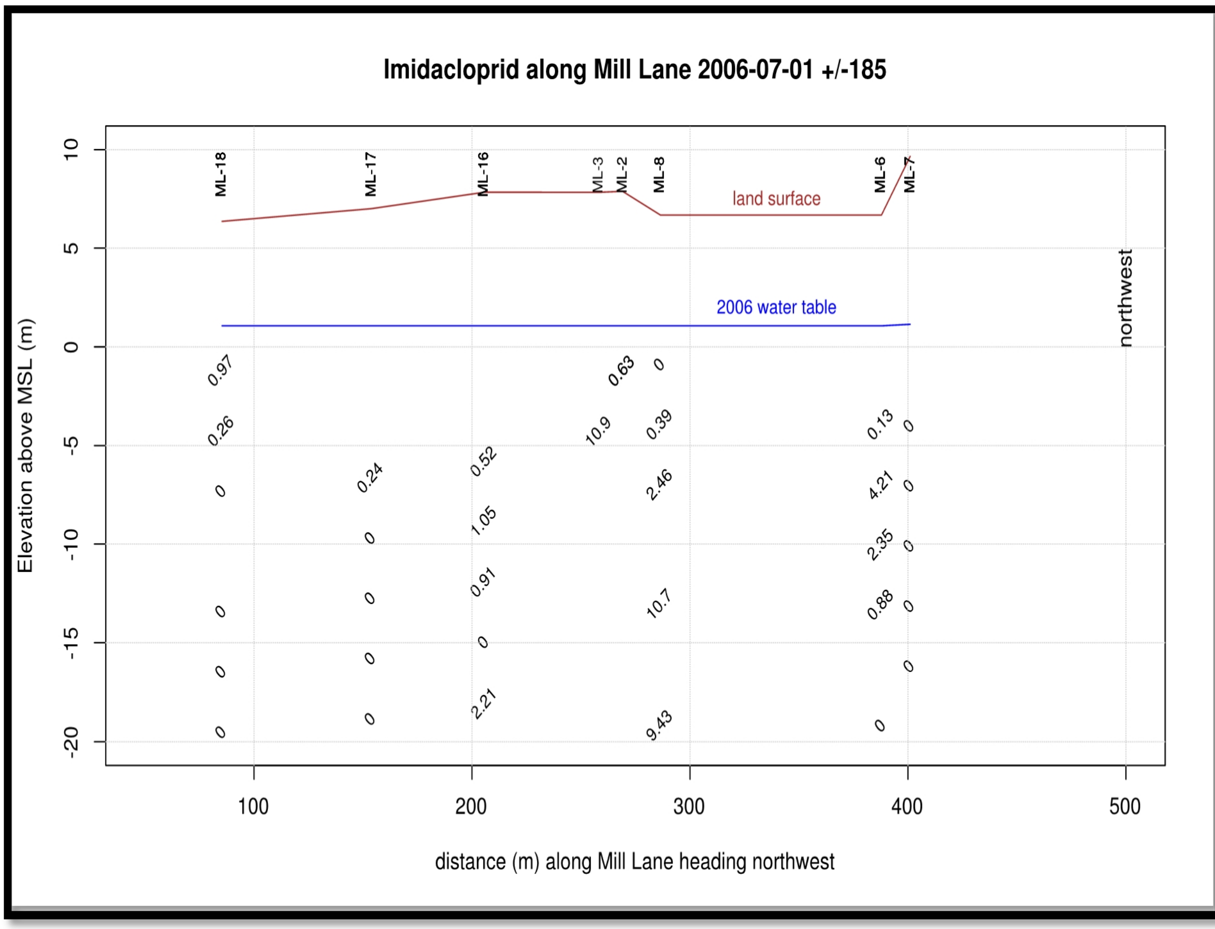


Figure 21: Imidacloprid at Mill Lane, 2006

<u>Figure 21 Caption</u>: A series of vertical profile samples were collected along Mill Lane in 2006 giving the best example of the plume. Note that wells are all projected onto Mill Lane even if they are not right along it. Well ML-8 near the center of the diagram is

projected about 130 meters upgradient. Over that distance the plume moved much deeper and shallower depth increments are cleaner.

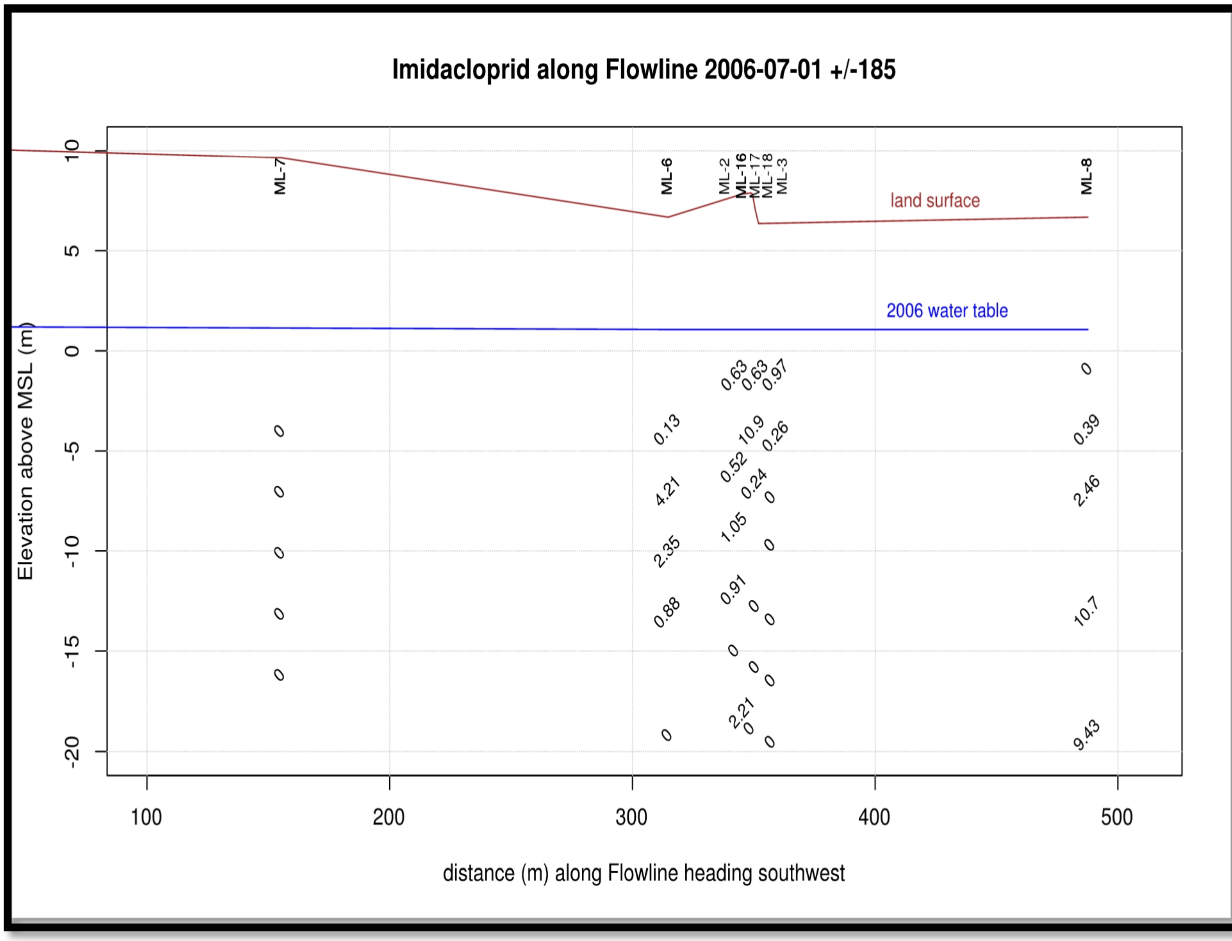


Figure 22: Imidacloprid along flowline crossing Mill Lane, 2006 (flow from left to right)

Figure 22 Caption: Similar to Figure 21, including the 2006 time coverage, except oriented parallel to the direction of ground water flow (from left to right, toward Mattituck Creek which is beyond the right edge in this portrayal).

Figure 22 and the map in earlier Figure 18 imply that the source of the higher contamination must have been at the greenhouse, not upgradient, downgradient, or alongside of it.

Concentrations at ML-6 (right side of plume) and ML-18 (left side) indicate considerable lateral spread. The greenhouse structure is wide and long enough for fugitive emissions through its floor to create a plume as large as that observed. However the concentrations seen are surprising compared to the significantly lower concentrations at the "clean" greenhouses analyzed in the previous section.

With the plume well characterized and nothing above 25% of the default drinking water criterion of 50 μg/L, only shallower sampling was done in 2007 (Figure 23) and 2008 (Figure 24). The downgradient ML-8 well showed a moderate concentration of 4.5 μg/L then 1.6; the wells closer to Mill Lane had lower concentrations. Probably the original source of contamination had been eliminated years earlier.

In 2009 sample concentrations from most Mill Lane wells (Figure 25) continued to fall, but persisted at ML-8 in a sample taken at -10m, which yielded 4.8 μg/L.

There was one sample taken in 2010, at the originally contaminated well ML-1, -10m, into the plume, and a non-detect resulted. The plume at Mill Lane was presumably gone by 2010. However, it could have persisted downgradient ML-8 until that time, or longer.

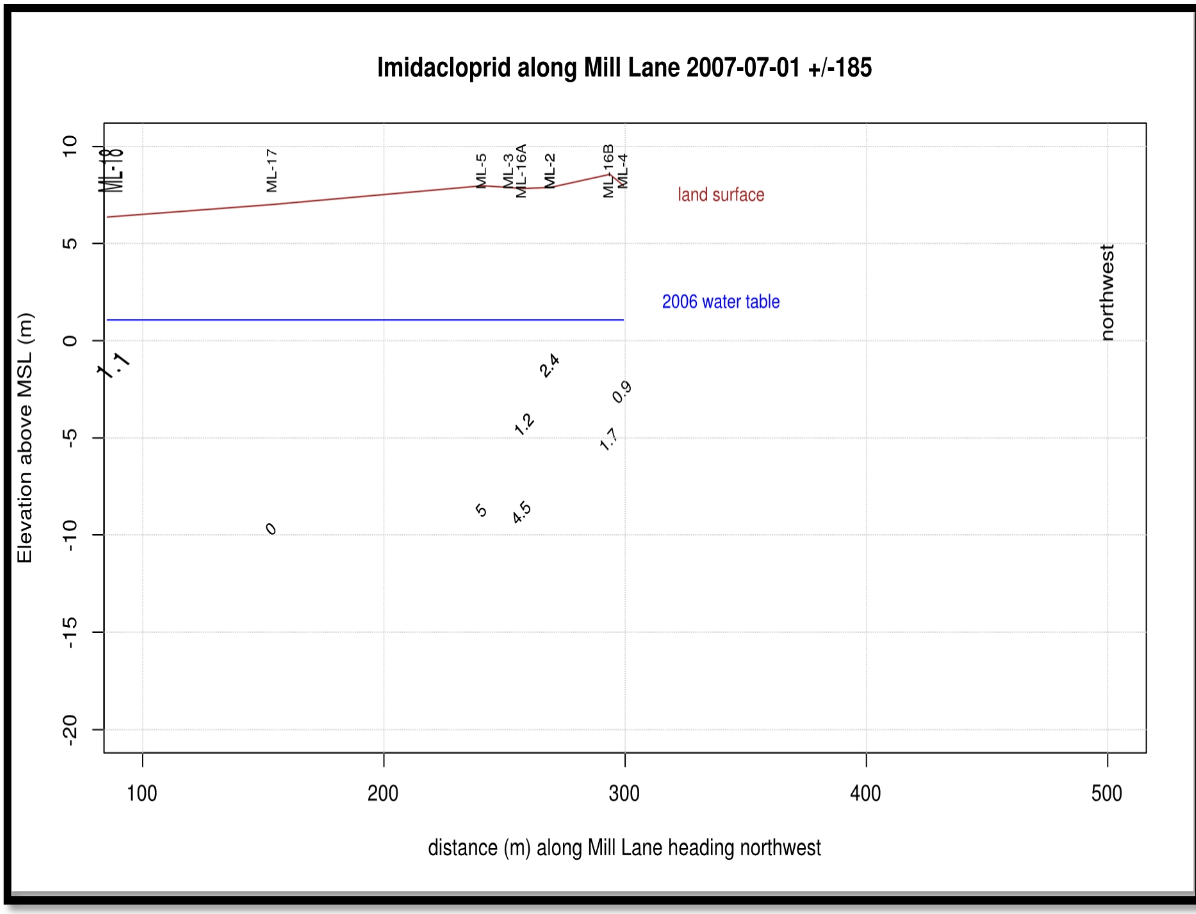


Figure 23: Imidacloprid at Mill Lane, 2007

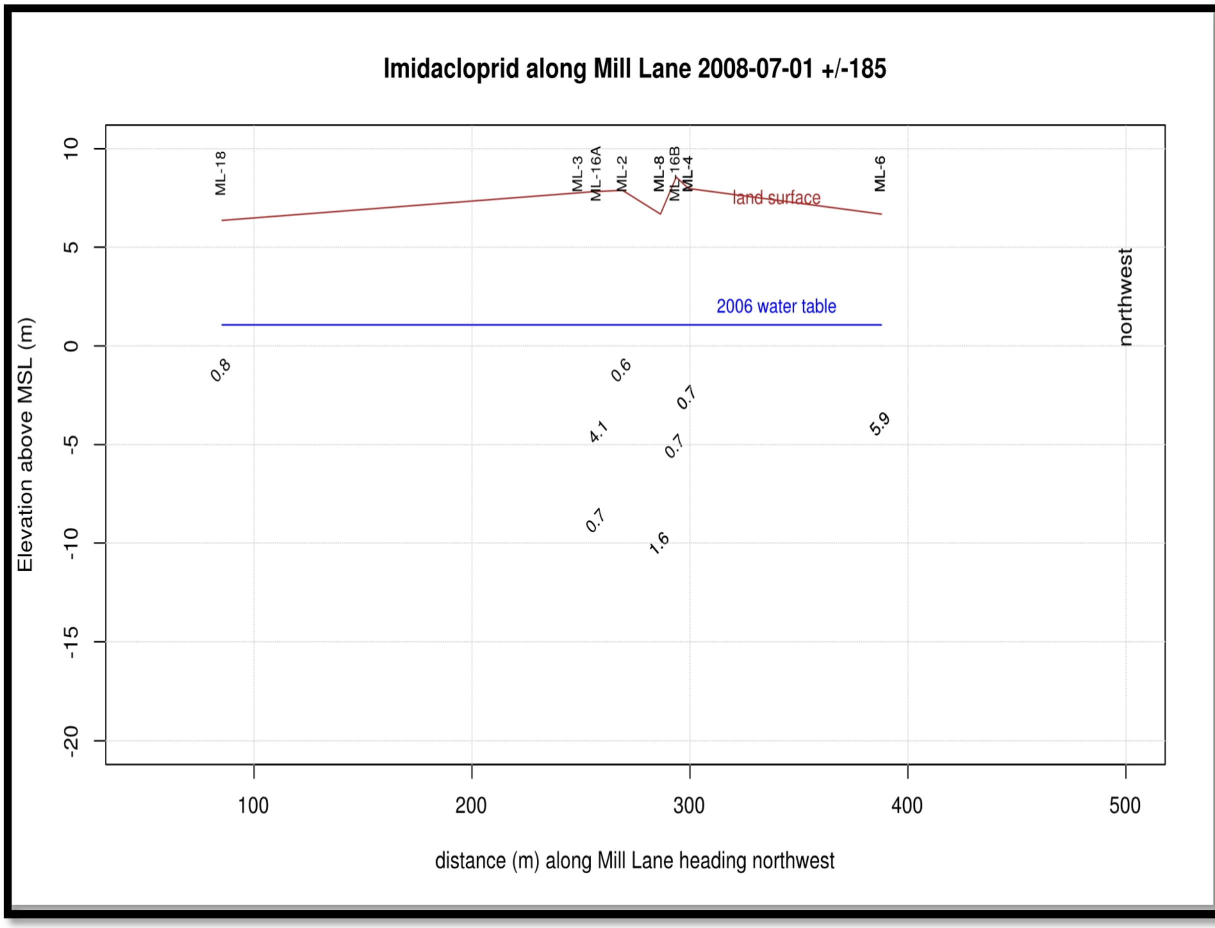


Figure 24: Imidacloprid at Mill Lane, 2008

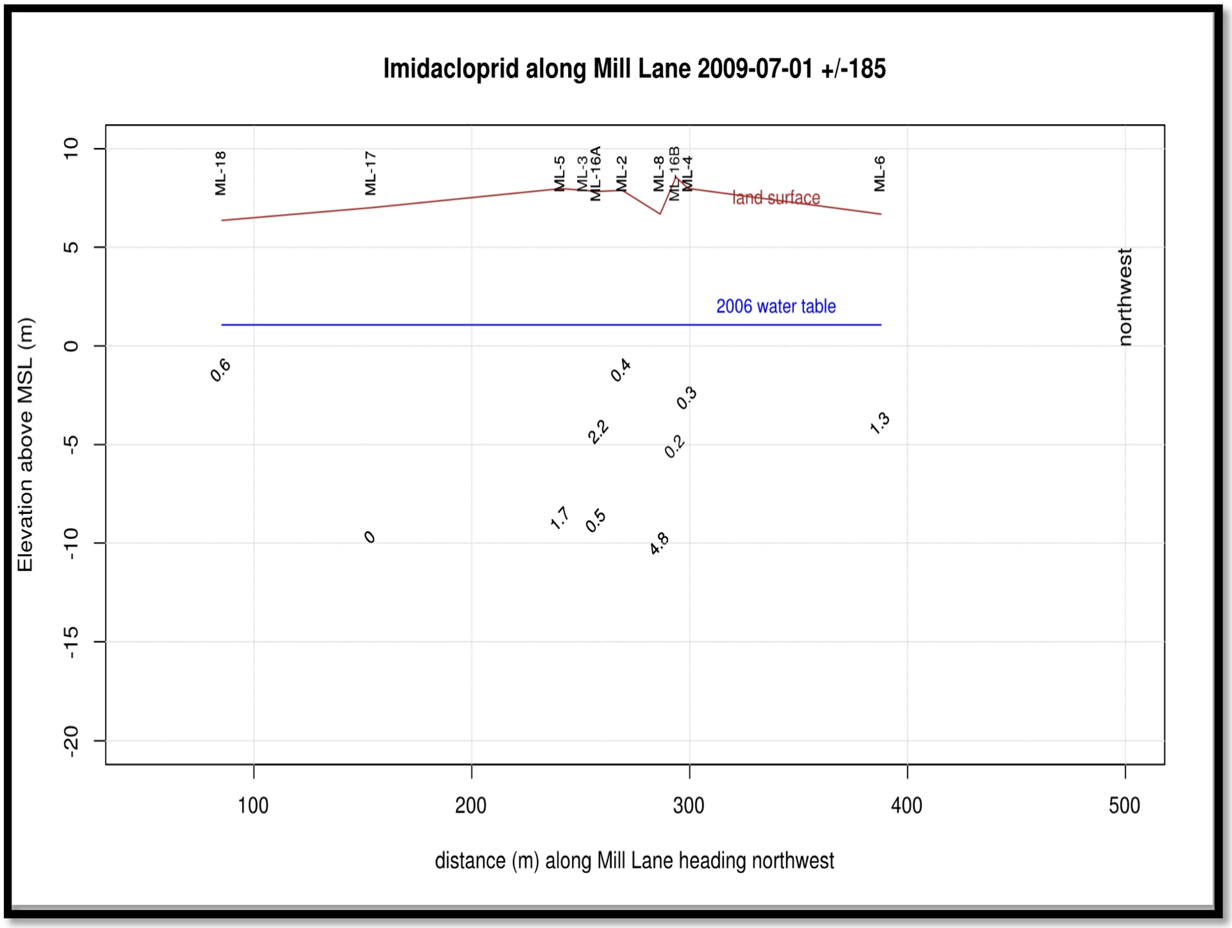


Figure 25: Imidacloprid at Mill Lane, 2009

Section 4.5 in the following chapter discusses management conditions that led to this transient plume. The width of the plume seems to indicate emissions over a moderately large zone among the greenhouses, which cover an area roughly 100m by 100m. This could represent emissions through sand floors in multiple buildings. Fugitive emissions were probably several times higher than those at the more typical greenhouses described in section 3.1, since the concentrations were 10-20x higher.

3.3 Concentrated Source Outlier: Lindenhurst

Many permitted uses of imidacloprid products are in residential and commercial landscapes, where it is applied to trees and shrubs to control numerous pests. For control of the Hemlock Woolly Adelgid, it is applied as a soil drench, or occasionally as a trunk injection or by foliar applications. Control of Boxwood and Holly Leaf Miners and some soft scale insects is achieved by soil application. This also provides season-long control of Japanese beetles, some aphids on large trees and, for exceptionally damaging aphid species, on trees of all sizes. Soil treatments are also used to control Lace Bugs in Andromeda, Sycamore, and Azalea species, Flatheaded Borer Beetles in Bronze Birch and Two Lined Chestnuts, and leaf-feeding beetles like the Viburnum Leaf Beetle, which only recently appeared in Long Island (NYS DEC, Bureau of Pest Management, 2015).

In the USDA Asian Longhorned Beetle (ALB) programs, it is used as a trunk injection to prevent the spread of ALB from contaminated trees to yet unaffected trees in the immediate vicinity. Chemical treatment is one component of the integrated strategy for eradicating ALB from the United States. Once treatments with Imidacloprid begin in an area, only a few years of consecutive annual applications are required to eliminate ALB populations. In 2014, there were 13,209 Ha of land in Nassau and Suffolk counties under quarantine for ALB (USDA APHIS, 2014).

Soil injection of imidacloprid is not permitted in Nassau and Suffolk counties, but is used elsewhere in the state and country. Soil drench is the only allowed soil treatment for trees and shrubs in this region. Field soil applications to nursery shrubs and trees are expensive and are consequently seldom used. Applications of imidacloprid to the grassy areas in field and forest nurseries are performed very rarely, if at all. A specific section of each product label is dedicated to describing these practices, even though they are rarely employed.

In November 2005, the New York State Department of Environmental Conservation (DEC) provided the USDA Animal and Plant Health Inspection Service (APHIS) test results from groundwater monitoring conducted by SCDHS. Suffolk County's Lab recovered imidacloprid at a 215 µg/L concentration from SCDHS well L2-54A in Lindenhurst. This very shallow well, tapping a water table less than 1 meter from the surface, was sampled in April 2005. The DEC expressed concern that this unexpectedly high concentration was possibly associated with the ALB program. An additional sample taken by SCDHS on May 17 (2005) at well L2-54 was reported to have 201 µg/L of imidacloprid, and investigation into the Lindenhurst site resulted after these initial high detects were discovered.

The locations of selected Lindenhurst monitor wells are shown in Figure 26 below. Lindenhurst is a suburban community on the south shore of Long Island. Homes in the neighborhood are small, tightly packed single-family dwellings, all with apparently actively maintained and possibly professionally landscaped and managed lawns.

Figure 26: Aerial photo of Lindenhurst ALB tree study region

Figure 26 Caption: Arial photo of the Lindenhurst ALB tree study region. Monitor wells and associated detects are shown. Well L2-54, which spawned further investigation and the instillation of other monitor wells in the area had the highest detects, as illustrated by the large pink circle marking it.

Well L2-54 and L2-54A are located at the edge of a homeowner's front lawn and adjacent to a paved driveway. A sycamore (Platanus) on this particular property has 0.61m Diameter at Breast Height (DBH), and is in close proximity to well L2-54 (also known as "well #16") (USDA/APHIS/PPQ, Emergency and Domestic Programs, Environmental Compliance, 2007).

This tree was first treated with a 48 ml Mauget product capsule by trunk injection in 2002, then again in 2004 and 2005 with 192 ml of Mauget. (Mauget is 10% imidacloprid by weight.) 14 other trees in close proximity also received trunk-injection treatments of 192ml Mauget in 2004 and 2005. These 14 trees are all within 8m of the initial well (L2-54), and up gradient from the wells installed along Grenada Parkway in later years.

USDA's assessments of application records, homeowner interviews, and onsite observations made during inquiry into the August 2004 and 2005 tree injections did not reveal any other imidacloprid uses, notable spills or other unusual events. The concentrations at certain other wells sampled in the SCDHS Lindenhurst investigation are shown in Figure 27 below, which also encodes their distance from the initial well (L2-54) along Granada Parkway.

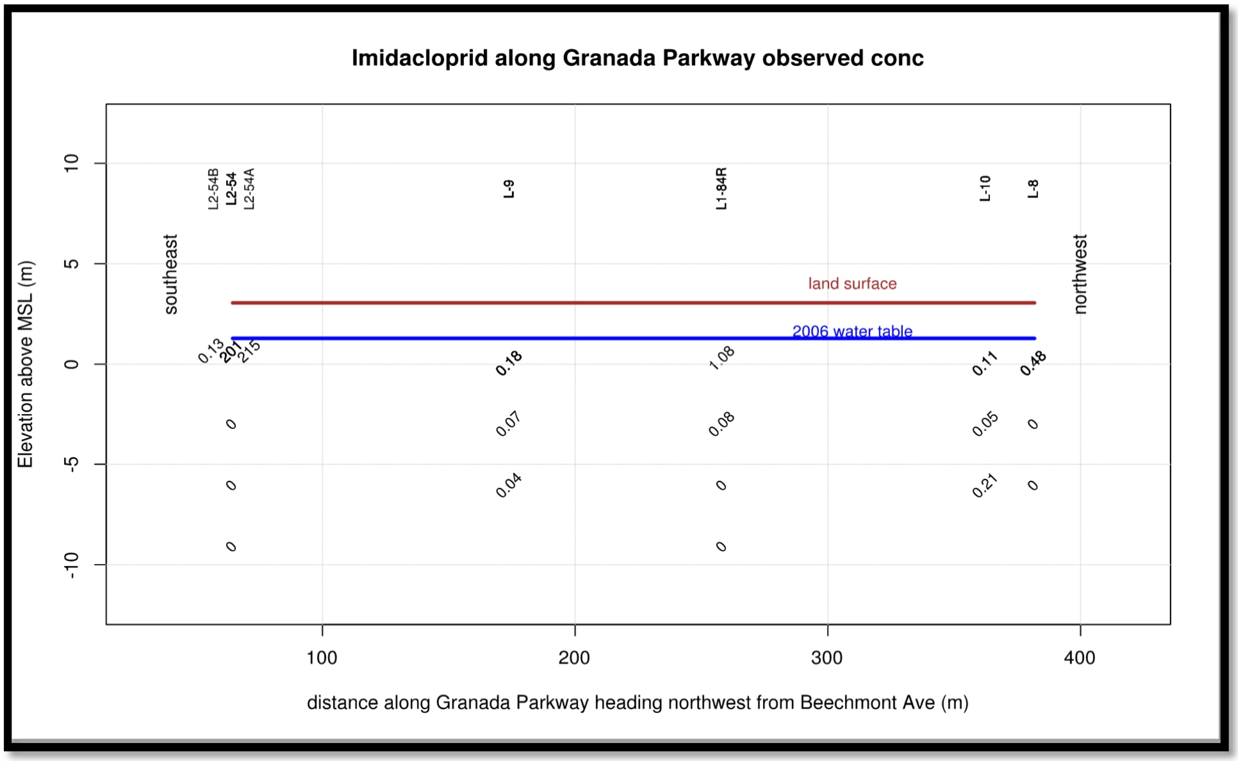


Figure 27: Imidacloprid monitoring at Lindenhurst, along a line

Figure 27 Caption: The wells associated with the ALB study area. The plotted numbers are the highest values observed at any time at the given depth and well position. Note: Wells L2-54A and L2-54 are moved by a few meters for plotting, so their results do not plot on top of L2-54B results. All three wells are probably on the same lot (possibly transiently, at different times) based on their numbering.

The high levels seen in SCDHS' well L2-54 in 2005, are drastically higher than residues found in any other well near an ALB Program-treated tree.

Figure 28 focuses on the time series of sample results at outlier-yielding well L2-54.

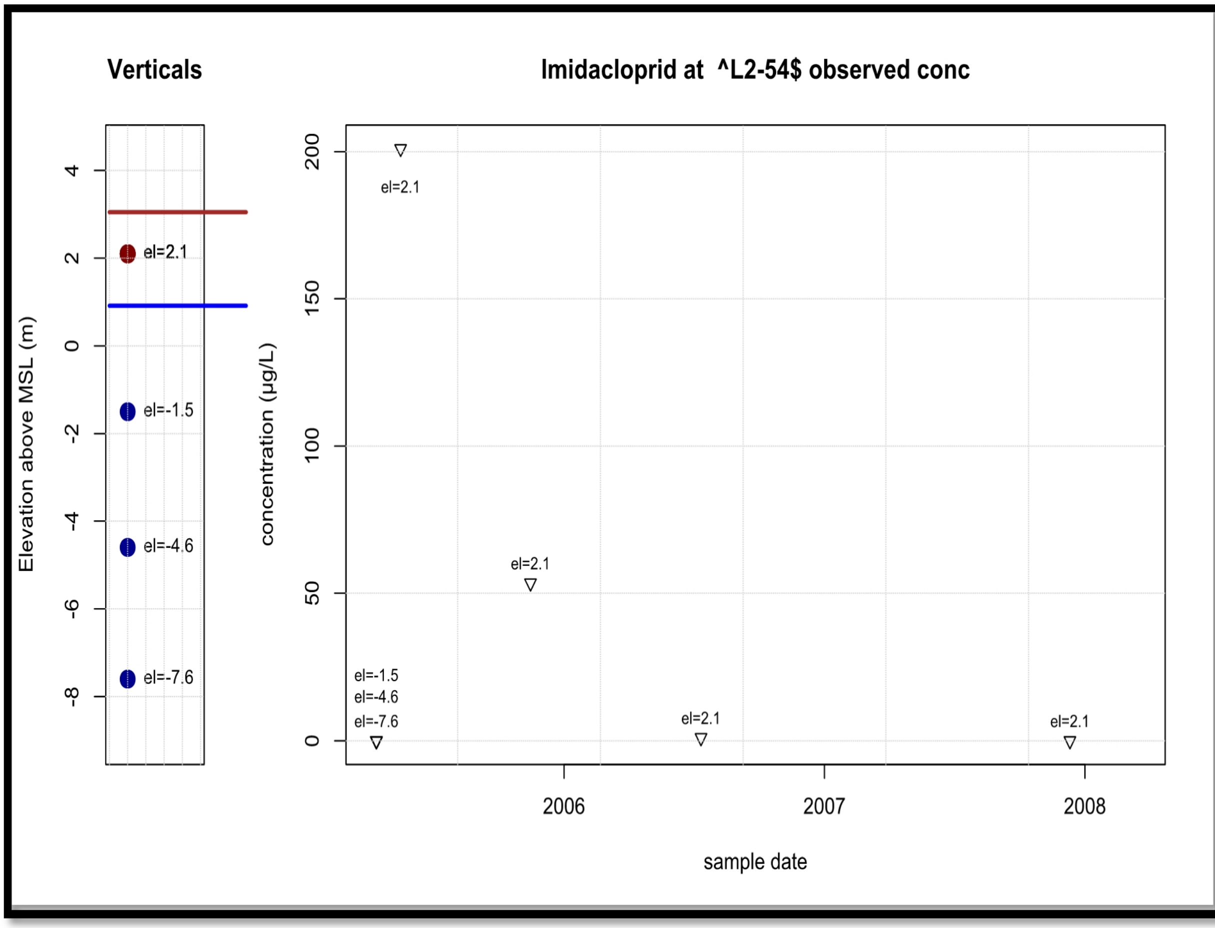


Figure 28: Imidacloprid at Lindenhurst site, well L2-54

Figure 28 Caption: The observed concentrations recorded at Lindenhurst monitor well L2-54, the depth at which the well was sampled (above MSL), the magnitude of the detections, and the sample dates are shown in this figure. Note the decline in detected concentration between the samples taken in April 2005, November 2005 and July of 2006.

L2-54 shows a high residue value that decreases through time following a tree treatment made on May 11, 2005, but this same pattern was not observed in well L2-54A (Figure 29), even though this well must be close to L2-54.

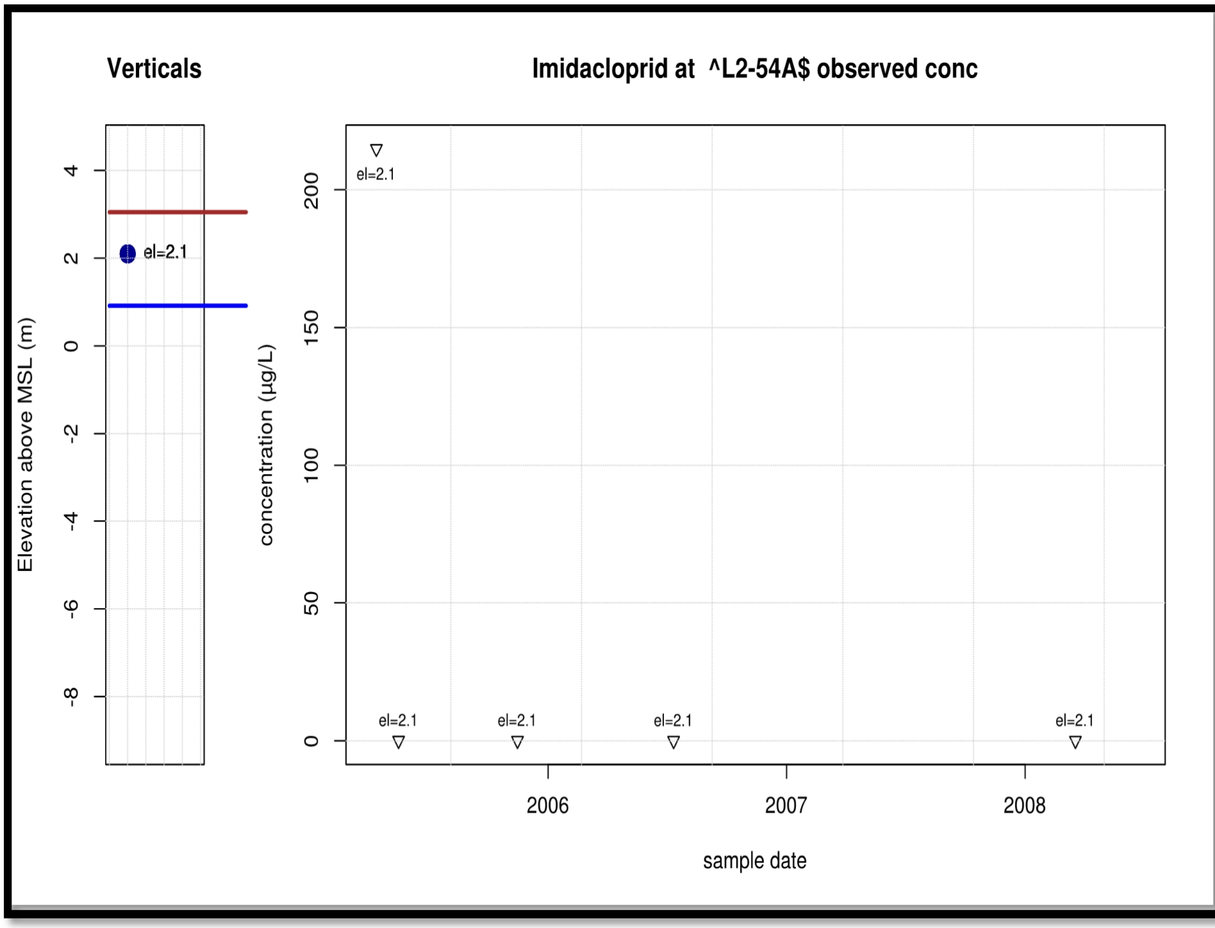


Figure 29: Imidacloprid at Lindenhurst site, well L2-54A

It should be noted that an April 2005 sample taken at L2-54 was taken at a much greater depth below the surface and thus would have missed nearest-surface contamination (if any). The consistent detected concentration between the April L2-54A sample and the May L2-54 sample on the same property and at the same depth, suggests that there is actual contamination, not mishandling of a sample or a lab error. L2-54A declined to nearly zero by May 2005, yet well L2-54 still had over 50 µg/L as late as November, again suggesting a brief contamination event followed by slow decline from degradation and dispersion.

The concentrations of imidacloprid in well L2-54 and L2-54A later dropped to levels similar to the other Suffolk monitor wells in the Lindenhurst area, and are consistent with comparable monitor wells in other ALB program study regions on Long Island. USDA's own results for samples taken from a nearby well, located in a wood lot and surrounded by 2500-3500 trees, all treated by trunk injection, ranged from non-detect to 3.9 μg/L.

USDA's samples from three wells on Indian Island near Riverhead (each sampled twice), and located down gradient of 3200-4500 trees also treated with imidacloprid by trunk injection, all yielded non-detects for imidacloprid residues. USDA states that the Indian Island treatment site had been selected because the groundwater could be isolated from that of the rest of Long Island. If imidacloprid had been found in the groundwater on Indian Island, it could reasonably be concluded that the source of contamination was likely from trunk-injected trees.

Because of the Indian Island results, and based on several years of similar environmental monitoring data, USDA concluded that it seems highly unlikely that residues found in Wells L2-54 (USDA well #16) in spring 2005 can be attributed to trunk injections. Ultimately, the USDA investigation report concluded that the finding of > 200 μg/L imidacloprid in Well L2-54 is likely the result of "a one-time event, well outside the standard operating procedures of the ALB Program" (USDA APHIS, 2014). This case is modeled as a one-time spill in Section 4.4.

3.4 Area Source: Potatoes

Potatoes are a historically important agricultural crop of Long Island. Production has decreased in recent years largely due difficulties related to pest control. The Colorado Potato Beetle, Aphids (especially, the Melon Aphid), and the Potato Leafhopper are the most prevalent and problematic pests for the potato industry in the region. Despite the persistence of these detrimental insects, the potato industry is still strong in Suffolk County. On the North Fork of Suffolk County, approximately 2,388 Ha of potatoes were cultivated in 1997, decreasing to 1,619 Ha in 2002 (Akhtar, 2002) and 1,055 Ha in 2012 (US Department of Agriculture, 2012).

Imidacloprid is an important part of controlling the pests that are affecting the potato industry in the area (Stivers, (undated)). Although local Colorado potato beetle populations have developed some resistance to Imidacloprid over time, most potato farmers in the region still regularly apply it both preventatively and to provide ongoing control. It is applied either as an in-furrow application (at planting), or as foliar applications (as needed throughout the growing season), or both (NYS DEC, Bureau of Pest Management, 2015).

Using PSUR data, and information from CCE associates and publications, it was determined that Admire and Provado (both from Bayer AG) are the most commonly used products in potato production in the region. Their labeled uses and the percent of potato crop area using each product on long Island are summarized in Table 12 below.

Table 10: Representative imidacloprid products for potatoes

Product	**Type of Application**	**Typical Rates, kg/AI/Ha**	**Timing of Applications**	**# of Applications per year**	**% Applied to LI potato crop area**
Admire	Soil, spray on seed pieces in furrow	0.26-0.56	At planting	1	95
Provado	Foliar, ground or air	0.0525	As needed during season	1-4	60

Source: (Stivers, (undated)).

A study area in the South Fork, in which potato fields are located directly up gradient of two monitor wells was selected and is shown in Figure 29. Like B-1 discussed earlier, the B-4 and B-5 wells had been installed by the Bayer Company in relation to the imidacloprid registration for New York.

Figure 30: South fork (Bridgehampton) potato focus area

Figure 30 Caption: Well locations from SCDHS database.

Figures 31 and 32 show time patterns of imidacloprid concentrations at the wells, where the water tables are roughly 5m below the surface. Concentrations in the range of 0.2-0.6 µg/L were found. Quarterly sampling was probably often enough to capture the higher concentrations given the averaging potential of the 5m thick vadose zone.

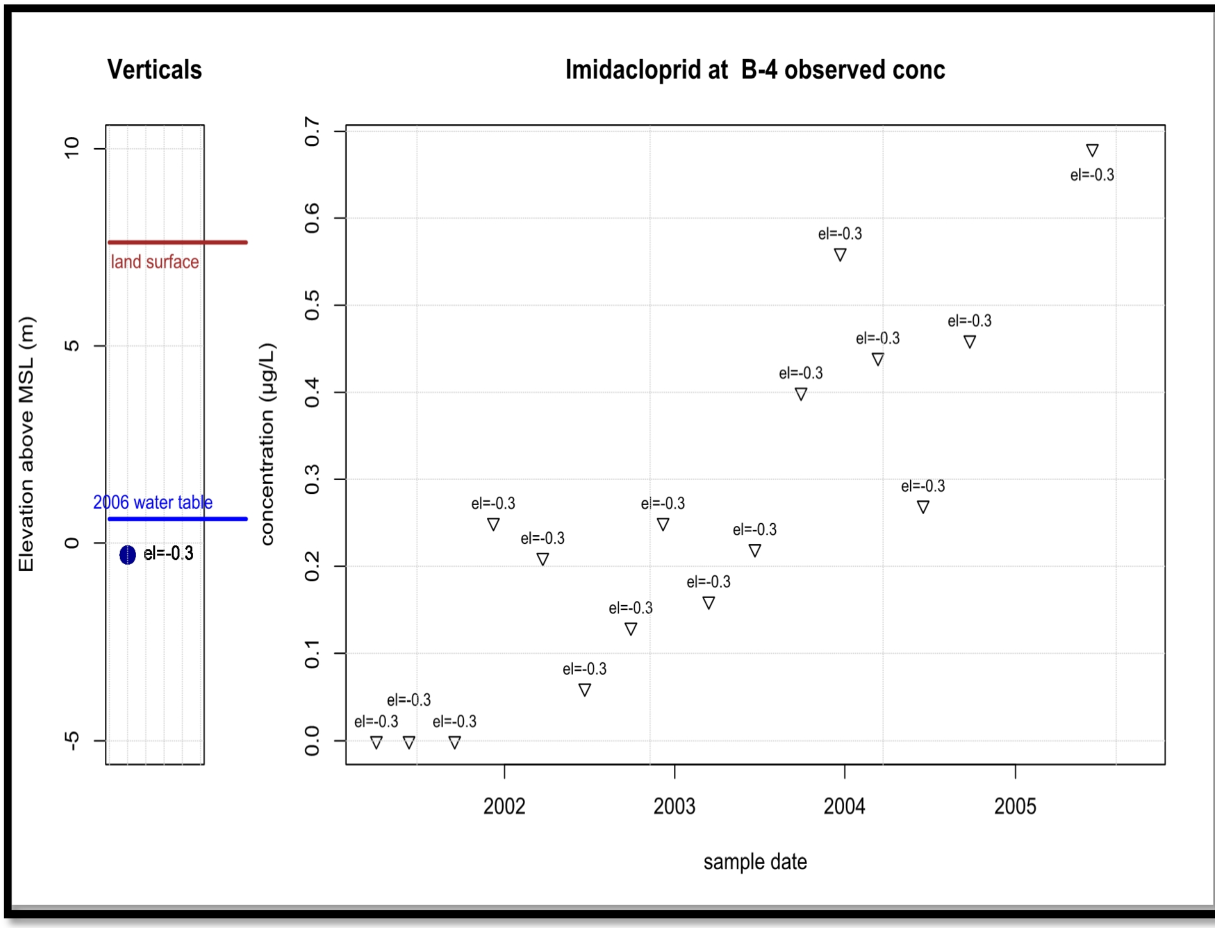


Figure 31: Concentrations at former Bayer well 4 (potatoes)

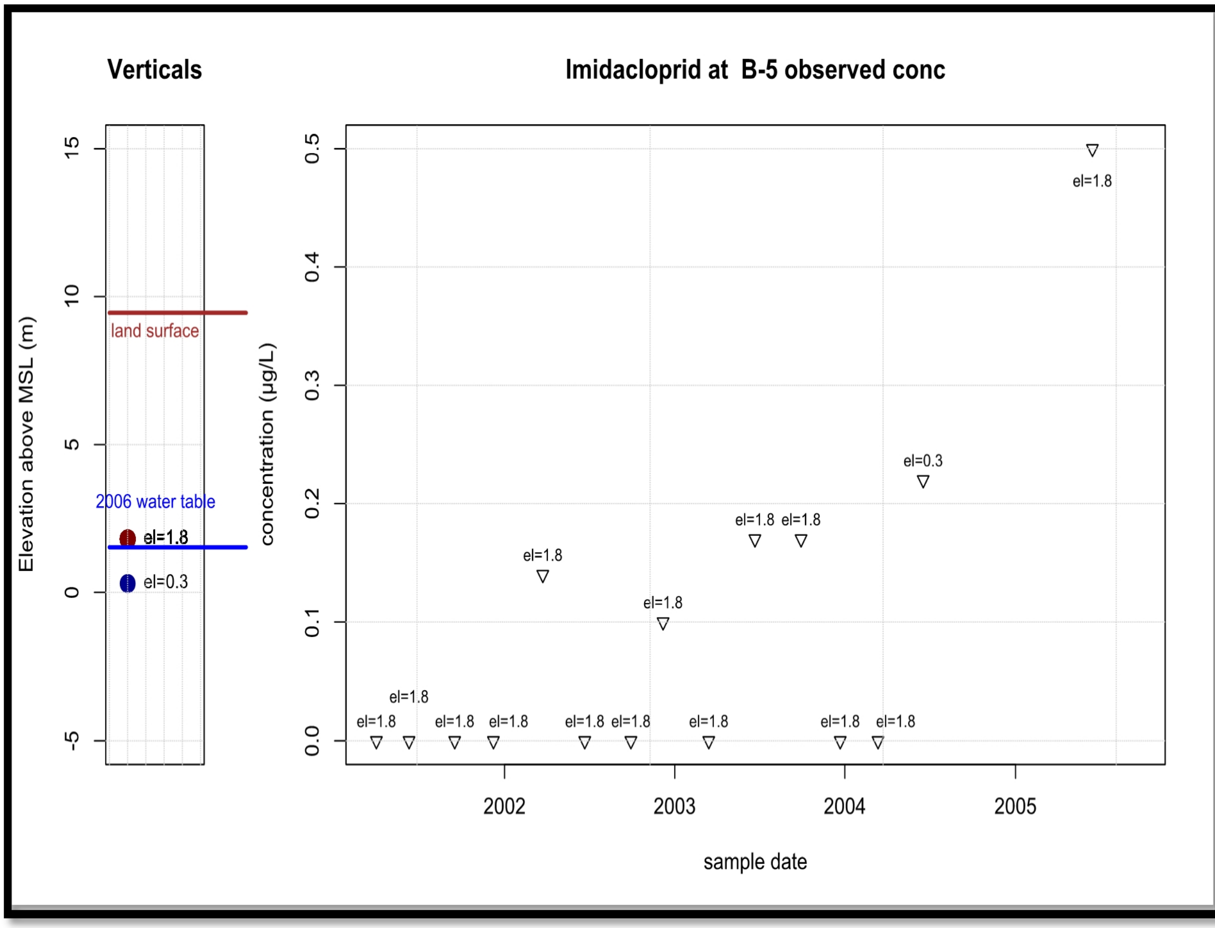


Figure 32: Concentrations at former Bayer well 5 (potatoes)

With non-detects until late 2001 and a fairly shallow water table that would have limited travel time to a year or two after first use, it is possible that these users were both only doing the low-rate Provado foliar applications until after imidacloprid became available in the mid 1990's. Perhaps the B-5 field was never treated with the more leaching-prone and 10x higher rate in-furrow Admire applications. It was in-furrow applications of aldicarb (for the same pest control) that caused the well contamination problems with that chemical.

Imidacloprid on potatoes is modeled using LEACHP for the B-4 and B-5 sites' general area (Bridgehampton weather and soil), in Section 5.3.

3.5 Area Source: Turf

Imidacloprid is widely used for control of white grubs, primarily the oriental beetle, and other common local species. It is used in established residential and commercial lawns, golf courses, athletic fields and other manicured and professionally maintained properties. It is not however, ordinarily or frequently used on sod farms, where white grubs are not a significant problem, as its production cycle does not offer enough time for invasive white grub populations to become established enough to merit treatment. When used, imidacloprid is customarily applied using broadcast or drop spreaders from granular formulations. As imidacloprid is also a component of several fertilizer-based products, it can also be applied in fertilizer-based form; spray applications of imidacloprid are seldom used (Personal communication with industry members of NY DEC Pesticide TRAC, 2015).

Since golf courses occupy a notable area of land in Suffolk County, there was concern about the consequences and impact of using imidacloprid in such large, highly manicured and maintained grassy areas. In order to explore the effects of imidacloprid uses in such areas, the SCDHS placed monitor wells on several different golf courses throughout the county. Table 11 inventories the golf courses in the Suffolk database that were monitored. Most of the well sites reported all non-detects or a single low detection and are thus are not useful for detailed interpretations.

Table 11: Golf courses in the SCDHS database

Locale	**Wells**	**Description**	**Sampling results**
Riverhead	CC-1	Golf course, 28m water table	Concentrations to 0.2 µg/L, four years
Manorville	PH-1	Golf course, 18m water table	Concentrations to trace level (0.1 µg/L)
Shirley	LS-1	Golf course, 5m water table. (Course is now closed.)	Concentrations up to 9.9 in 2007, most samples under 1.0
Stony Brook	SG-1	Golf course, 8m water table, at regional groundwater divide	Concentrations up to 0.2 µg/L
several other golf courses	various		All non-detect results in wells.

The LS-1 well had one sample yielding 9.9 µg/L in May 2007 after a 1.5 year unmonitored period, the observed concentrations for this well are shown in Figure 33. This was followed by 3.7 µg/L detect a few weeks later. The detects then returned to trace levels (0.1 µg/L) in October of 2007. The lack of monitoring data before the initial 9.9 µg/L detection prevents this from being a useful case study. This probably was a one-time release that might even have been a moderate spill if it had been a year earlier than May 2007, or a result from routine use near the well if the use was just before the May 2007 sampling. Given that three other 4 golf courses with repeat detections yielded maximum imidacloprid residue concentrations ≤0.2μg/L, it is probable that the significantly higher concentration of 9.9μg/L recorded at the LS site is an outlier, and not the result of normal use, which is better represented by the other three sites with detections.

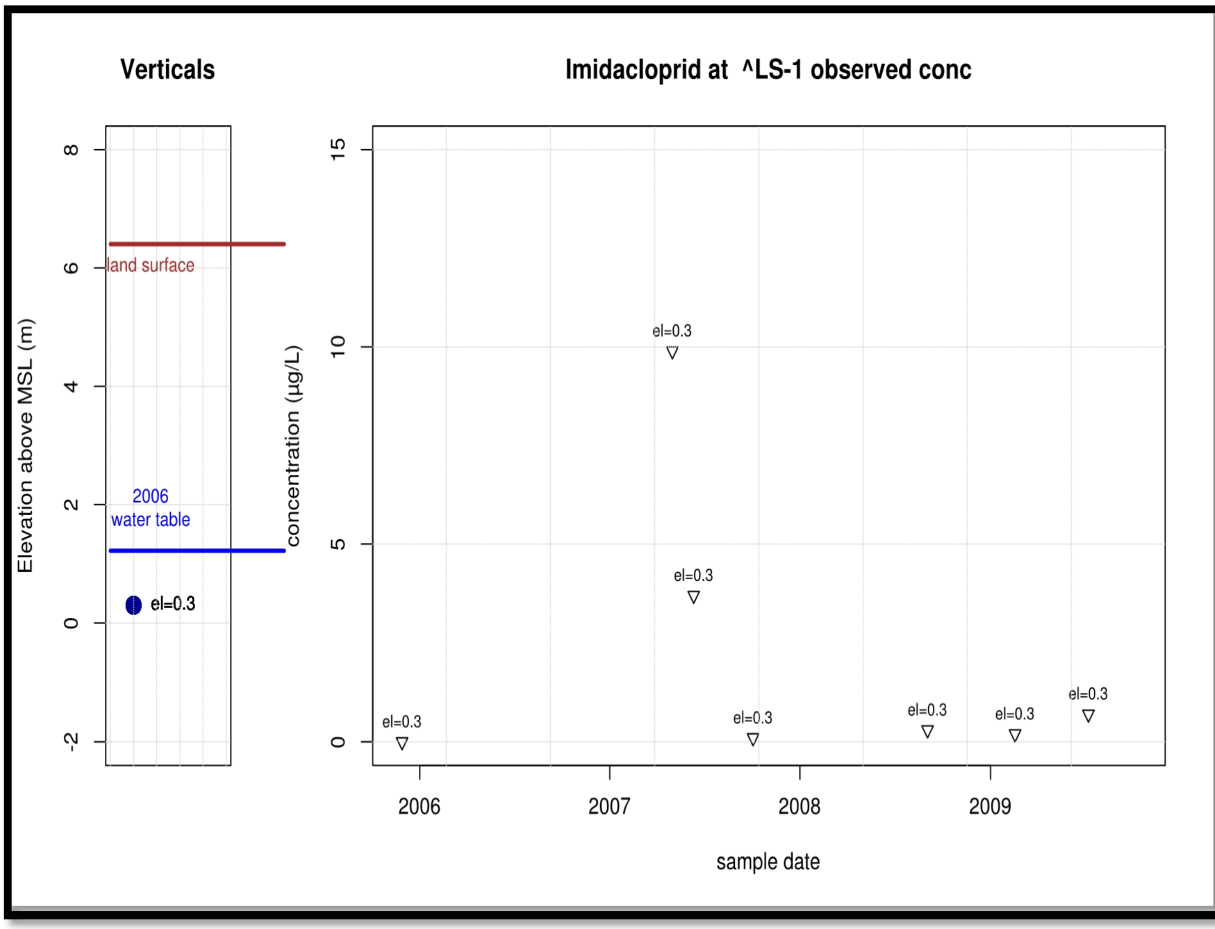


Figure 33: Outlier concentrations at golf course monitor well, LS-1

The other three sites with more than one detection all had values at the lowest routinely quantified level of 0.2 μg/L or traces at 0.1 μg/L. The consistency across locations and times makes this an interesting example for exploring turf management, a major imidacloprid user. The CC-1 monitor well in Riverhead was chosen for elaboration. Figure 34 locates the well and some other nearby monitor sites. (CC-SW would be a surface site such as a pond and is probably mis-located.)

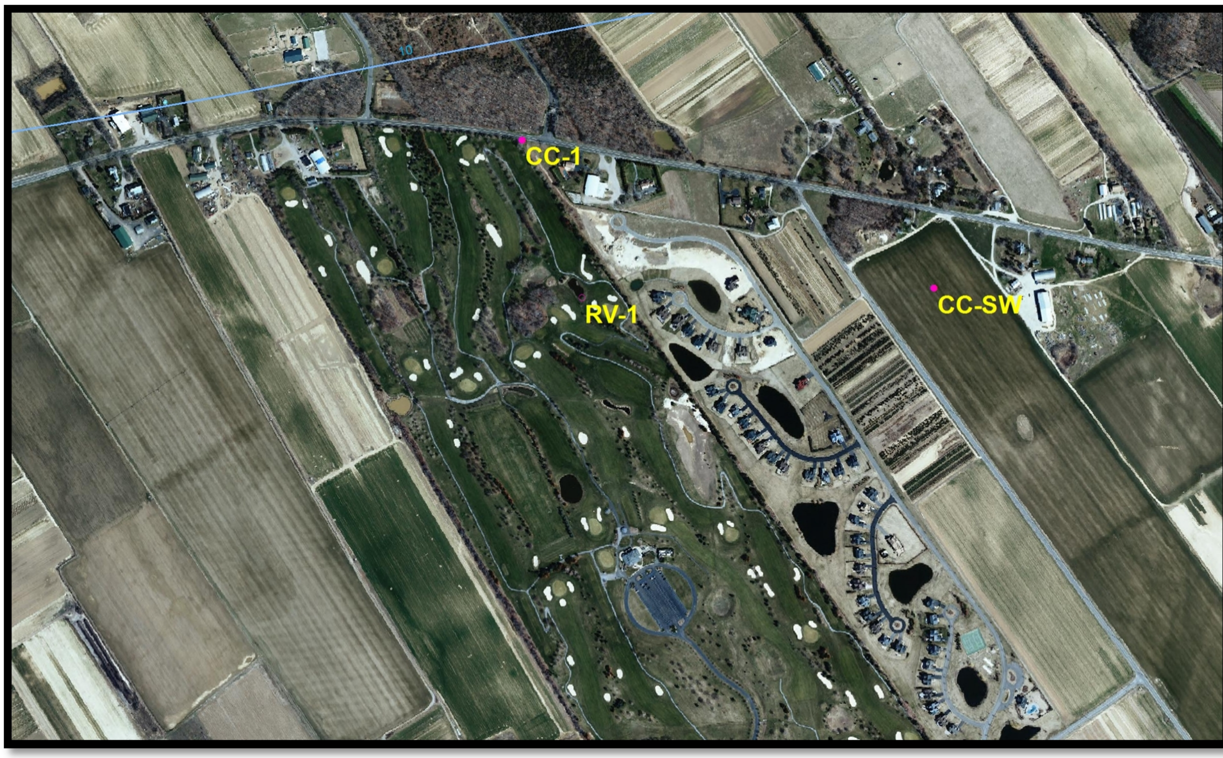


Figure 34: Turf case area (Riverhead golf course)

Figure 35 provides the time series plot. In 2005, when the well was first sampled, a concentration of 0.12 μg/L was detected. Later concentrations stabilized at 0.2μg/L for over two years, suggesting repeating modest inputs.

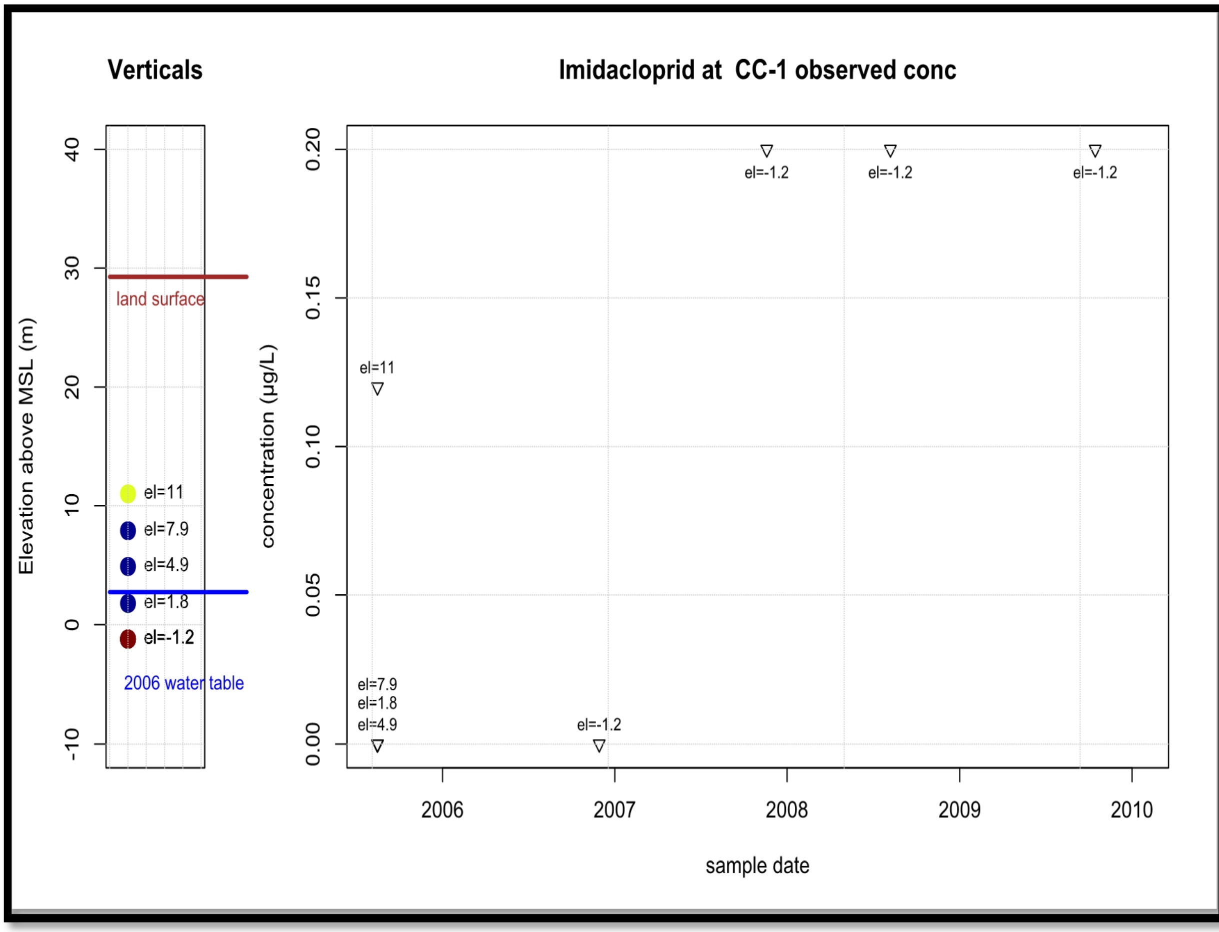


Figure 35: Imidacloprid near Riverhead golf course

Either there are not well-situated monitor wells for turf where imidacloprid is applied, or it indeed is a very minimal leacher because of low dosage or rapid environmental transformation to other forms. Section 5.4 models imidacloprid applied to turf grass using LEACHP.

3.6 Area Source: Vineyards

Long Island is becoming an increasingly popular location for winemaking, and thus vineyards and grape growing. Figure 36 locates the array of vineyards, which concentrate on the North Fork.

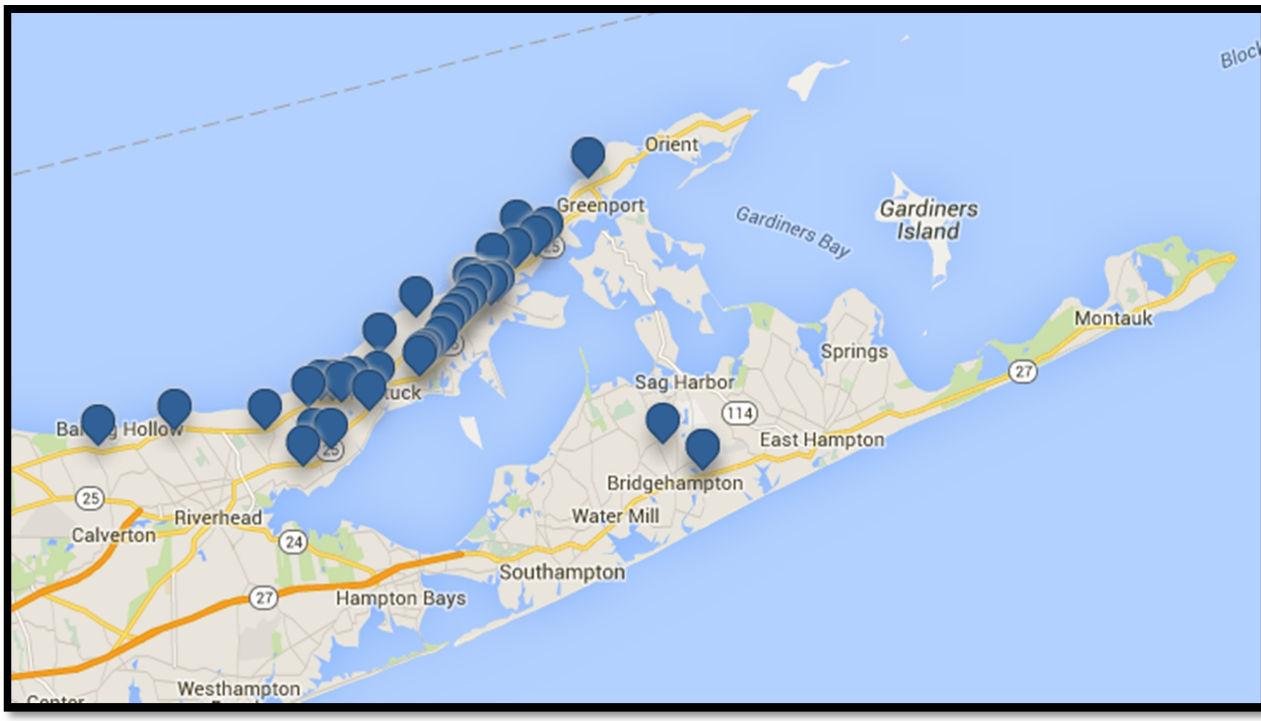


Figure 36: Wineries of eastern Long Island

Figure 36 Caption: Source: Google Maps, reached via http://www.liwines.com/planner/ (C) 2016 Google.

Organic insecticides are preferentially used and are increasingly popular in vineyards as it is believed that any chemical additives to vines or soil undesirably affects the taste, flavor, and quality of the grapes and wine. Unfortunately, organic alternatives to pesticides are generally considered less effective, require more applications, and are more expensive than imidacloprid based products (Cornell University, Cooperative Extention and Penn State Extension, various, grapes). Nevertheless, as of June 2012, roughly 263 Ha (25%) of the total 1,052 Ha vineyard lands had enrolled in the Long Island Sustainable Wine Program, and are committed to organic growth and production practices. The remaining 789 Ha (75%) (USDA National Agricultural Statistics Service, 2012) of vineyards are not organic and still apply pesticides such as imidacloprid as needed.

In vineyards, imidacloprid is used to control Sharpshooters, Leafhoppers, Mealybugs, Aphids, White flies, Fruit flies, and Phylloxera. The most prevalent grape pests in Long Island are Flea Beetles, Cutworms, Grape Plume Moths, European Redmites and Japanese Beetle Grubs (Cornell University, Cooperative Extention and Penn State Extension, various, grapes). On vinyard grapes in Long Island, Japanese Beetle grubs are the most frequent pest requiring imidacloprid based treatments. In New York State imidacloprid, can be applied to grapes any time from May-July, when flowers are not in bloom and pollinators cannot be affected. On Long Island, it may only be used if applied by a certified pesticide applicator.

In vineyards, Imidacloprid is most effective for longer-term pest regulation, especially when applied by soil applications such as chemigation through drip irrigation systems, where the insecticide is systemically taken up by the grapevines. When applied through the root zone, through soil applications, imidacloprid is systemic throughout the entire grape vine. It is only locally systemic when applied directly to the foliage (as a foliar spray), which provides more instantaneous but shorter-term pest control.

Admire Pro (BayerCropSci) is the most commonly used imidacloprid formulation for soil applications in vineyards (Cornell University, Cooperative Extention and Penn State Extension, various, grapes). Admire Pro is sold under a number of different trade names, including Alias, Merit, Gaucho, Provado, Montana, Nuprid, and Marathon and by numerous manufacturers.

Imidacloprid based treatments of grape pests, until recently, were labeled separately for foliar (Provado 1.6F and Provado Solupack) and soil/chemigation (Admire Pro) applications. As of 2012, the label for Admire Pro was changed, and has since been allowed for both foliar and soil application. This eliminates the need for Provado and related generic versions of this product, which became available when imidacloprid went off Bayer's initial patent in 2006, are also labeled for both foliar and soil uses (Loeb, 2012).

The specific area employed in this study, chosen to isoloate the impact of imidacloprid uses on grapes and vineyards, is shown in Figure 37. Other monitored vineyard wells had no detections. A 13.35 Ha vineyard (Vineyard 48) is the only up-gradient potential imidacloprid user directly contributing to the recharge in the monitoring wells considered.

Figure 37: Imidacloprid in monitor wells near a North Fork vineyard

Figure 37 Caption: The pink circles indicate the location of the SCHD monitoring wells, and the maximum imidacloprid detections at these wells are encoded in the relative size of each circle.

A profile of maximum concentrations in monitor wells along Oregon Road is provided in Figure 38, indicating that only two wells contained detectable concentrations. Figure 39 traces time series of concentrations at wells OR-2 and OR-2B. Well OR-2 had the highest detected peak concentrations of 0.2 µg/L-0.3 µg/L at 5m below the water table in fall samplings in 2005 and in 2007, and a little lower detected value at 12 m below the water table. All samples nearest the water table from these wells contained detected amounts, though some were at a trace level of 0.1 µg/L. As with turfed areas, wells either are not situated to pick up highest concentrations or the usage regime and environmental fate processes combine to yield very low concentrations.

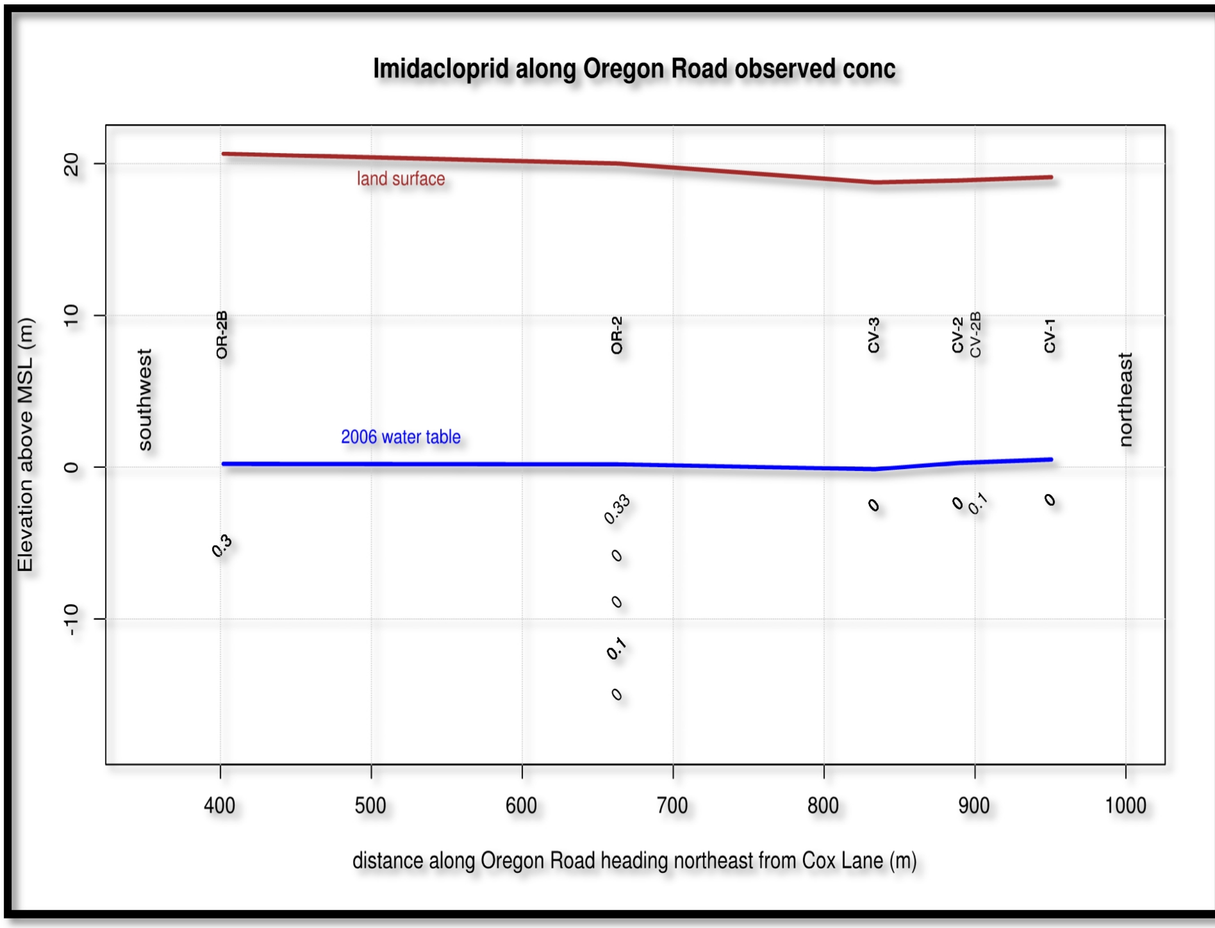


Figure 38: Imidacloprid in monitor wells along Oregon Road

Figure 38 Caption: Lateral plot of monitor well data, moving northeast from well OR-2 along Oregon Rd, toward Mill lane. The depths and concentrations of each detect are shown along the vertical axis.

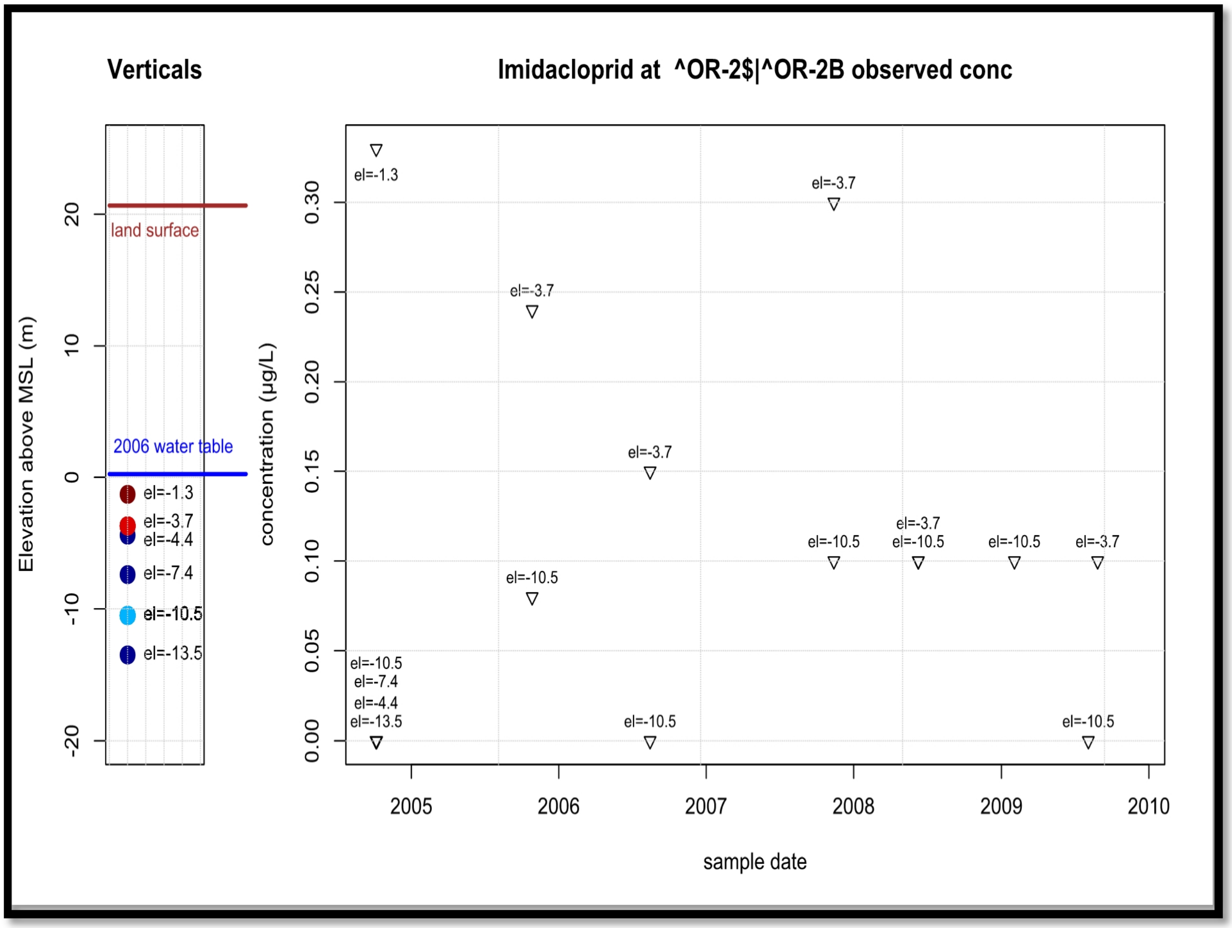


Figure 39: Imidacloprid time pattern in monitor well near a vineyard

Section 5.5 models imidacloprid applied in vineyards using the Sinkevich model, attempting to back-calculate a surface loading rate from the observed 0.1-0.3 µg/L concentrations in the shallowest depths at Oregon Road.

3.7 Summary of Monitoring Data Interpretations

It was extremely helpful to have access to the large set of monitoring well data up to 2010, provided by the SCDHS through the DEC. This unusually consistent data set was used at whole-county and site specific levels. Having the specific geographic locations of each well, and an understanding of the surrounding land uses over time permits the data to be mapped in proximity to possible pesticide emission areas, and then organized and categorized for area and countywide summaries.

Monitor well data after 2010 exist, and are being processed by the SCDHS with the same destination in mind: the DEC's EQuIS system. It would be helpful to combine the 2001-2010 data with these later data in a way that could extend the interpretations in this report with more sites or longer time series at the same sites.

Monitor well data before 2001 exist in various forms, but would be difficult to combine with the 2001-2010 data due to different laboratory techniques and monitoring strategies. Perhaps selective data about the North Fork could be organized similarly to how the 2001-2010 data were organized.

As noted in Chapter 2, the only monitor well results anywhere near the applicable drinking water criterion of 50 µg/L are associated with isolated incidents. The majorities of greenhouses or tree treatment users seemingly do not have problems with their handling or disposal, and work with the chemical according to product labels. Typical detections are at a concentration 10-fold below the criterion or lower. Land near outdoor area users yields the lowest concentrations, typically under 1 μg/L, and land nearest to concentrated, point source users yields concentrations up to 10 μg/L in a few cases.

Unfortunately, monitor well data obtained for public health protection purposes are biased in at least two ways: 1) They are skewed towards expected higher concentrations, such as from known intensive pesticide users. Sampling was repeated where the detected initial concentrations are high, but were not repeated as often where initial detected concentrations were low. 2) The data are from monitor wells, which tend to be shallow and sample from the top of the water table in order to measure the more immediate effect of the most recent and nearest pesticide uses. They are not representative of drinking water. Public drinking water wells draw from much below the surface of the water table, which are rarely located near areas of intensive pesticide use. This bias is normal and desirable solely for a public health assessment as pesticide use regulations must balance many factors, most importantly, the economic benefit of pesticide use versus the environmental impact aspects.

The SCDHS has many more related data sets including analytical results from private wells. It would be beneficial for these data to be more accessible to provide insights beyond the initial collectors. Note how valuable it is to have completely open databases from the US Geological survey water resources division and the NOAA weather bureau. It is expensive to prepare data for the public, but the public desire for transparency favors more openly accessible government-held environmental data. A partial improvement in the existing data bias for pesticide management purposes would be to merge SCDHS data from private household wells with the existing monitoring well data. Although limiting the ability to associate samples with nearby pesticide sources, appropriate measures to protect the privacy of these landowners should be assured.

Monitor well data are not easily accessible beyond the SCDHS database. A Cornell University group and the SCDHS prepared the data used in this report for submission to DEC's EQuIS. This is a second data system also inaccessible to the public and at this writing, not even accessible to contributors after their data submissions. Further, EQuIS will exclude perhaps 60% of these data from admission into their database because all the criteria for completeness are not met. This report demonstrates that valuable interpretations are possible, even without the full rigor of EQuIS admission criteria.

In different laboratories and data systems the term "detection limit" is not necessarily applied uniformly, which complicates interpretation. For example, Suffolk's imidacloprid data all cite a method detection limit (MDL) of 0.2 µg/L (and results for other pesticides cite other MDL values), but many trace values between 0.05 µg/L and 0.2 µg/L are included in the data as numbers flagged as "trace" or "below detection limit." For EQuIS purposes the MDL in the SCDHS reports have to be called a <u>quantification</u> limit, and the true <u>detection</u> limit is 0.2 µg/L or the numeric value associated with the trace, whichever is lower. Thus, "not detected" is an ambiguous result: definitely below 0.2 µg/L and possibly below 0.05 ug/L. There is indeed quantitative information reported in the SCDHS results between 0.05 µg/L and 0.2 ug/L, but it is relatively less precise than for values at 0.2 µg/L and above.

4. Concentrated Source Model Case Studies

The following case studies reflect the combined effects of input loading, depth to water table, and degradation and each provides insight into the observed imidacloprid magnitudes in the nearby SCDHS monitor wells. These cases all have unknown imidacloprid releases because they involved unsuspected, fugitive emissions to the environment or an undocumented spill.

4.1 Common Data used in Concentrated Case Assessments

The Sinkevich vadose zone model uses parameters similar to LEACHP. The main difference in applying the two models (Chapters 4 and 5 respectively) is that LEACHP is used in a "forward" sense, simulating the concentrations in soil water at 1.1 m depth that would result from known imidacloprid input rates related to labels. The Sinkevich model is used in a backward sense, trying to infer what imidacloprid releases would be consistent with the observed orders of magnitude of concentrations at the near-downgradient water table. The Sinkevich model is applied to cases with water tables as deep as 33 m.

Table 12 enumerates the main Sinkevich model parameters used and their sources. Table 13 details the soil parameters used in the Sinkevich models. Site-specific details are provided in each case study subsection.

Table 12: Sinkevich model parameter sources and values for case studies

Parameter	**Sources**	**Processing and Assumptions**
Depth to water table (*x*)	USGS (Monti & Busciolano, 2009) Taken from near case study.	Water table level assumed stable at 2006 level.
Duration of simulation (*tmax*)	As long as necessary to break through to the local water table for several years.	In most cases year zero is 1995 when imidacloprid first was allowed to be used. Actual usage period is unknown in most cases.
Recharge rate (*R*)	From LEACHP Riverhead and Bridgehampton potatoes water budget output.	48 and 62 cm/year respectively. Most Sinkevich cases are in Riverhead or North Fork thus 48 was used for most simulations.
Distribution (mixing) layer thickness (*dthick*)	Assumption.	5 cm for greenhouses, Lindenhurst tree, and turf, 20 cm for potatoes (Chapter 5)
Imidacloprid input rates and timings (*M* vector, *tv* vector)	Case-specific. Working backwards from observed concentrations in monitor wells.	Most cases assume five years each having three equally spaced inputs in time at same magnitude. This represents a greenhouse seasonally leaking from treated pots onto sand floor, or a vineyard having repeat treatments during the year, possibly for different pests. The Lindenhurst Tree case uses a single application representing a spill.
Organic matter and bulk density (*fom, fomT, rho, rhoT*)	USDA digital soil survey. (Soil Survey Staff, Natural Resources Conservation Service, USDA, 2013)	Ignore topmost organic horizon, use values for 0-20 cm to represent distribution zone and at least 1 m deep to represent transmission zone; assumes that deep values apply all the way to the water table. See Table 13.
Active flow fraction of saturation moisture content (*Af*)	Assumed. Corroborated by breakthrough time when available.	0.1 for Lindenhurst Tree case, 0.2 - 0.3 for others.
Distribution zone degradation rate (*decay*)	European pesticide properties database (Lewis, et al., 2016)	0.004/day = 1.5/year
Transmission zone degradation rate (*decaystar*)	Assumption, centering on 25% of the distribution zone rate.	0.2 - 0.6/year
Linear sorption partition coefficient (*koc*)	Table 1 in Chapter 1.	Midpoint 220 mL/g of range 135-310 in Table 1.

Table 13: Sinkevich-related soil parameters

Soil	Organic matter % shallow	Bulk density shallow (g/cm^3)	Organic matter % deep	Bulk density deep (g/cm^3)
Riverhead	3%	1.3	0.25%	1.63
Haven	4%	1.31	0.5%	1.48
Plymouth	3%	1.31	0.25%	1.63
Bridgehampton	5%	1.18	0.25%	1.81
Cut and fill ("Fs") at Lindenhurst (near Riverhead soil whose properties were used except lower surface organic matter)	2%	1.31	0.25%	1.63

Source: USDA digital soil survey (Soil Survey Staff, Natural Resources Conservation Service, USDA, 2013)

4.2 Sensitivity Analysis of Sinkevich Model

The two primary models, LEACHP and Sinkevich, used to link imidacloprid releases at the surface to observed concentrations in wells are each sensitive to various parameters that are uncertain to different degrees. This section explores the sensitivity of predicted concentrations at the bottom of the modeled profile -- the water table for Sinkevich -- to locally uncertain parameters. A later section 5.2 explores the sensitivity of the LEACHP model at 1.1m depth.

Both explorations are for potatoes at Bridgehampton. Similar relative results should be expected for Riverhead soil and weather, for turfgrass, and for regular non-incident greenhouse emissions.

All of the Sinkevich sensitivity runs use the same input loading of 1 kg/ha, once per year for several years. The results scale linearly with input loading. Peak values from once per year inputs would be slightly higher than values from thrice per year inputs at one third strength, particularly when the water table is shallowest.

A main difference between Sinkevich and LEACHP applications is the different depth of the lower bound of the model. Figure 15 in Chapter 2 demonstrated the different effect of 1 kg/ha/yr annual inputs at different depths below the surface using the Sinkevich model. The shallower concentrations are more time variable and the initial breakthrough is earlier. The deeper concentrations are quite smoothed and the peaks are closer to the averages due to cumulative dispersion. The average concentrations fall with depth due to degradation. The averages would be roughly the same at any depth if degradation below the surface mixing layer were zero.

A basic sensitivity analysis for potatoes using Bridgehampton soil and climate was performed. Parameters held fixed in the Sinkevich model were:

- *rho*=1.3 g/cm^3 bulk density of distribution zone
- *rhoT*=1.63 bulk density of transmission zone
- *fom*=0.03 fraction organic matter of distribution zone

- *R*=62 cm/year recharge rate (Bridgehampton weather and soil)

Parameters varied include:

- *x*=200, 500, 1500 cm; depth to water table
- *dthick*=5, 20 cm; thickness of distribution zone
- *koc*=132, 310 mL/g; organic carbon sorption partition coefficient
- *fomT*=0.0025, 0.001, 0.0005; fraction of organic matter in transmission zone
- *Af*=0.2, 0.4; active fraction of saturation moisture content through which water flows in transmission zone; effectively an average volumetric moisture content
- *decay*=0.75, 1.5, 3.0/year in distribution zone, reduced to one quarter of these in the transmission zone

The results in Table 14 explore four factors at work among the parameters: mobility (*Af*, *koc*, *fomT*), distance (x), distribution zone thickness (dthick), and decay (decay and *decaystar*). These result in differential smearing, disappearance, and lag. (Lag is invisible when using peak concentrations.) Concentrations are generally higher for the thinner distribution zone, slower degradation, and faster mobility. It is important to note that the Sinkevich model will smear out peak concentrations due to assuming that water is moving all the time at the annual average rate, unlike LEACHP which moves water intermittently in response to storm events and with a seasonal rhythm determined by evaporation and soil moisture depletion.

Table 14: Sensitivity of Sinkevich model peak concentrations at 2-15 meters+ distribution thickness to degradation and mobility parameters

Average of peak concentrations			Peak concentration (µg/L)		
water table depth (cm)	distribution zone thick-ness (cm)	mobility	decay		
			faster	moderate	slower
200	5	1-fastest	177.9	235.5	279.2
		2-fast	162.2	225.3	273.6
		3-moderate	105.8	161.9	209.9
		4-slow	106.3	161.5	209.7
		5-slowest	65.2	113.2	159.1
	20	1-fastest	52.8	77.5	107.5
		2-fast	49.9	77.5	110.2
		3-moderate	32.7	57.8	89.5
		4-slow	33.6	57.7	88.6
		5-slowest	19.3	38.1	64.6
500	5	1-fastest	99.0	163.6	219.6
		2-fast	78.4	142.7	201.8
		3-moderate	44.9	94.0	147.1
		4-slow	44.2	90.8	142.3
		5-slowest	20.6	59.1	108.3
	20	1-fastest	30.4	56.7	89.9
		2-fast	25.3	52.4	87.6
		3-moderate	13.9	34.6	66.7
		4-slow	14.8	34.9	65.1
		5-slowest	6.4	21.1	46.9
1500	5	1-fastest	22.5	66.8	126.0
		2-fast	13.5	47.2	100.2
		3-moderate	6.7	28.1	68.8
		4-slow	4.7	23.7	59.4
		5-slowest	0.8	10.1	40.9
	20	1-fastest	7.2	24.8	56.3
		2-fast	4.6	18.9	48.5
		3-moderate	2.0	10.3	32.5
		4-slow	1.7	10.2	30.6
		5-slowest	0.3	3.9	19.3

Source: Generated by R function call:

```
x=SAmassbal( R=c(48,62), x=c(200,500,1500), dthick=c(5,20),
koc=c(132,310),fomT=c(0,0.0025,0.0005), Af=c(0.2,0.4),
decay=c(0.75,1.5,3.0), decayratio=0.25 )
```

The Sinkevich model's evident sensitivity to locally unknown parameters *Af*, *decay, decaystar*, and *fomT* mean that a wide tolerance should be attached to peak concentration predictions. The smearing effect of a thicker vadose zone narrows the uncertainty somewhat compared to LEACHP outside of the shallowest water table areas, thus a factor of 5-10 uncertainty from nominal is appropriate.

In general, it is best when comparing uncalibrated models like Sinkevich and LEACHP against observed data, to operate at the level of order of magnitude, such as 0.1 versus 1.0 versus 10.0.

4.3 Routine Use: Greenhouses with Nearby Detections, or All Non-detects

The simpler greenhouse cases have in common:

- Timings (earliest use, seasonality) and rates of imidacloprid use are unknown;
- Routes of fugitive emissions are unknown;
- Outdoor uses on the same property are unknown;
- Depth to ground water is known for late fall 2006;
- Positions and land surface elevations of monitor wells are known;
- Sample depths below the surface are known;
- Soil type is known;

- Actual degradation rates and unknown, less so for the near surface where literature values are available;
- Deeper vadose zone organic matter, water content, and other properties are unknown;
- Estimated recharge rate from LEACHP is the same, all using Riverhead meteorology and soil.

The differences between cases are:

- Different locale thus different soil type and different depth to water table;
- Different position of monitor well relative to property (all are downgradient, most immediately);
- Different mean, variability, and timing of concentration patterns observed in wells.

The long list of unknowns is daunting, but it is still possible to gain order-of-magnitude insights by adapting a Sinkevich model to each site.

Nursery with Greenhouse in Aquebogue

With just a single trace-value (0.1 µg/L) detection as discussed in Section 3.1, the fugitive emissions reaching the 5 meter water table at this site were tiny.

Figure 40 shows the Sinkevich model results for 0.0004 to 0.0010 kg/ha (0.4 to 1.0 g/ha) imidacloprid emissions three times per year for eight years using soil and water table data for this site. (The loading rates correspond to different transmission zone degradation rates.) A thin distribution zone 5 cm was used to reflect surface rather than buried applications. At any of the three transmission zone degradation rates represented (0.3/year to 0.6/year), the concentrations peak around the single observed monitoring result of 0.1 (trace level). The first breakthrough to the water table was after two years, a value strongly affected by the assumed *Af* parameter value of 0.3. A lower value of *Af* translates into a faster first arrival and less smoothing of time-variable concentrations. The single trace detection was at the end of the monitoring period, in 2009, thus the greenhouse probably used imidacloprid after the simulation cutoff of 1995+8 = 2003 and may not have used it as early as 1995.

The simulated amounts emitted are minuscule. The main lesson of this case is that it demonstrates the possibility of reaching 0.1 μg/L detectable (semi-quantified trace) values in shallow recharge with a minuscule fugitive emission, when taking account of degradation. Also notable is the time lag before surface releases will show up even at adjacent monitor wells.

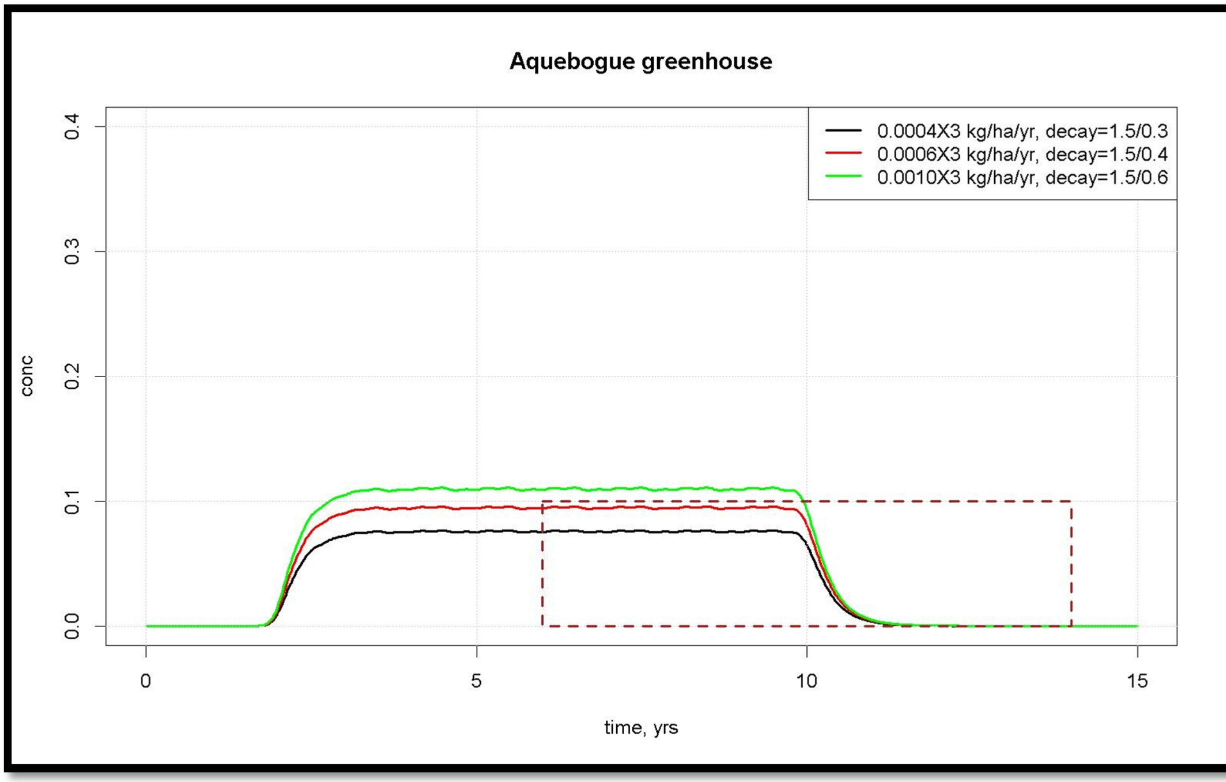


Figure 40: Sinkevich model result (µg/L) for Aquebogue nursery

Figure 40 Caption: The solid lines represent the time series of simulation results at 5 meters for different parameter combinations of input loading and degradation in root zone/subsoil in 1/year units. In all cases the input loading was 3x per year for 8 years. The dashed box represents the range of observed data assuming that year 0 is 1995, the first year of imidacloprid sales on Long Island. The box's vertical height spans all analytical results from wells HA-1 and B-1. The box's horizontal span represents the period of monitoring.

```
Model:
   slineit2S( x=500, M=rep(0.0004,24), M2=rep(0.0006,24),
   M3=rep(0.0010,24), tv=c(0.33,0.66,1.0, 1.33,1.66,2.0,
   2.33,2.66,3.0, 3.33,3.66,4.0, 4.33,4.66,5.0, 5.33,5.66,6.0,
   6.33,6.66,7.0,7.33,7.66,8.0), cmax=0.4, decay=1.5,
   decaystar=c(0.3,0.4,0.6), tmax=15, R=48, rho=1.31, rhoT=1.66,
   Af=0.3, dthick=5, koc=220, fom=0.03, fomT=0.001, tinc=0.02,
   main="Aquebogue greenhouse", cap=c("0.0004X3 kg/ha/yr,
   decay=1.5/0.3","0.0006X3 kg/ha/yr, decay=1.5/0.4",
   "0.0010X3 kg/ha/yr, decay=1.5/0.6"), legendPos="topright",
   obsRect=c(6,0,14,0.1), obsCol="brown",
   plotfile="sink-aquebogue-4" )
```

Greenhouse Case SA: Home and Garden Store with Small Greenhouse

Section 3.1 indicated that there were consistent detections at this northern Riverhead site from 0.40 to 0.94 µg/L between 2006 and 2009. Except for an early profile well, there were detections in every sample. These confirm that the greenhouse was an actual imidacloprid user.

Imidacloprid emission was assumed to be from three equal applications per year. The observed 10x higher concentrations here, compared to Aquebogue, would require an emission rate much higher. Reflecting the much thicker vadose zone with its likely greater gravel content at depth, the *Af* value was reduced to 0.25 and transmission zone organic matter was reduced from 0.25% to 0.1%.

Figure 41 portrays the simulated result. A deep water table at 28 meters meant a long time until imidacloprid first reached the water table -- over 8 years simulated. Emission rates 0.04 kg/ha to 0.35 kg/ha (40 to 350 g/ha) three times per year are consistent with the observed concentration magnitude when transmission zone degradation rates *decaystar* are set to 0.3 to 0.6/year.

Because imidacloprid originally became available on Long Island in the mid 1990's, it is possible that the initial monitoring in late 2005 may have missed the earliest detections in that well (unless the greenhouse owner delayed in using imidacloprid).

The main lesson of this case is that to reach the magnitude of 1 microgram per liter at a deep water table, 10x higher that at Aquebogue, recurring emissions of tens to hundreds of grams per hectare of imidacloprid would be needed unless degradation in the deeper vadose zone is slower than the slowest values assumed. (Note that an emission zone smaller than 1 hectare (10,000 m^2) would have correspondingly smaller emission amounts.)

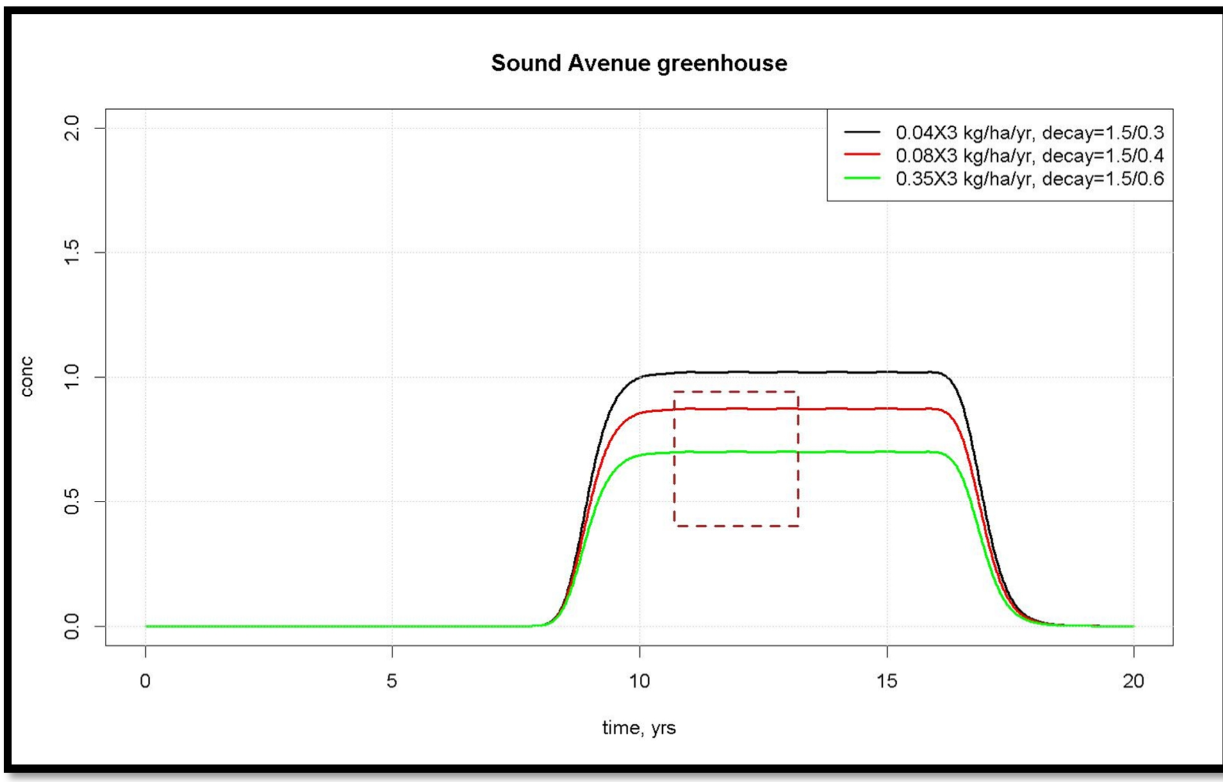


Figure 41: Sinkevich simulation results for Sound Avenue greenhouse

<u>Figure 41 Caption:</u> Model:

```
slineit2S( x=2800, M=rep(0.04,24), M2=rep(0.08,24),
M3=rep(0.35,24), tv=c(0.33,0.66,1.0, 1.33,1.66,2.0,
2.33,2.66,3.0, 3.33,3.66,4.0, 4.33,4.66,5.0, 5.33,5.66,6.0,
6.33,6.66,7.0, 7.33,7.66,8.0), cmax=2, decay=1.5,
decaystar=c(0.3,0.4,0.6), tmax=20, R=48, rho=1.31, rhoT=1.66,
Af=0.25, dthick=5, koc=220, fom=0.03, fomT=0.001, tinc=0.02,
main="Sound Avenue greenhouse",
cap=c("0.04X3 kg/ha/yr, decay=1.5/0.3",
"0.08X3 kg/ha/yr, decay=1.5/0.4",
```

```
"0.35X3 kg/ha/yr, decay=1.5/0.6"), legendPos="topright",
obsRect=c(10.7,0.4,13.2,0.94), obsCol="brown",
plotfile="sink-soundave-4" )
```

Baiting Hollow Major Greenhouse

As noted in Section 3.1, observed concentrations in the LL-1 well reached 1.9 µg/L and were rising over the monitored period; perhaps the monitor wells were picking up the initial arrival then sustained emissions. With an even deeper water table (33m) and concentrations double those at Sound Avenue, the loadings had to be higher. The inferred loadings 0.1 kg/ha through 2.3 kg/ha (three times per year) are indeed much higher (Figure 42). The 2.3 is implausible because it implies very careless handling, indicating that the transmission zone degradation rate 0.6/year is much too fast. (A rate like that could apply in a much thinner transmission zone.)

The main additional lesson of this case is that the unknown vadose zone degradation rate is very important to narrow down the possible emission magnitude. Literature based on field experiments by manufacturers is very available to estimate degradation in the surface soil; however, there is no literature about deeper vadose zone degradation of pesticides. The two unknown parameters -- emission rate and degradation rate -- cannot be estimated separately without independent, site-specific data starting from known imidacloprid use rates and timings, and thorough characterization of how indoor usage becomes environmental emissions. With such data for multiple sites at a range of depths to water tables, it may be possible to narrow down the range of uncertainty of the degradation rate.

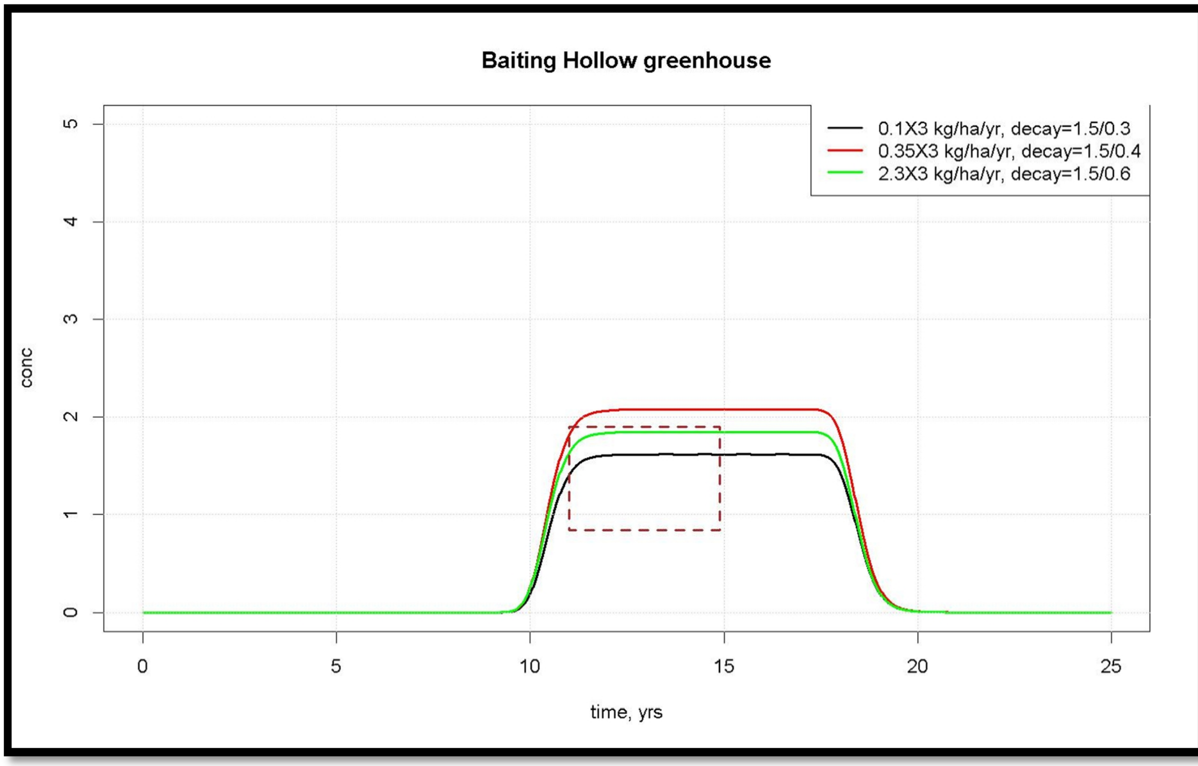


Figure 42: Sinkevich model results for Baiting Hollow greenhouse complex

Figure 42 Caption:
Model:

```
slineit2S( x=3300, M=rep(0.1,24), M2=rep(0.35,24),
M3=rep(2.3,24), tv=c(0.33,0.66,1.0, 1.33,1.66,2.0,
2.33,2.66,3.0, 3.33,3.66,4.0, 4.33,4.66,5.0, 5.33,5.66,6.0,
6.33,6.66,7.0, 7.33,7.66,8.0), cmax=5, decay=1.5,
decaystar=c(0.3,0.4,0.6), tmax=25, R=48, rho=1.31, rhoT=1.66,
Af=0.25, dthick=5, koc=220, fom=0.03, fomT=0.001, tinc=0.02,
main="Baiting Hollow greenhouse", cap=c("0.1X3 kg/ha/yr,
decay=1.5/0.3","0.35X3 kg/ha/yr, decay=1.5/0.4","2.3X3
kg/ha/yr, decay=1.5/0.6"), legendPos="topright",
obsRect=c(11,0.84,14.9,1.9), obsCol="brown",
plotfile="sink-baiting-4" )
```

Greenhouse at Bellport (all non-detects)

There were no detections at this greenhouse (monitor well SCR-2A) over several years of monitoring, indicating low to nonexistent use or very tight containment (minimal fugitive emissions). Hypothetically, for a 6-meter water table, it is possible to have some emissions and never get above the detection threshold of 0.1 µg/L. The model in Figure 43 illustrates that continuing fugitive emissions of 0.2 to 0.4 grams per hectare three times per year are compatible with reaching 0.05 µg/L (half the detection limit) at the water table.

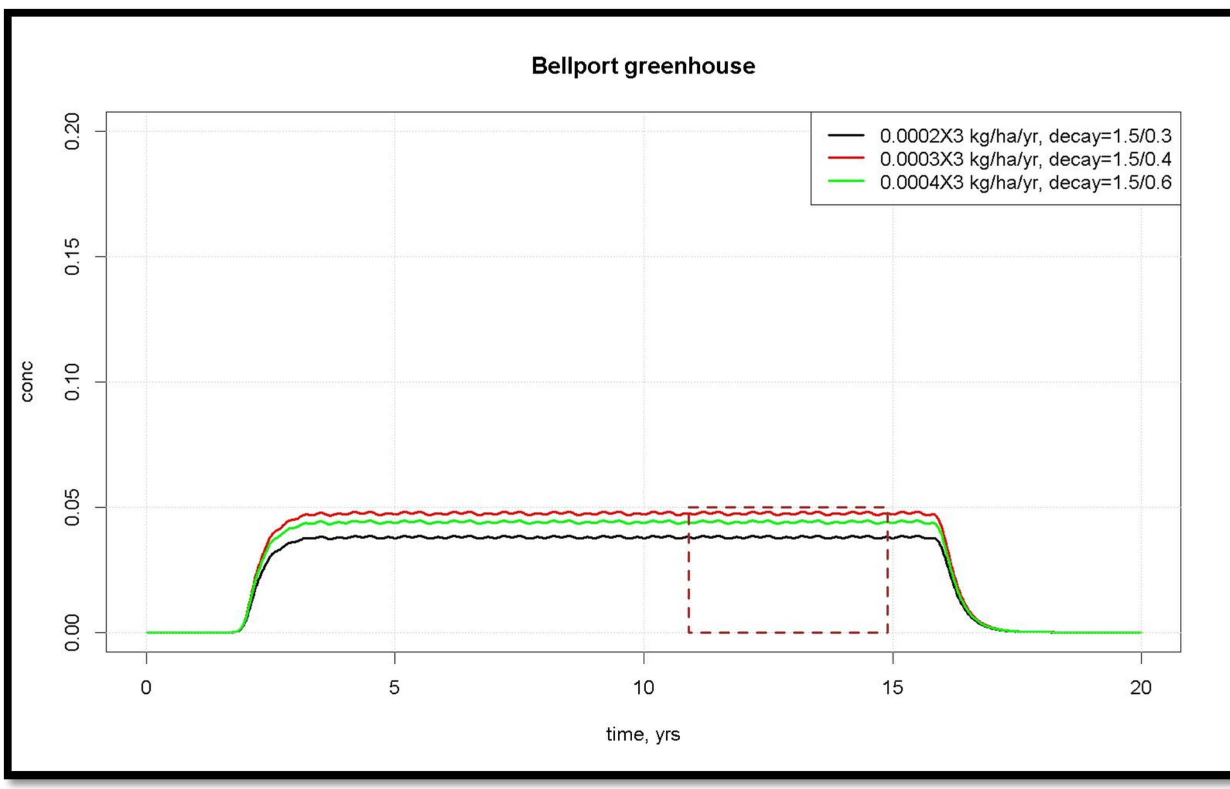


Figure 43: Sinkevich model results for Bellport greenhouse

<u>Figure 43 Caption</u>: Model:

```
slineit2S( x=600, M=rep(0.0002,42), M2=rep(0.0003,42),
M3=rep(0.0004,42), tv=c(0.33,0.66,1.0, 1.33,1.66,2.0,
2.33,2.66,3.0, 3.33,3.66,4.0, 4.33,4.66,5.0, 5.33,5.66,6.0,
```

```
6.33,6.66,7.0, 7.33,7.66,8.0, 8.33,8.66,9.0, 9.33,9.66,10.0,
10.33,10.66,11.0, 11.33,11.66, 12.0,12.33,12.66, 13.0,13.33,
13.66,14.0), cmax=0.2, decay=1.5, decaystar=c(0.3,0.4,0.6),
tmax=20, R=48, rho=1.31, rhoT=1.66, Af=0.25, dthick=5,
koc=220, fom=0.03, fomT=0.001, tinc=0.02, main="Bellport
greenhouse", cap=c("0.0002X3 kg/ha/yr, decay=1.5/0.3",
"0.0003X3 kg/ha/yr, decay=1.5/0.4",
"0.0004X3 kg/ha/yr, decay=1.5/0.6"), legendPos="topright",
obsRect=c(10.9,0.0,14.9,0.05), obsCol="brown",
plotfile="sink-bellport-4" )
```

4.4 Possible Spill? Lindenhurst Asian Longhorn Beetle Treatment Area

Section 3.3 reviewed the unusual 200 µg/L finding in two samples in mid April and mid May 2005, which were followed by one sample in November at 53 µg/L, and ultimately by a sample in June 2006 at 1.0. This is a classic exponential decay pattern following a sudden input. The Sinkevich model releases exponentially from its distribution zone into its transmission zone, thus its mathematics match the shape of the observed data in a very shallow system like this.

This was unlikely to escape from being injected into a tree given the very clean ground-water results at Indian Island and single digit concentrations elsewhere in Lindenhurst. It must have resulted from a small spill onto soil, not far from the monitor wells near the tree being treated. USDA's investigation following the findings of high concentrations in wells found no record of accidental spills (unsurprising since a contractor's spill would have no visible effect and would be extremely unlikely to be discovered).

The Sinkevich model can be applied to illustrate this case with the following assumptions:

- 1.5 meters depth to ground water based on a 1 m water table elevation (Monti & Busciolano, 2009) and a 2.5m land surface elevation from the USGS topographic map;
- a spill not long before sampling;
- the soil is sandy cut and fill, near a Riverhead soil: Riverhead parameters were used except for 2% instead of 3% upper layer organic matter;
- 5 cm thick distribution zone (mixing layer);
- steady flow recharge 100 cm/year (much higher than usual since April 2005 had over 20 cm of rain); and
- three pairs of degradation rates ranging from 1.5/year in distribution and 0.5/year in transmission, to zero in both layers.

Effective loading rates of 1.0 kg/ha to 0.6 kg/ha, depending on the degradation parameters, generate the time traces in Figure 44. The initial distribution zone concentration for the 1.0 kg/ha rate is around 500 µg/L, which translates to a peak

The A_f active fraction of the cross section had to be set quite low at 0.1, to make the plume appear early enough at the water table for a March spill to show up by April. If A_f is set to 0.2, the travel time is lengthened; the spill would then have occurred in the previous October and have been larger in magnitude (except with zero degradation).

Figure 44 provides one conceivable explanation for the pattern including the dual 200 µg/L findings in April and May. The time trace intersects the observed data range at around 200 twice at around the right times. The considerably higher peak is simulated somewhere between those two times, and the earlier sample caught the plume on the way up and the later sample caught the plume on the way down. The real plume degraded to around 25% of its original concentration by November, and to under 0.5% by the following June. The model tracks this pattern but "dies off" somewhat quickly. There are enough parameters in the spartan Sinkevich model to make this match more closely, a purely mathematical exercise. However the shape would remain very similar and corroborates the hypothesis of one sudden release at the surface around a month before the first sample. A similar case could be made for a sudden, perhaps larger release in late summer of 2004; the spring 2005 samples both could have caught the trailing edge of the mini-plume.

Perhaps the contractor personnel making the applications were reloading their injectors from a bulk supply, and spilled 20-50 mL of 10% imidacloprid. The spill would go unnoticed after it disappeared into grass or sand -- out of sight, out of mind. Perhaps wash it into the soil with a little water to dilute it. *Why report something that is invisible?* The forensics of this case are formidable.

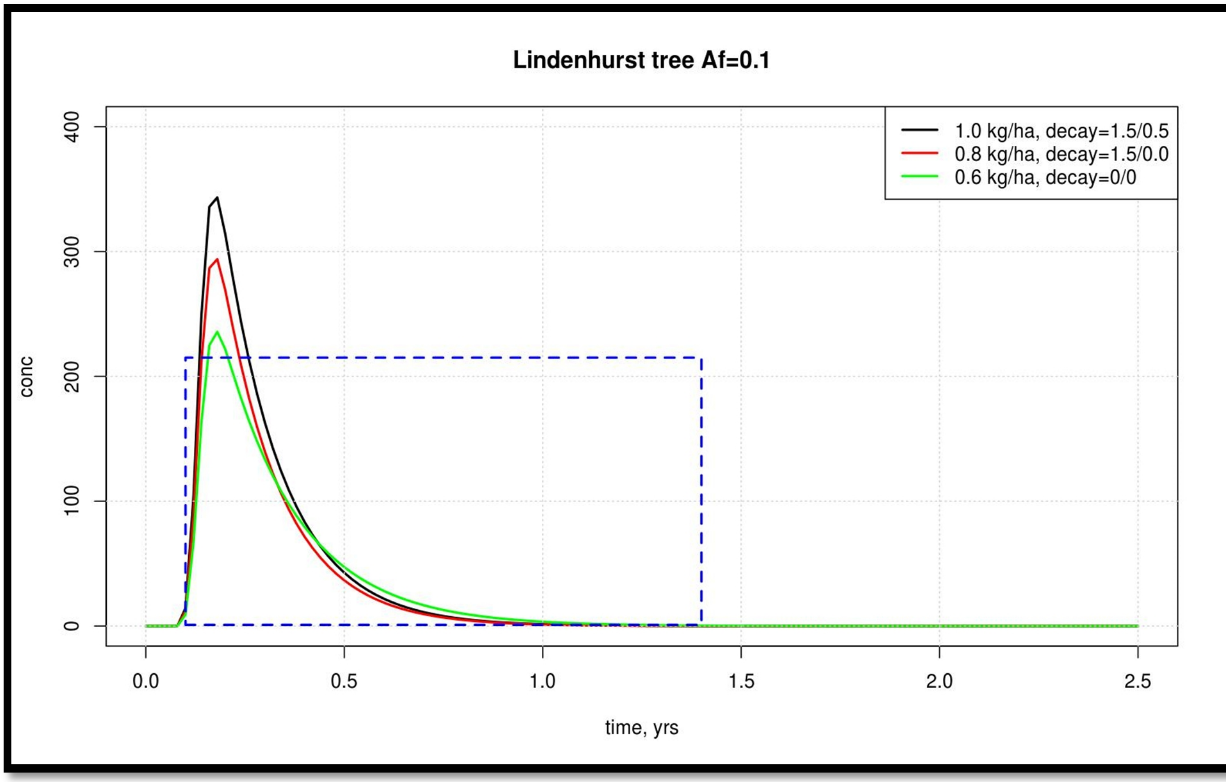


Figure 44: Sinkevich model results for spill near monitor well

Figure 44 Caption: Model code:

```
slineit2S( x=150, M=c(1.0,0), M2=c(0.8,0), M3=c(0.6,0),
tv=c(0,1), cmax=400, decaystar=c(0.5,0.0,0.0),
decay=c(1.5,1.5,0), tmax=2.5, R=100, rho=1.31, rhoT=1.66,
Af=0.1, dthick=5, koc=220, fom=0.02, fomT=0.0025, tinc=0.02,
main="Lindenhurst tree Af=0.1",
cap=c("1.0 kg/ha, decay=1.5/0.5",
"0.8 kg/ha, decay=1.5/0.0",
"0.6 kg/ha, decay=0/0"), legendPos="topright",
obsRect=c(0.1,1.0,1.4,215), obsCol="blue" )
```

4.5 Concentrated Source Outlier: Mattituck Greenhouse

Setting

Figure 40 illustrates the apparent geometrical configuration of the plume observed downgradient from the Mattituck greenhouse.

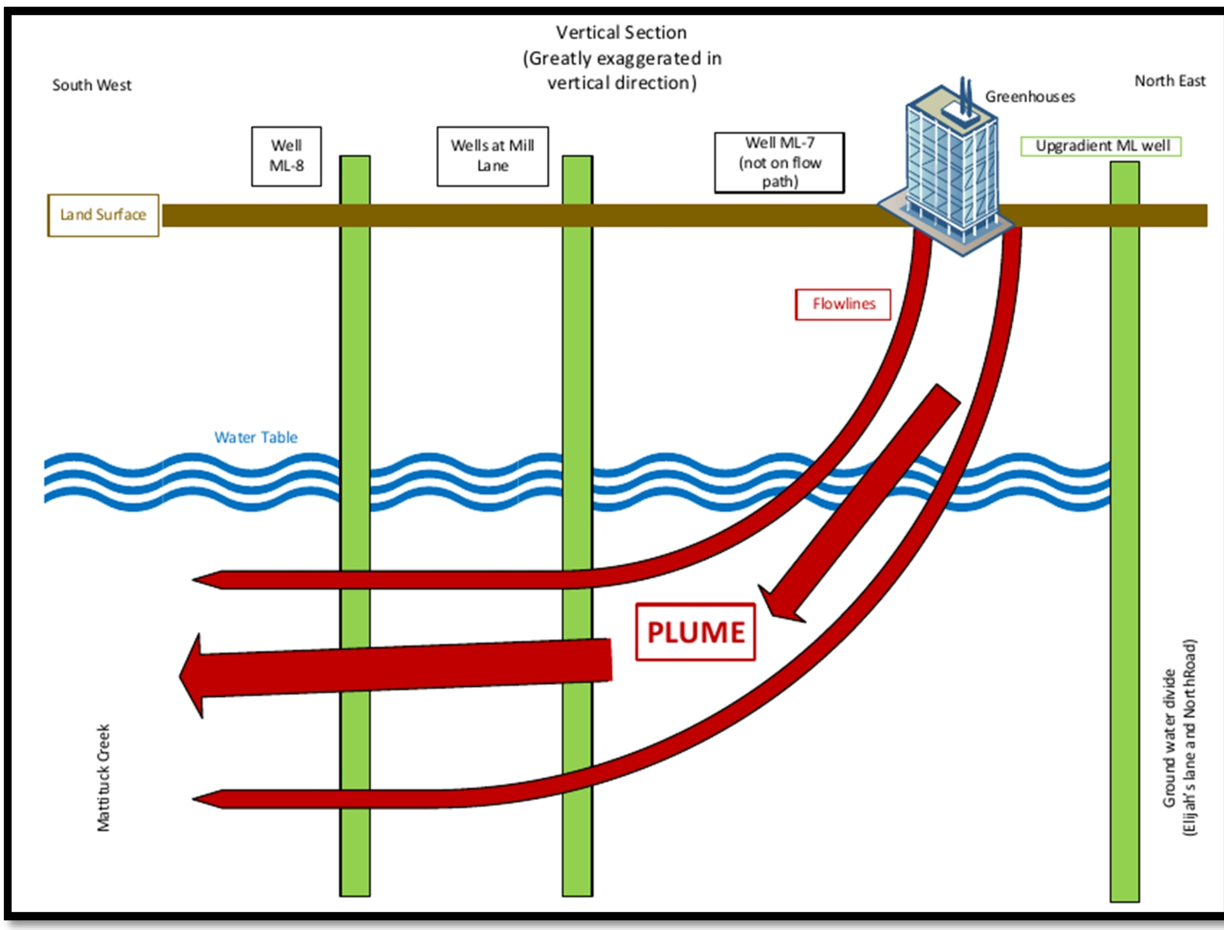


Figure 45: Schematic of North Fork greenhouse plume

To understand the conditions that led to the plume, a DEC incident file was obtained via FOIA (with some redactions). In these reports, the proprietor claimed to have applied Marathon for two seasons, starting in 1994. As Marathon was only first approved for use in February of 1995, it is more likely that it was used in 1995 and 1996. The formulation available at that time was Marathon 1% granular greenhouse and nursery insecticide (EPA product ID: 3125-452-5908), and was reportedly applied by hand in scoops for those two seasons to control whiteflies and aphids on the poinsettias and chrysanthemums being grown. The proprietor then claimed to discontinue use until 2001, when the liquid formulation became available. Marathon II greenhouse and nursery insecticide (EPA ID: 3125-549-59807) was then used until 2003, when the investigation of the operation and its downgradient plume began. The owner claims to have used only one container -- of unspecified size. The product label says 250 mL of product volume that contains 60g weight of imidacloprid. The owner claimed to have applied from the container 5 times in 2002, in accordance with the label, and stated that no accidental spill events occurred. More detailed records of applications were not kept by the owner (a violation) and were thus not available in the case file.

The DEC site investigation revealed that all the greenhouses had soil floors (very sandy in this area), and no run-off collection systems. The soil floors and lack of any runoff collection systems in the greenhouse suggest that the overflow from the initial granular applications fell directly onto the dirt floor and was allowed to soak into the ground everywhere it was used in the facility. Irrigation water may also have leached some dissolved imidacloprid through the plant containers.

The site's100m x 100m footprint includes several closely spaced buildings. This entire rectangle represents the probable potential source of the plume, given the observed width of the plume.

Additionally, a 757L (200 gallons) mixing tank was located inside one building. This tank, used to mix pesticides for the facility, was situated directly above an indoor drywell. The drywell was approximately 0.61m by 0.61m and extended roughly 1.5m below the unpaved greenhouse floor and land surface. After mixing and using the liquid formulation in this tank (for the 2002 applications), the tank was flushed to remove the remaining, unused solution, and the rinsate from this tank was disposed directly down into the drywell and ground below it. Out of sight, out of mind again: The archived Marathon II product label (Olympic Horticultural Products, 2000) does says that "*wastes resulting from the use of this product may be disposed of on site or at an approved waste disposal facility*." Because the drywell was located indoors, below the mixing tank, it was not exposed to any sunlight and no photo degradation would occur. As Imidacloprid primarily degrades via sun exposure, this direct indoor injection below the soil surface prevented any of this from occurring and enhanced it as a point source of contamination. (A glass greenhouse, that will not pass UV light, would also inhibit photodegradation of spillage onto floors.)

The Marathon II labeled rates for greenhouse use range from 13 - 50 mL of product in 100 gallons of water. This equates to 8,000 and 32,000 μg/L starting concentrations in the tank. While the disposal of mixed product would have created a tiny plume given the small size of the drywell, it would have been an intense plume.

An important opportunity for understanding imidacloprid's environmental fate near a greenhouse was lost when the owner of the greenhouse did not keep the required records of actual imidacloprid use.

Toward Modeling

It would be useful to work backwards toward emission rates from the observed concentrations as was done for the greenhouses with immediately adjacent monitor wells. However the ML-series monitor wells tapping the plume are over 200m distant thus the Sinkevich model is not enough; the saturated zone must also be represented. Additionally, the plume is clearly not uniform geometrically as it might be from a spatially large and uniform source, thus to interpret the concentrations requires taking account of mixing (dispersion) with cleaner water above, below, and alongside the finite source.

An axisymmetric 3-D model like Domenico's (Domenico, 1987) might be useful, if coupled to the Sinkevich model and its plume warped geometrically to account for ground-water streamlines that are not horizontal. Domenico's analytical model represents a step-function contaminant source having a fixed concentration starting at time 0, through a rectangular aperture, in the direction of steady-state ground-water streamlines. Superposition could extend this to successive finite-duration inputs, such as a succession of inputs from the vadose zone.

Geometric transformation could be used to "warp" the flat plume along a streamline that is vertical at the water table and moves deeper below the water table in the downgradient direction because of cleaner recharge above the plume as it becomes horizontal.

Building then fitting a new model is infeasible within the scope of this work, but it is nevertheless useful to discuss what data are necessary and available (in this vicinity) to apply such a model. Again, the objective of such a model would be to connect a source at the land surface to wells not too far away. In this case the farthest well of interest is 500m away. (Note: Two of the three authors of this report built conceptually similar root zone + vadose zone + saturated zone teaching software in the 1980's (Steenhuis, et al., 1987). That software used a vertically oriented 2-D saturated zone.)

It seems reasonable to use a lag time between release at the surface and appearance at Mill Lane of 3.5-7.5 years, based on data discussed below.

For a Sinkevich model application to transfer solute vertically downward to the water table, the following site specific data are necessary:

- Timing of solute inputs to soil: (*tv[]*). There were two distinct periods of imidacloprid introduction: 1995-96; a five-year gap; then the second use period, at most 2001-2003 and possibly only 2002. One must begin by considering lag time in the vadose zone, 10 meters thick at this site. 0.5 m/year recharge flowing through 0.1-0.2 water content (*Af*) would have taken 2-4 years to break through at the water table, longer if there is much organic matter. Then there is lag for the solute to move laterally over 200m, which would take additional years. The earlier peak concentration in wells was no later than 2004. Concentrations even at last-affected ML-8 fell after 2006. Probably the observed plume is only from the first usage period. There might be a second peak but it should have been detected by the last monitoring in 2010 -- if the samples were deep enough.

- Magnitude of solute inputs to soil, possibly different over time (*M[]*). This would be inferred by sensitivity analysis to try to match the magnitude of concentrations at monitor wells, as in the Sinkevich-only cases.
- Degradation rates in distribution and transmission zones (*decay* and *decaystar*): as for the earlier cases in section 4.3.
- Bulk density (*rho* and *rhoT*): Haven soil numbers.
- Surface and subsurface organic matter content (*fom* and *fomT*): The soil in this area is Haven, derived from glacial outwash.
- Unsaturated thickness (*X*). About 10m in 2006.
- Recharge rate (*R*): Use the Riverhead average from LEACHP 48cm/yr.
- Fraction of the cross section through which water and solutes flow (*Af*): vary 0.1 to 0.3.

For a Domenico extension of the Sinkevich model that picks up at the water table and carries solute slightly downwards and mostly toward Mattituck Creek, the following additional data are needed:

- Map-view flow direction: from the water table configuration in multiple USGS reports, this is perpendicular to Mill Lane; the origin of the flow system is near the upgradient wells ML-20;
- Longitudinal distances along the flow direction to various monitor wells: from map;
- Pore water velocity: computable from porosity, horizontal gradient of the water table, and hydraulic conductivity:
    - Porosity: 0.25. (Bohn-Buxton, et al., 1996);
    - Bohn-Buxton et al showed a gradient in this area of 0.001 (1.64 m elevation drop in 1600 m between the ground water divide and Mattituck Creek), It should also be noted that the 1988 conditions modeled by Bohn-Buxton et al were drier than average, leaving to lower than average gradients and slower flow than would have occurred during the wetter 2000s;
    - Bohn-Buxton et al concluded a horizontal hydraulic conductivity of 400 ft/day for their cross section near Cutchogue; A more commonly cited (Schubert, et al., 2004) horizontal conductivity is 200 ft/day.
- Solute retardance factor for sorption: assume very low organic matter, thus solute moves with water;
- Width, height, and along-streamline dispersivities; unknown; most of the flow is horizontal thus the height dispersivity should be much lower than the along-streamline dispersivity; the width dispersivity would be between the other two values; treat as calibration parameters;

- Dimensions of the rectangular aperture through which the solute is introduced: 100m x 100m or smaller, i.e. the area of greenhouse floor;
- Anisotropy ratio: 10x cited by many for Long Island (Schubert, et al., 2004), up to 50x (Bohn-Buxton, et al., 1996);
- Recharge rate: as for Sinkevich model, 48 cm/year;
- Imidacloprid degradation rate in the saturated zone. Unknown, calibration parameter.

The Domenico model is axisymmetric around a centroid which originates at a streamline at the center of the rectangular aperture through which the solute enters. It would be useful to try to match Figure 22 which is a vertical plane at Domenico's Y=0.

A very preliminary attempt to build a Domenico extension of the Sinkevich model, along the lines of the above, yielded the conclusion that there are too many uncertain parameters in the above list to yield usable insights about the magnitudes of this site's emissions *M[]* at the surface that could have resulted in the observed magnitudes of the plume. The conclusion of this case remains that the emissions must have been much higher than the ones at any greenhouse covered in section 4.3. Thus no results will be presented for this case.

4.6 Summary of Concentrated Source Interpretations

From the cases of 4.3 with shallow to deep water tables and notably different concentration results, and from other greenhouse sites where there were no detections at 0.1µg/L or above at all, it is apparent that the routine effect of greenhouses is at most inconsequential emissions. To reach double digits would take a far higher routine rate (if even permitted on labels), probably beyond economic rationality, or it would take very sloppy housekeeping. The main reason could be degradation near the surface. Compared to an earlier problem chemical aldicarb, imidacloprid degrades faster and it sorbs more strongly to organic matter thus staying longer in the upper soil where it has a much higher probability of degrading than in the subsoil.

The averaging effect of a thick vadose zone (28-33 m) smoothens concentrations at the water table, attenuating concentration peaks. The first appearance of imidacloprid is also later than in areas with thinner vadose zones, as shown prominently by comparing Figures 42 and 43.

All of the highest observed well concentrations (e.g. above 30 μg/L) are from misuse incidents or probable accidents, which affect relatively small areas. The Lindenhurst tree case affected one lot, and the Bianchi-Weiss (Winwood Oaks) high imidacloprids were in one well.

The Sinkevich model employed uses a minimal parameter set necessary to represent a sorbing, degrading chemical entering in surface soil. It is helpful to have a tool available complementing the LEACHP model to represent the entire vadose zone thickness because Long Island has many areas with water tables over 10 meters deep. Unfortunately, even in this data-rich geographic area, there are major gaps in characterization of the vadose zone. Therefore, major assumptions about parameter values had to be made which require that wide error margins be associated with all calculated concentrations. The key assumed parameter values include: organic carbon content below the surface soil, moisture content below the surface, and degradation rate of imidacloprid below the surface.

Even with such a limited data set, important modeling inferences can be made. When the timing and extent of surface application are known, it is possible to estimate a chemical's potential earliest arrival time (within a few years), and the expected order of magnitude of its average concentration when it reaches the water table.

Instead of, or in addition to root zone or vadose zone modeling, a tool for diagnosis of saturated zone plumes would be useful to have in the pesticide assessment repertoire. The Domenico plume model is used in Pennsylvania for analysis of pesticide plumes as well as plumes of other hazardous materials (Helmke, 2015).

The trees case in Lindenhurst was a notable outlier. This could be explained if a loading spill had occurred. According to related product labels, the allowed injection rate into trees per unit of land area is many times higher than the allowed field and greenhouse usage rates. Thus, a lot of material might have been handled outdoors in the area being treated. Even if only a small fraction of the volume handled had been spilled, a concentration in the hundreds of micrograms per liter can result nearby as was observed in Lindenhurst.

A notable aspect of the greenhouse impact reconstruction in chapter 4 is that there is no way to quantify the actual emissions from the greenhouses. As has been shown in chapter 3, monitor well data imply that there are recurring pesticide emissions from some of Long Island's conventional greenhouses, probably through their sand floors. It is important not to assume that indoor use of pesticides results in zero emissions to the outdoor environment. It is equally important not to assume that handling of large quantities per unit area of pesticides for tree injection will result in zero spills. Statistically there will be some escape from these imperfect containments. Observation well monitoring at varied sites is probably the only way to measure these effects. It is very helpful to have SCDHS continue to operate a broad monitoring program that includes focal areas with concentrated sources.

Data from monitor wells in areas with shallow water tables (thus having short lag times before first appearance) can be used together with the Sinkevich model to address the difficulty associated with observing greenhouse emissions directly. As already noted, a deeper vadose zone degradation rate and specific application times and rates are important to narrow down the range of uncertainty. To the extent that a greenhouse owner cooperates with monitoring, their handling practices could be documented and paths of escape from the greenhouse mapped. It must be considered, that only the most environmentally friendly greenhouse operators will allow such scrutiny.

5. Area Source Model Case Studies

The following case studies reflect the combined effects of input loading and degradation within the root zone, and in one case deeper. Each provides insight into the observed imidacloprid magnitudes in the nearby SCDHS monitor wells. These cases, with one exception, are based on label rates and timings of imidacloprid for a specific landscape or crop thus the LEACHP model is quite helpful similarly to how DEC uses it for regulatory purposes. Vineyards are approached as in the previous chapter, using the Sinkevich model to back-calculate possible emission rates.

5.1 Common LEACHP Model Input Data used in Area Source Assessments

The LEACHP model requires extensive input data to characterize site meteorology, soil, chemical behavior in soil, and the chemical's management. Table 14 summarizes the sources of most parameters used with LEACHP for these assessments. They are evolved versions of the standard NYS DEC pesticide modeling data set, to improve flexibility and documentation of underlying sources.

Table 15: Common LEACHP parameters

LEACHP Parameter	**Sources**	**Processing and assumptions**
Precipitation (daily) - Riverhead Research Farm and Bridgehampton	NOAA National Climatic Data Center, Climate Data Online (National Climate Data Center, 2016)	Fill in missing daily values from other station of the two. Raw values are passed through a degree-day snow fall and melt algorithm to convert from total precipitation into rainfall + snowmelt, then those two are combined as LEACHP "precipitation". Delete days with zero rain + snowmelt.
Air temperature (weekly) - Riverhead Research Farm and Bridgehampton	(included with daily precipitation)	Fill in missing daily values from other station of the two. Average over weeks.
Potential evapotranspiration (weekly)	Hamon's method based on air temperature (Hamon, 1961)	
Soil texture, saturated hydraulic conductivity, organic matter content, bulk density	USDA digital soil survey for Suffolk County (Soil Survey Staff, Natural Resources Conservation Service, USDA, 2013)	Adapt profile to 100 mm layers used in LEACHP (11 layers, 1100 mm total)
Vertical root distribution per crop and soil layer	DEC defaults for potatoes (provided by J. Hutson, LEACHP developer, originally).	Potatoes: roots=c(0.25,0.30,0.30,0.10,0.05,0,0,0.0,0.0,0.0,0.0) Turf: roots= same as potatoes
Imidacloprid properties: solubility, vapor density, Freundlich sorption KOC and exponent	European Pesticide Properties Database (Lewis, et al., 2016)	Solubility: 610 mg/L Vapor density: 0.1E-8 Freundlich kfoc:225 Frendlich exponent: 0.802
Initial moisture content of soil profile, as suction	Assumed partly saturated.	Set to -10 kPa in every layer.
Imidacloprid degradation rates, upper and lower	European PPD for upper layers.	Upper degradation rate (top 30 cm) set to 0.004/day. Lower degradation rate arbitrarily set to 1/4 of upper rate = 0.001/day.
Imidacloprid application rates, timings, and depths	Product labels and discussions (see individual cases)	

Table 16 presents the detailed soil properties per soil, as interpreted from the USDA digital soil survey (Soil Survey Staff, Natural Resources Conservation Service, USDA, 2013). The uppermost organic layer in the soil survey data was not included in the LEACHP profile.

Table 16: Detailed LEACHP soil layer parameters (R Project notation)

Property	**Riverhead Sandy Loam**	**Bridgehampton Silt Loam**
Symbol	RdA	BgB
Layering	11 layers x 100mm each	11 layers x 100mm each
Texture	clays= c(10, 10, 10, 10, 10, 10, 10, 5, 5, 2, 2), # % silts= c(21, 21, 21, 23, 23, 23, 23, 17, 17, 2, 2), # %	clays= c(12, 12, 12, 12, 12, 12, 12, 12, 12, 12, 12), # % silts= c(59.7, 59.7, 59.7, 67.3, 67.3, 67.3, 67.3, 67.3, 67.3, 67.3, 67.3), # %
bulk density	bd= c(1.3, 1.3, 1.3, 1.5, 1.5, 1.5, 1.5, 1.5, 1.5, 1.6, 1.6), # g/cm^3	bd=c(1.18, 1.18, 1.18, 1.39, 1.39, 1.39, 1.39, 1.39, 1.39, 1.39, 1.39), # g/cm^3
saturated hydraulic conductivity	kh= c(2419.0, 2419.0, 2419.0, 2419.0, 2419.0, 2419.0, 2419.0, 2419.0, 2419.0, 12182.0, 12182.0), # mm/day	kh=c(778.0, 778.0, 778.0, 778.0, 778.0, 778.0, 778.0, 778.0, 778.0, 778.0, 778.0), # mm/day
organic carbon	ocs <- c(1.7, 1.7, 1.7, 0.6, 0.6, 0.6, 0.6, 0.3, 0.3, 0.15, 0.15) # %	ocs <- c(5.0, 5.0, 5.0, 0.75, 0.75, 0.75, 0.75, 0.75, 0.75, 0.75, 0.75) # %

Table 16 source: (Soil Survey Staff, Natural Resources Conservation Service, USDA, 2013)

5.2 Sensitivity Analysis of LEACHP

The most available critical input data for LEACHP in Suffolk County are soil characteristics, meteorology, and crop type, which determines the imidacloprid use regime. The less available critical input data are sorption parameters and degradation rates, which interact to determine the near-surface division of imidacloprid among the fates of plant uptake, degradation, soil carryover, and deep leaching.

Later sections in this chapter explore different application rates, timings, and depth of incorporation as a function of land type, such as potato fields or golf courses.

A brief LEACHP sensitivity analysis was performed to illustrate the effect of uncertainty in degradation and sorption parameters. Nominal parameter values are based on an international pesticide properties database. The sensitivity analysis varied degradation and sorption parameters by halving and doubling from the nominals. Table 17 enumerates all cases including a LEACHP runID value, which serves to distinguish simulations from one another.

This was for a hypothetical potato field near Bridgehampton on Bridgehampton soil. The field was assumed to receive a total of 3.08 kg/ha imidacloprid over four years 1995-1998 (maximum label rates for in-furrow plus later foliar treatments), then four additional years were simulated with no input which serves to wash the earlier-applied imidacloprid deeper in soil, or be taken up by subsequent crops, or degraded.

Table 17: LEACHP sensitivity analysis combinations

	Degradation: 0.002/day surface, 0.0005/day deeper	**0.004/day surface, 0.001/day deeper (nominal values)**	**0.008/day surface, 0.002/day deeper**
Freundlich sorption multiplier: 112.5	case 472 (*mobile and persistent*)	case 372 (*mobile and nominal*)	case 772 (*mobile and ephemeral*)
225 (nominal)	case 572 (*nominal and persistent*)	case 272 (*both nominal*)	case 872 (*nominal and ephemeral*)
450	case 672 (*sticky and persistent*)	case 172 (*sticky and nominal*)	case 972 (*sticky and ephemeral*)

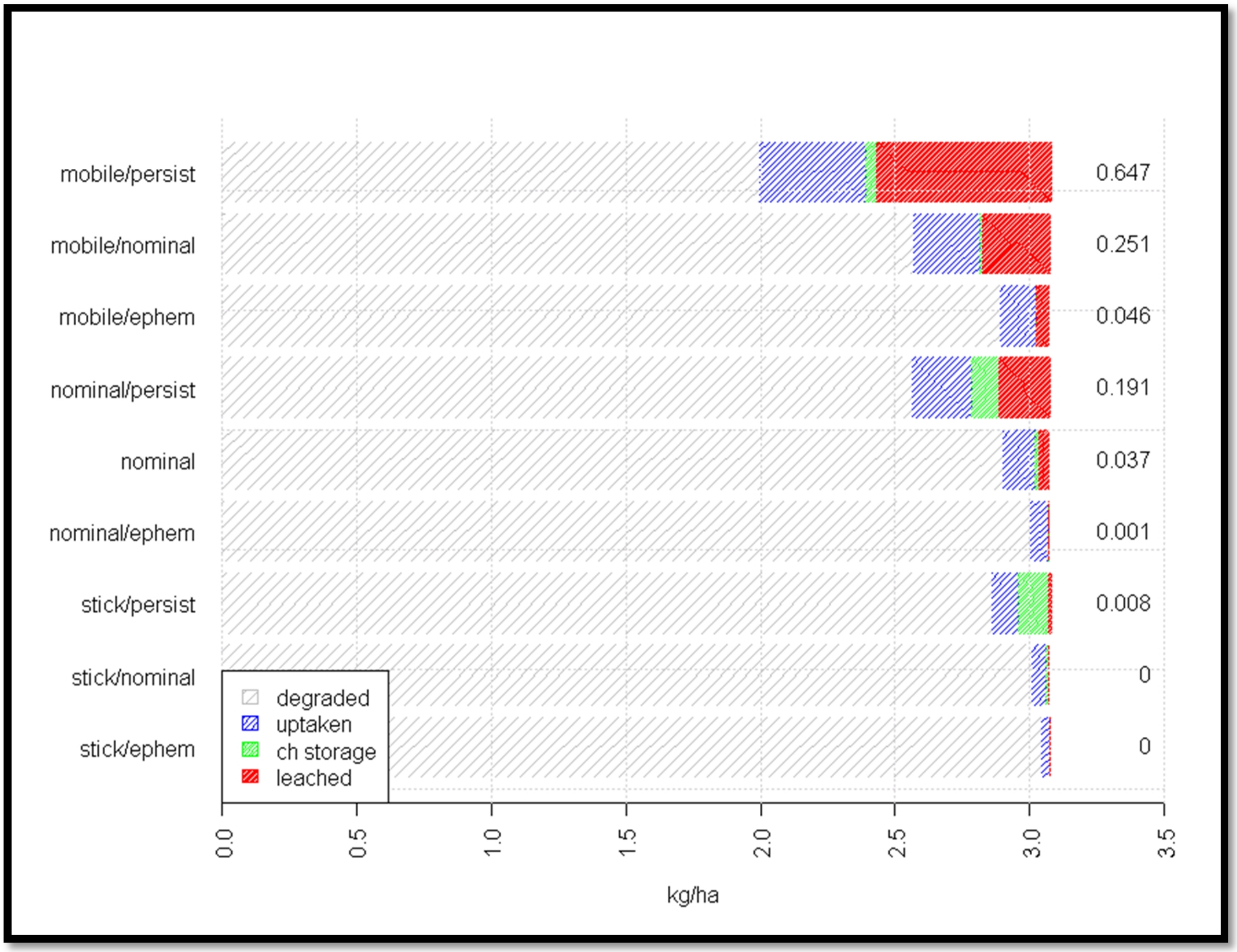


Figure 46: 8-year mass balances for potatotes as a function of sorption and degradation

Figure 46 Caption: Total length of each bar represents the input loading (all same in this case). The four possible fates of the input are represented by stacked bar segments. The amount leached is in the red segments, repeated as a number at right.
R-Project code:

```
plotMassbalL4( runids=c(972,172,672, 872,272,572, 772,372,472),
xlim=c(0,3.5), density=c(15,30,50,100), cap=c("stick/ephem",
"stick/nominal", "stick/persist", "nominal/ephem", "nominal",
"nominal/persist", "mobile/ephem", "mobile/ephem",
"mobile/persist" ), ylab="")
```

Figure 46 presents mass balance results of all cases. The most mobile and most persistent case has the highest leaching at around 20% of the 3.08 kg/ha cumulative input. Leaching is essentially zero for the sticky and ephemeral and the sticky and nominal cases. The sticky cases also make plant uptake more difficult. There is some carryover in soil past the eighth year (green segments) when degradation is at its lowest rates.

Figures 47, 48, and 49 present time series results for three combinations of sensitivity cases, always including the centered nominal case.

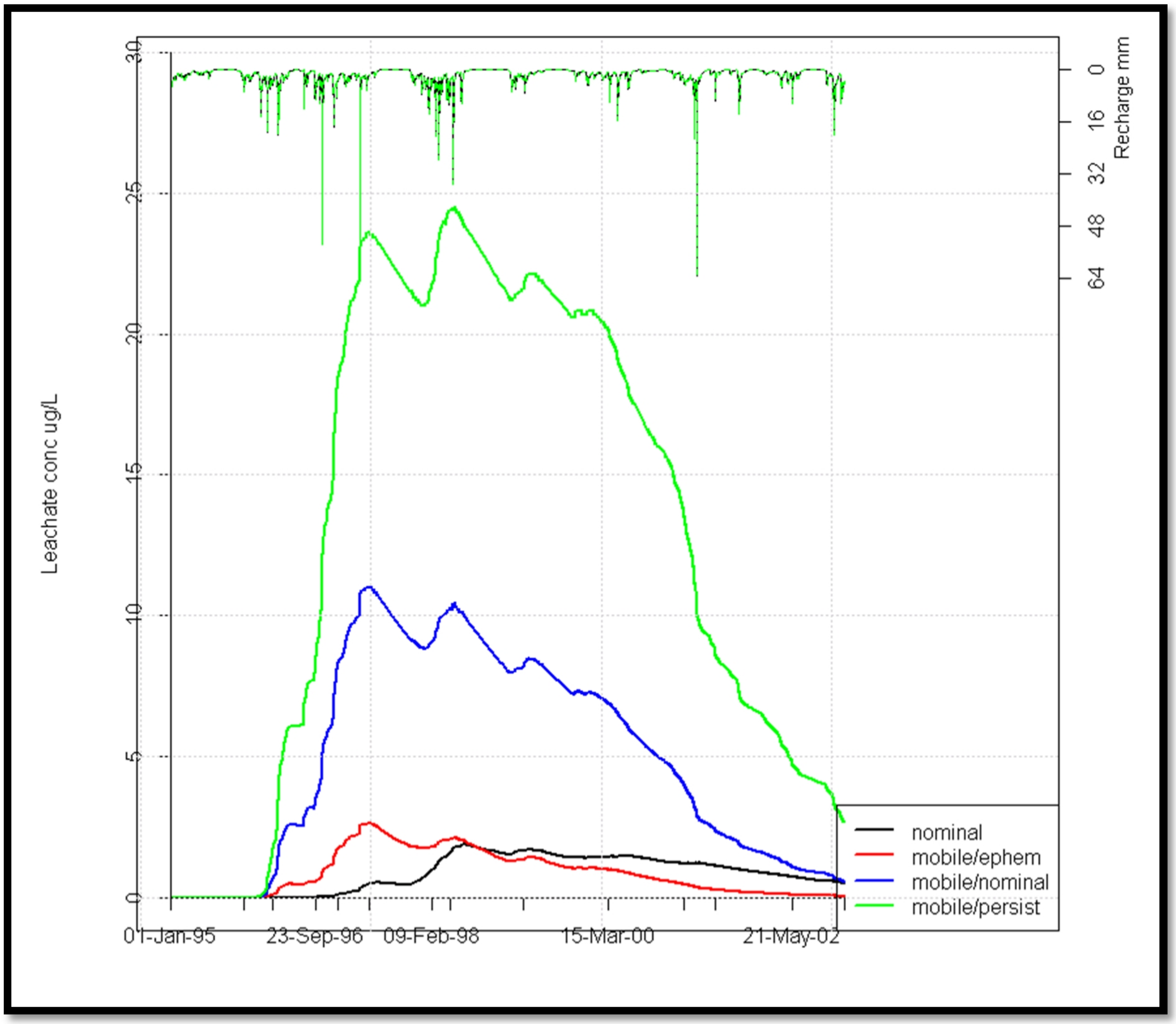


Figure 47: Effect of degradation on peak concentrations (low sorption)

With low sorption, peak concentrations appear about one year earlier than nominal. The slowest degradation rate led to 12x higher peaks than nominal, and the fastest degradation yielded results similar to nominal (including nominal sorption).

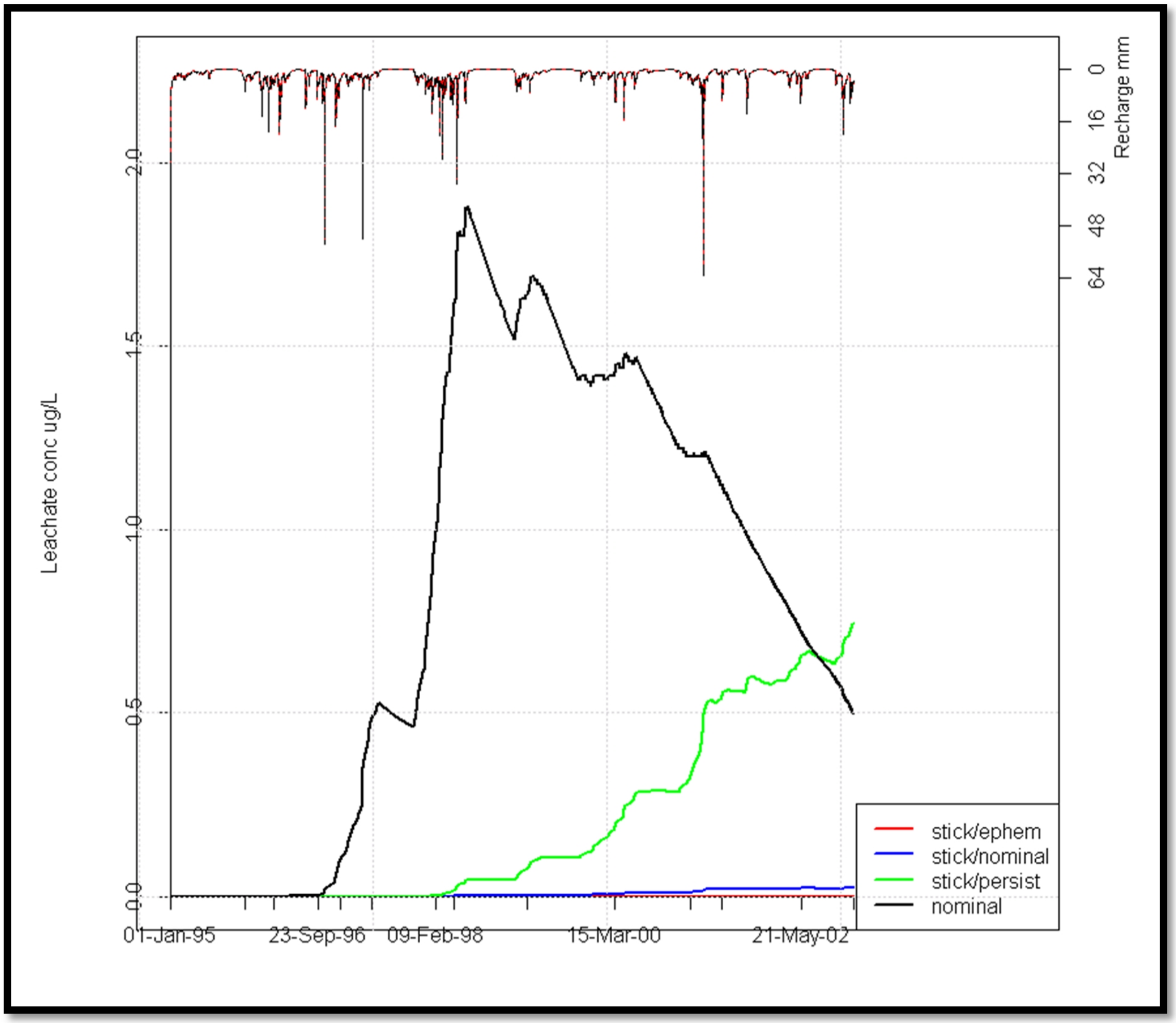


Figure 48: Effect of degradation rates on peak concentrations (stickiest sorption) (with nominal)

The doubled sorption leads to a much longer time lag before breakthrough to 1.1m depth, providing more time for degradation compared to the nominal sorption case. Concentrations were still rising at 8 years after the simulation began in the highest-persistence cases. There was almost no leaching with nominal to short degradation times.

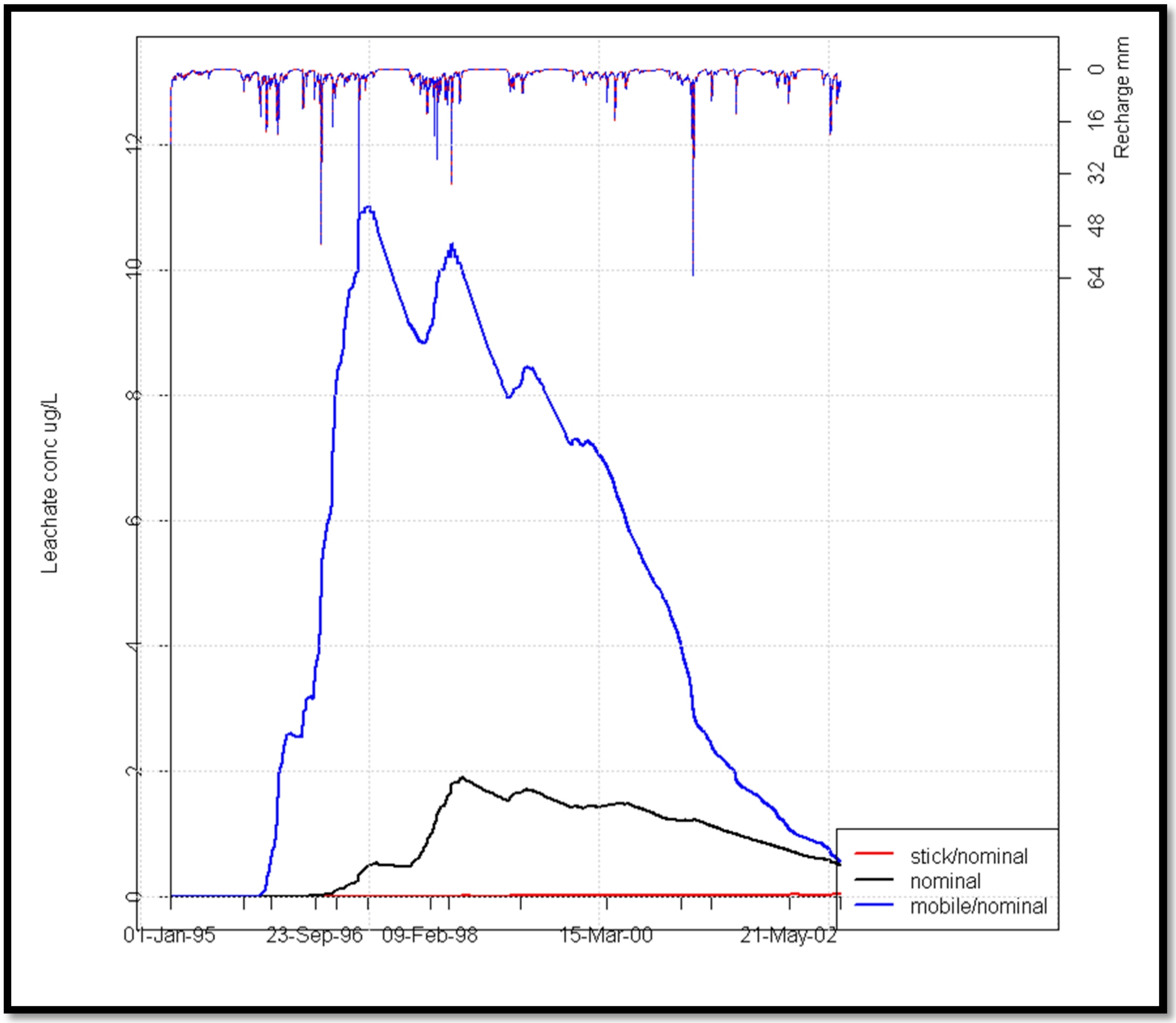


Figure 49: Effect of sorption on peak concentrations (nominal degradation)

At nominal degradation the sorption range has a major effect, the most mobile case yielding a peak concentration at 5x the peak of nominal. At its stickiest, essentially no solute broke through.

These results demonstrate the robust integration of processes in LEACHP -- the parameters interact and affect leaching realistically.

The various sensitivity cases demonstrate that there is considerable uncertainty about peak concentrations at 1.1 meters and the earliest peak's arrival when applying LEACHP with no local data about sorption and degradation rates. It is sensible to attach a confidence band of at least a factor of 5 to simulated peaks, and a somewhat lower factor to simulated averages and mass balances.

5.3 Note: Recharge Differences Between Riverhead and Bridgehampton

The diagnostic simulations with LEACHP use data from two sites, Riverhead and Bridgehampton. These are 29 km apart. The latter (Runids 278 and 1) had considerably more rainfall during the modeled period 1996-2003, which translated into an extra meter of recharge over eight years (Table 18 and Figure 50). Evapotranspiration was around 300 mm greater at Riverhead. The soils also contribute some difference, Bridgehampton soil (runid 278) contributing 80mm more recharge than Riverhead (runid 1).

As just one illustration, during a storm on July 31 and August 1, 1996, Bridgehampton reported 132 mm of rain and Riverhead reported 48mm.

Table 18: Water budget differences between Bridgehampton and Riverhead weather (1996-2003) and soil

Run ID	Weather station	Soil series	Precipitation (mm in 8 yrs)	Recharge (mm)	Evapotrans-piration (mm)	Change in storage (mm)
278	Bridgehampton	Bridgehampton	10165	5010	5216	-66.7
1	Bridgehampton	Riverhead	10165	4930	5158	63.2
277	Riverhead	Riverhead	9459	3877	5511	57.7

The stronger cumulative recharge from Bridgehampton weather would wash more pesticide deeper into lower-degradation subsoil and out of the bottom of the 1.1 meter soil column. This demonstrates the sensitivity of site selection for simulating pesticide leaching.

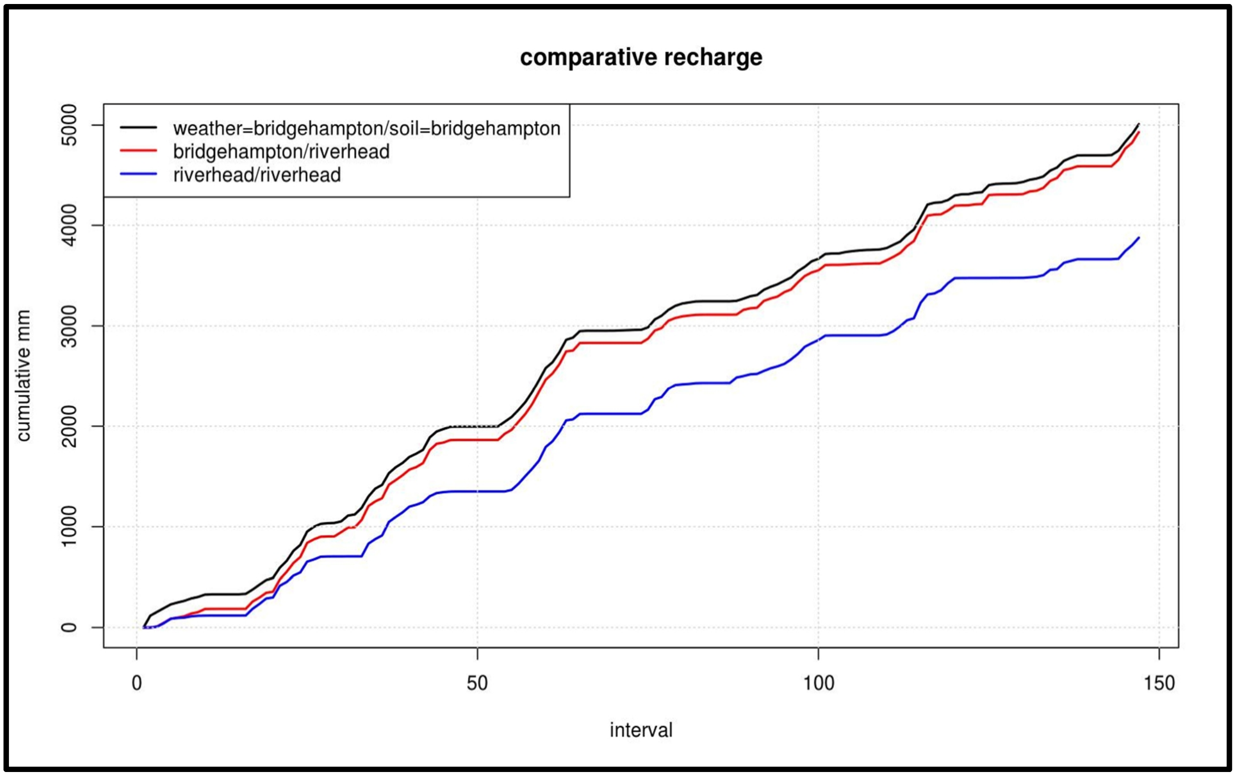


Figure 50: Cumulative simulated recharge at Bridgehampton and Riverhead (20 day intervals)

5.4 Potatoes (LEACHP)

Using “Cornell Recommends field guides” (Cornell University, Cooperative Extension, various, Vegis), regional planting and potato life cycle dates, and the registered pesticide labels for these products, application schedules representing differing potential allowed, recommended and problem use patterns were formulated, and represented as LEACHP input data. Both maximum and minimum application rates for both products, used singularly or in combination were examined for annual crops and rotated crops. Since "Cornell Recommends" guides and labels both recommend alternating years of product use, such as for crop rotation, application schemes and case scenarios for annual and rotated use of each product individually and both products together were devised.

The models were each simulated for an 8-year period beginning in 1995 when Imidacloprid first became available for use in the region. Treatment was for the entire period, instead of interrupted after four years as it was in the sensitivity analysis. The approach is very similar to that used for DEC registrants' simulations, in which real weather and soil data for a specified period is combined with chemical properties and application rates representing what could be on a label. DEC requires applications each year to be evaluated unless the label restricts to alternate years. Variations from DEC specifications for LEACHP were made to exactly match the beginning of imidacloprid use on Long Island instead of 1965-1972, and cover Riverhead plus Bridgehampton locales to explore intra-regional differences.

For potatoes, Admire is labeled for a single application per year at an application rate range of 0.26-0.56 Kg/AI/Ha; it is applied in furrow, at planting, only. A selected few Admire-only application scenarios modeled are shown in Table 19.

Table 19: Application schemes for Admire only (from product label and Cornell Recommends) (eight years)

Model ID (runID)	Admire (8 years)					
	Application rate (kg/ha)	# of appli-cations / year	Application Mode	Model Depth Layer	Rotation?	Location
Ad1xBr (56)	0.56	1	In Furrow	2 (10-20 cm)	No	Bridge-hampton
Ad2xBr (52)	1.12	1	In Furrow	2	No	Bridge-hampton
Ad1xRi (55)	0.56	1	In Furrow	2	No	Riverhead
Ad1xAlt Br (62)	0.56	1 every other year	In Furrow	2	Yes	Bridge-hampton

Model Ad2xBr is a deliberate exaggeration: double the label's maximum application rate applied once per year, every year. While it is unlikely that a farmer would over-apply deliberately, the doubled rate serves as a worse case for comparison to the maximum legal rates. Cases Ad1xRi andAd1xBr apply each year at the labeled rate using Riverhead and Bridgehampton soil and weather respectively. Case Ad1xAltBr is the maximum application rate applied once in alternate years.

In contrast with Admire, which is labeled for a single application each season in furrow at planting, and is labeled for a range of application rates, Provado is applied by foliar spray applications after planting, is only labeled for one application rate (0.0525 kg/Ha), and can be applied as many as four times per season. Greater numbers of applications at the labeled rate are known to cause crop damage and are thus not beneficial. The scenarios modeled for when

Provado is used alone are detailed in Table 20 and are each modeled for the maximum of four applications, each year of use. (Pr1xAltBr represents rotated use thus skips every other year.)

Important: LEACHP does not represent photodegradation thus a surface application like Provado's will lead to unrealistically high net input to soil unless there is rain right away to wash the imidacloprid deeper out of reach of the sun. The rate could be reduced to take this factor into account.

Table 20: Provado-only application schemes modeled for potatoes (five years)

Model ID (runID)	Application rate (kg/ha)	# of appli-cations per year	Application Mode	Depth Layer	Rotation?	Location
Pr1xBr (66)	0.0525	4	Foliar	0 (at surface)	No	Bridge-hampton
Pr2xBr (64)	0.1050	4	Foliar	0	No	Bridge-hampton
Pr1xRi (65)	0.0525	4	Foliar	0	No	Riverhead
Pr1xAltBr (70)	0.0525	4 every other year	Foliar	0	Yes	Bridge-hampton

These cases are analogous to the Admire cases in that one of the four goes beyond actual labeled maximum rates.

As discussed earlier, and understood from discussions with CCE staff, local farmers and literature, most potato growers in Suffolk County use both Admire and Provado together each year, or in alternate years. When Admire and Provado are used together, the first application of Provado follows the initial Admire application at planting by approximately 5 weeks, when plants have emerged and root structures have been established. The application schemes modeled when both products are used together are shown in Table 21 below.

Table 21: Application schemes modeled for combined Admire and Provado use for potatoes

Model ID (runID)	Provado			Admire			
	Appli-cation rate (kg/ha)	Applications per year	Rotation?	Application rate (kg/ha)	Applications per year	Rotation ?	Location
Ad1xPr1xBr (78)	0.0525	4 foliar, layer 0	No	0.56	1 in furrow, layer 2	No	Bridge-hampton
Ad2xPr2xBr (72)	0.1050	4 foliar, layer 0	No	1.12	1 in furrow, layer 2	No	Bridge-hampton
Ad1xPr1xRi (77)	0.0525	4 foliar, layer 0	No	0.56	1 in furrow, layer 2	No	Riverhead
Ad1xPr1xAltBr (82)	0.0525	4 foliar, layer 0	Yes	0.56	1 in furrow, layer 2	Yes	Bridge-hampton

The mass balances generated by LEACHP for each scenario in Tables 19, 20, and 21 are shown in Figure 50.

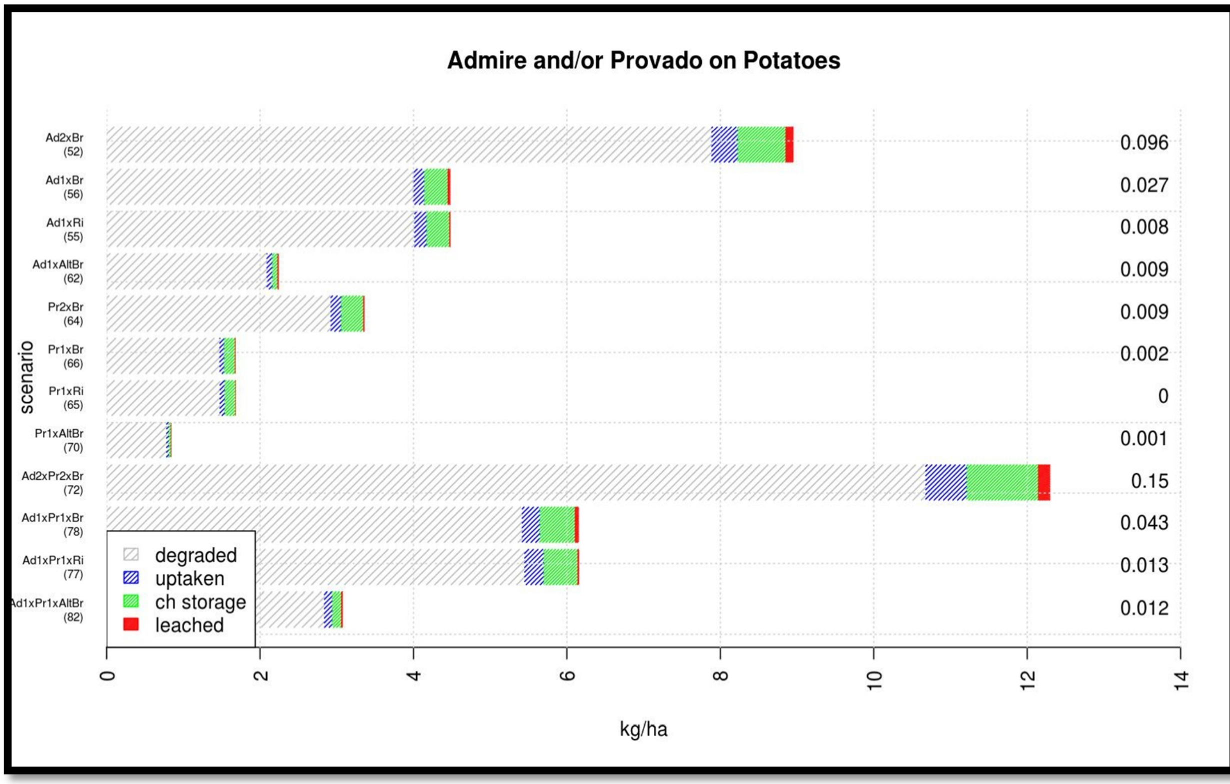


Figure 51: Mass Balances for Modeled Potato Cases

Figure 51 Caption: See Figure 46 caption for explanation of symbolism.
R-project code for plotting:

```
plotMassbalL4(
runids=rev(c(52,56,55,62,64,66,65,70,72,78,77,82)),
xlim=c(0,14), main="Admire and/or Provado on Potatoes",
cap=rev(c("Ad2xBr\n(52)","Ad1xBr\n(56)","Ad1xRi\n(55)",
"Ad1xAltBr\n(62)", "Pr2xBr\n(64)", "Pr1xBr\n(66)",
"Pr1xRi\n(65)", "Pr1xAltBr\n(70)", "Ad2xPr2xBr\n(72)",
"Ad1xPr1xBr\n(78)", "Ad1xPr1xRi\n(77)", "Ad1xPr1xAltBr\n(82)"
)), plotfile="lp-potatoes-massbal-2" )
```

Interpretation of the mass balance begins with the greatly varied input amounts over the 8-year simulations period, as represented by the total widths of the stacked bars. Inputs ranged from 1.0 kg total to 9.0 kg. Table 22 normalizes for the different inputs to display the percentage of the applied imidacloprid that leached.

Table 22: Fractions leached for potato scenarios

Product(s)	Model	RunID	Input (kg)	Leached (kg)	Leached %
Admire	Ad1xBr	56	8x0.56=4.5	0.027	0.6
	Ad2xBr	52	8x1.12=9	0.096	1.1
	Ad1xRi	55	8x0.56=4.5	0.008	0.2
	Ad1xAltBr	62	4x0.56=2.2	0.009	0.4
Provado	Pr1xBr	66	8x4x0.05=1.6	0.002	0.1
	Pr2xBr	64	8x4x0.105=3.3	0.009	0.3
	Pr1xRi	65	8x4x0.05=1.0	0.000	0
	Pr1xAltBr	70	4x4x0.05=0.8	0.001	0.1
Admire + Provado	Ad1xPr1xBr	78	8x0.56+32x0.05 =6.1	0.043	0.7
	Ad2xPr2xBr	72	8x1.12+32x0.105 =12.3	0.150	1.2
	Ad1xPr1xRi	77	8x0.56+32x0.05 =6.1	0.013	0.2
	Ad1xPr1xAltBr	82	4x1.12+16x0.05 =5.3	0.012	0.2

Solute degradation dominates in all cases. The doubled in-furrow Admire introduced the most chemical and produced the second highest leaching; for Bridgehampton about 1% (0.096 kg/ha) was leached over eight years. The highest amount leached was also around 1% of the applied 12 kg/ha amount for the doubled-legal Admire+Provado cases.

The difference between Riverhead and Bridgehampton is interesting. Bridgehampton had 62 cm of recharge per year for the period, compared to Riverhead's 48 cm. This has two causes. First, the Bridgehampton soil retains water much more tightly than the Riverhead, thus inhibiting transpiration. If the water doesn't evaporate, it will flow downwards. Second, there was a major storm spanning July 31 and August 1, 1996, which dropped 131mm of rain at Bridgehampton and just 47mm of rain at Riverhead. July had been wet thus there was extra recharge from this intense storm, much more at Bridgehampton.

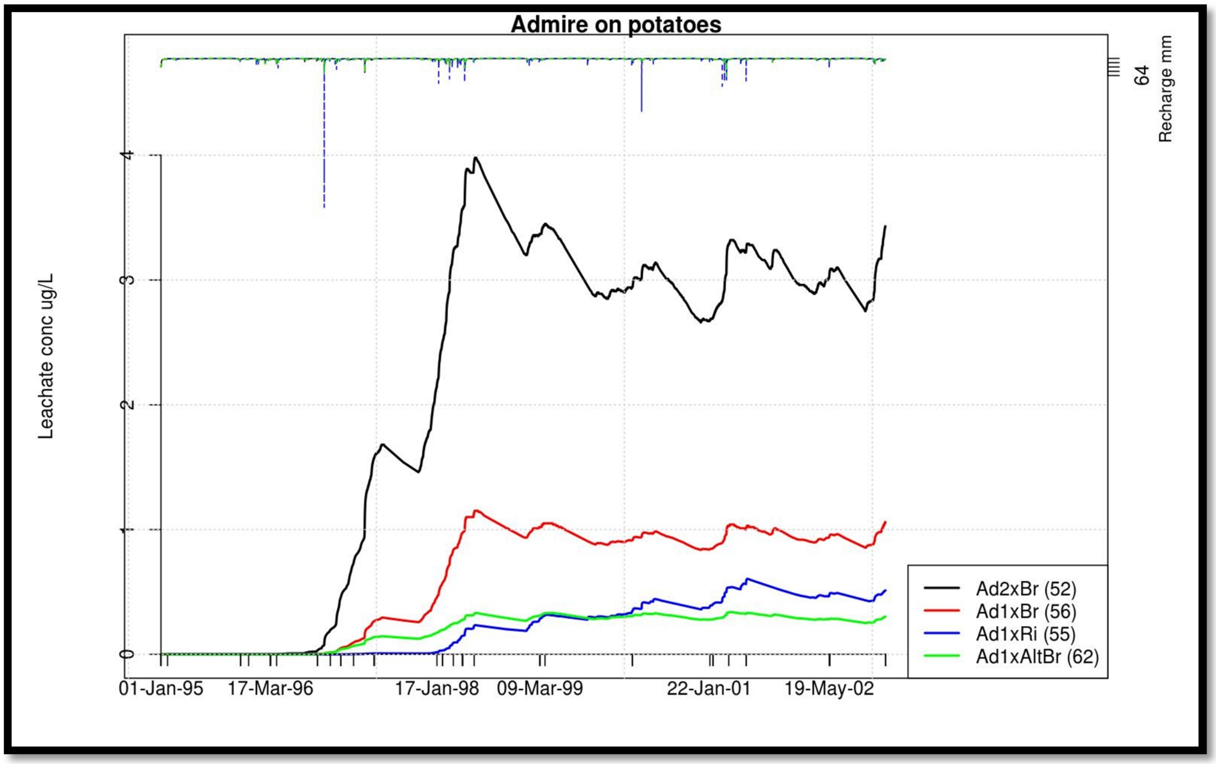


Figure 52: LEACHP time series for Admire only potato cases

For the Admire-only cases (Figure 52), the highest leachate concentrations predictably resulted from case Ad2xBr which included annual applications at double the maximum-labeled application rate (compare to the red trace at exactly the label rate). The peak leachate concentration for this scenario was 4 µg/L. Alternating years at label rates (green trace) was about half as intense as single rates every year (red trace).

Figure 53 indicates that Provado-only foliar regimes yielded much lower concentrations, starting off with over 4x less inputs than the Admire cases and introducing the imidicloprid higher in the profile where it would have a greater chance to degrade or be taken up. At its highest, the doubled-legal (black trace) leachate concentration was 10x lower than using Admire alone at doubled-legal.

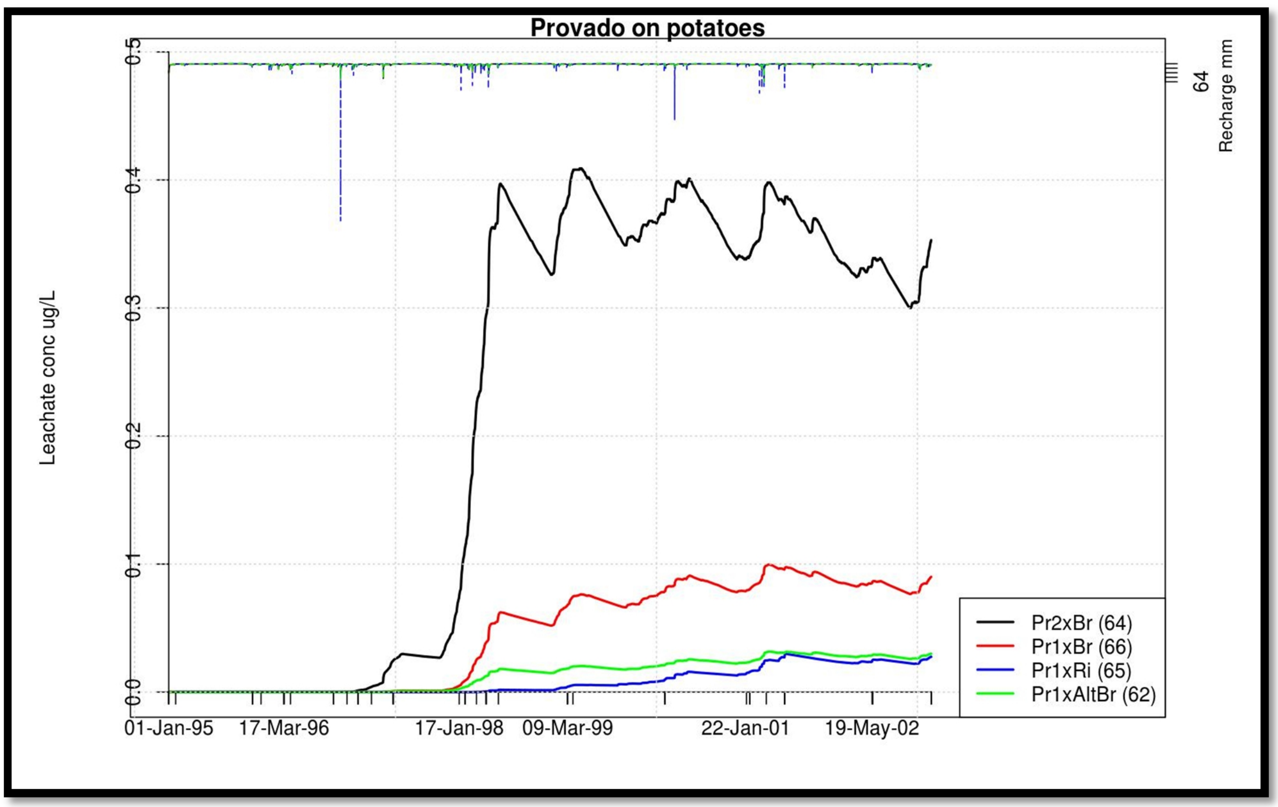


Figure 53: LEACHP time series plots for Provado only cases

Combining the two types of treatments over 8 years of application, the cases in Figure 53 have peaks up to 6 µg/L from doubled label rates.

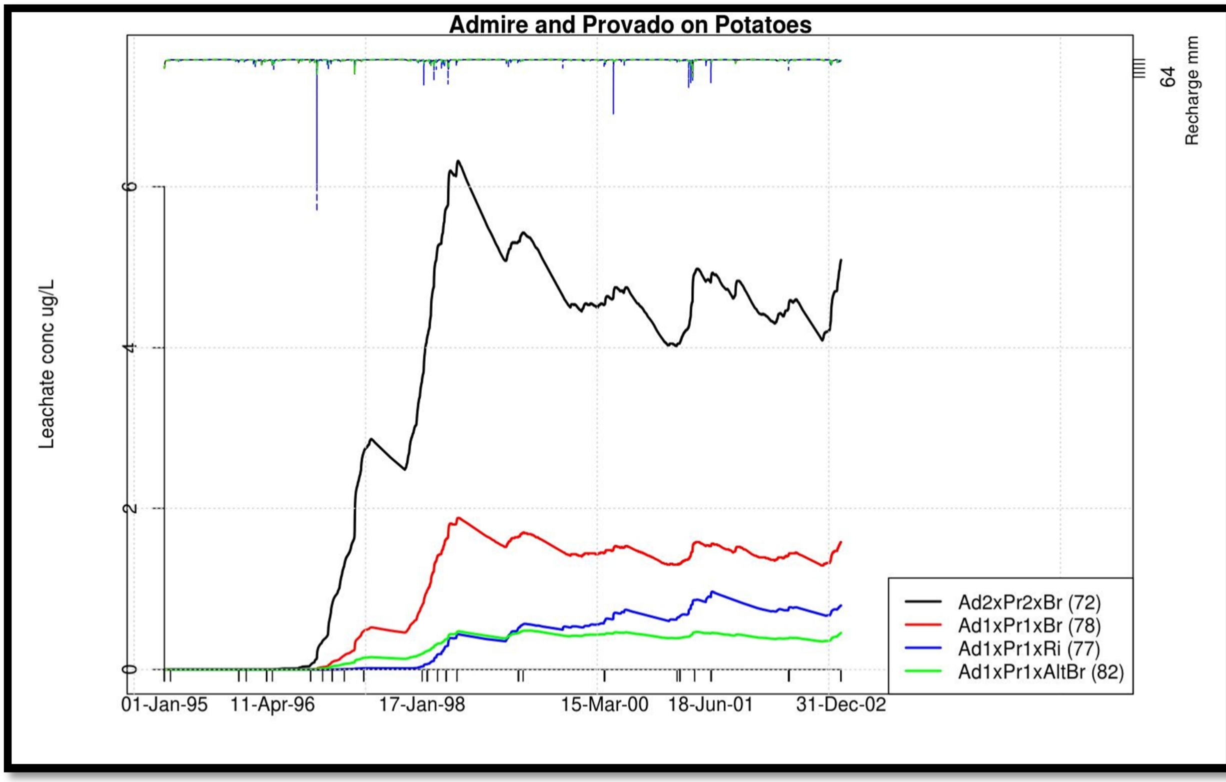


Figure 54: LEACHP time series output for combined Admire and Provado cases for potatoes

When Admire is applied at its maximum labeled rate, once annually, and Provado is also applied 4 times annually at the labeled rate, the highest concentrations of residue at the same 1.1m depth is near 2 μg/L. Figure 54 combines this scenario plus the label-rate Admire-only and Provado-only scenarios together with the monitor well (B-4 and B-5) data. With the monitor wells tapping a water table at 7-10 meters below the land surface, the travel time needed for the root zone leachate to reach the water table allows for additional solute degradation. The highest detection recorded was sampled from well B-4 was 0.68 μg/L at > 10 meters below the land surface. This magnitude is consistent with dual usage of Admire and Provado at the adjacent field, or perhaps Admire only. Note that the observed 0.68 was after the end of the modeled period though the box rises that high. The modeled scenario reaches a sort of equilibrium after about four years of repeating input, thus we would expect that an extension of the modeling period would continue to yield results around what occurred in the latter three years of the modeled period (1995-2002)

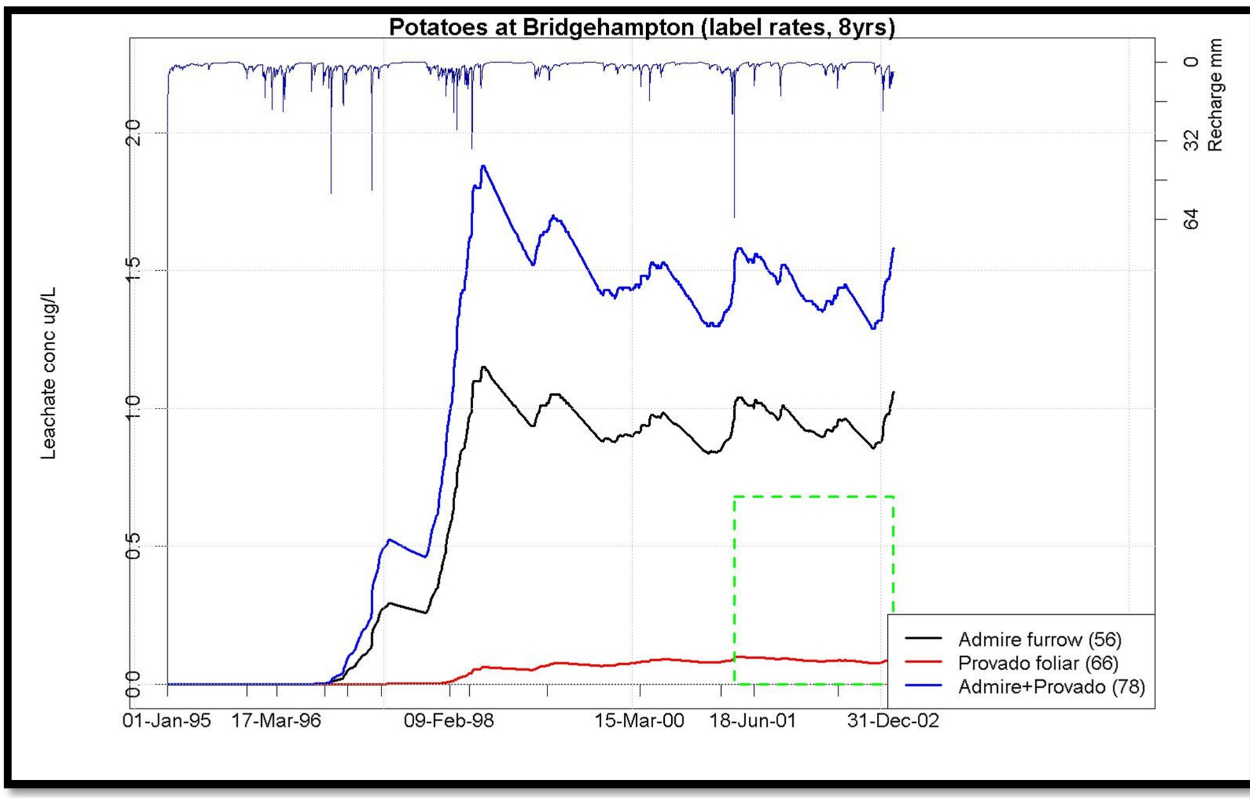


Figure 55: LEACHP output for potatoes at legal rates, vs. observations at 5m wells

Figure 55 Caption: The green dotted rectangle represents the range of observed concentrations in wells B-4 and B-5 at 5m depth, non-detect to 0.68 µg/L, from April 2001 through June 2005 (past the end of the simulated period). The solid lines represent LEACHP results at 1.1m for 8 years of use of the two products indicated at label rates.

The main conclusion from the LEACHP potatoes simulations is that the simulated concentrations from ordinary, maximum labelled use are consistent with monitor well data. As with aldicarb, LEACHP and available data to estimate parameters with no curve fitting simulate realistic magnitudes of imidacloprid in recharge. Ordinary use of imidacloprid on potatoes provides better than 10-fold headroom below the applicable drinking water criterion of 50 µg/L, as long as users obey the labels.

5.5 Golf Courses, Turf, and Lawns (LEACHP)

From PSUR data, it was determined that Merit 2F (BayerAG) is the most commonly used product for treatment and maintenance of grub populations on lawns and turf and in golf courses. Using the product label, "Cornell recommends" guides (Cornell University, Cooperative Extension, various, Turf) and information provided by members of the Nassau Suffolk Landscape Gardeners Association, application schedules for golf course, lawn and turf uses were devised. In golf courses, a single yearly application, usually during the first week of July, is standard. The labeled application rate for Merit 2F ranges from 0.35-0.45 kg/Ha per application and the application schemes modeled for golf course applications are detailed in Table 23. The Riverhead weather station is the default for the turf simulations instead of Bridgehampton used for potatoes, with Bridgehampton provided as an alternate.

Table 23: LEACHP imidacloprid inputs for commercial and institutional turf, one application per year (emphasizing golf courses)

Model ID (runID)	Merit 2F					
	Application Rate	# of Applications per year	Application Mode	Depth Layer	Weather Station	Description
1@MaxRi (154)	0.45	1	soil drench	0	Riverhead	Maximum Application Rate
1@2xMaxRi (156)	0.9	1	soil drench	0	Riverhead	2x Maximum Application Rate
1@4XMaxRi (158)	1.8	1	soil drench	0	Riverhead	4xMaximum Application Rate
1@4XMaxBr (157)	1.8	1	soil drench	0	Bridgehampton	4xMaximum Application Rate
1@4XMax/2Ri (171)	1.8	1 in alternate years	soil drench	0	Riverhead	4xMaximum Application Rate, every other year.

Most of the simulations exaggerate 2x or 4x beyond the legal labeled rate because it was found that label rates would be simulated to result in trace or non-detectable concentration ranges (below 0.2 µg/L). This is because of the modest base rate (below half a kilogram per hectare) and the application at the surface which provides extra soil residence time thus more opportunity for degradation or plant uptake. (And for the unmodelled process of photodegradation.)

The turf simulations thus have more of a flavor of "what does it take to reach single digit concentrations at 1.1m" than the potatoes simulations.

For lawn care, Merit 2F is labeled for a maximum of two treatments per year: first in early summer and second in late August. Twice annual applications of Merit 2F, are common in professionally maintained residential, commercial and institutional lawns and playing fields. The application rate for Merit 2F for lawn uses is the same as for golf courses and ranges from 0.35-0.45 kg/Ha per application. Though none of the SCDHS monitor wells can be sufficiently isolated to model only lawn application patterns, private and institutional lawn uses are significant and must be considered. The application schemes modeled for private and professional lawn care use scenarios are detailed in Table 24.

Table 24: LEACHP imidacloprid inputs for turf, two applications per year (emphasizing lawns)

Model ID (runID)	Merit 2F					
	Application Rate	# of Applications per year	Application Mode	Depth Layer	Weather Station	Description
2@MaxRi (166)	0.45	2	soil drench	0	Riverhead	Maximum Application Rate
2@2xMaxRi (169)	0.9	2	soil drench	0	Riverhead	2x Maximum Application Rate
2@4XMaxRi (177)	1.8	2	soil drench	0	Riverhead	4xMaximum Application Rate
2@4xMaxBr (178)	1.8	2		0	Bridge-hampton	4xMaximum Application Rate
2@4XMax/2Ri (170)	1.8	2 in alternate years	soil drench	0	Riverhead	4xMaximum Application Rate, every other year.

Figure 56 and Table 25 summarize the mass balances for these two sets of turf scenarios. The different amounts applied correlate well with the mass leached over eight years. The Bridgehampton recharge difference from Riverhead again yields a notably higher (over 2x) leached mass at Bridgehampton. Doubling and quadrupling the application rates (per time applied) lead to much higher than doubling and quadrupling the leached masses. Finally, two applications per year more than double the mass loss to recharge. Combining these factors, two applications at 4x label rate (2@4xMaxRi) compared to on application at label rate (1@MaxRi), together an 8x increase in input, led to nearly a 100x increase in leached mass.

This is realistic for the type of application regime being modeled. When there are several smaller applications the fractions that can be taken up by turf or degraded are at their highest. A high single application is most subject to a leaching event that washes the solute molecules away from their fastest/degrading/most-uptaken top layer into deeper layers with fewer roots and the lower degradation rate, before the slower processes of degradation and uptake can destroy or sequester them. Smaller, more frequent applications have a better chance of evading leaching events.

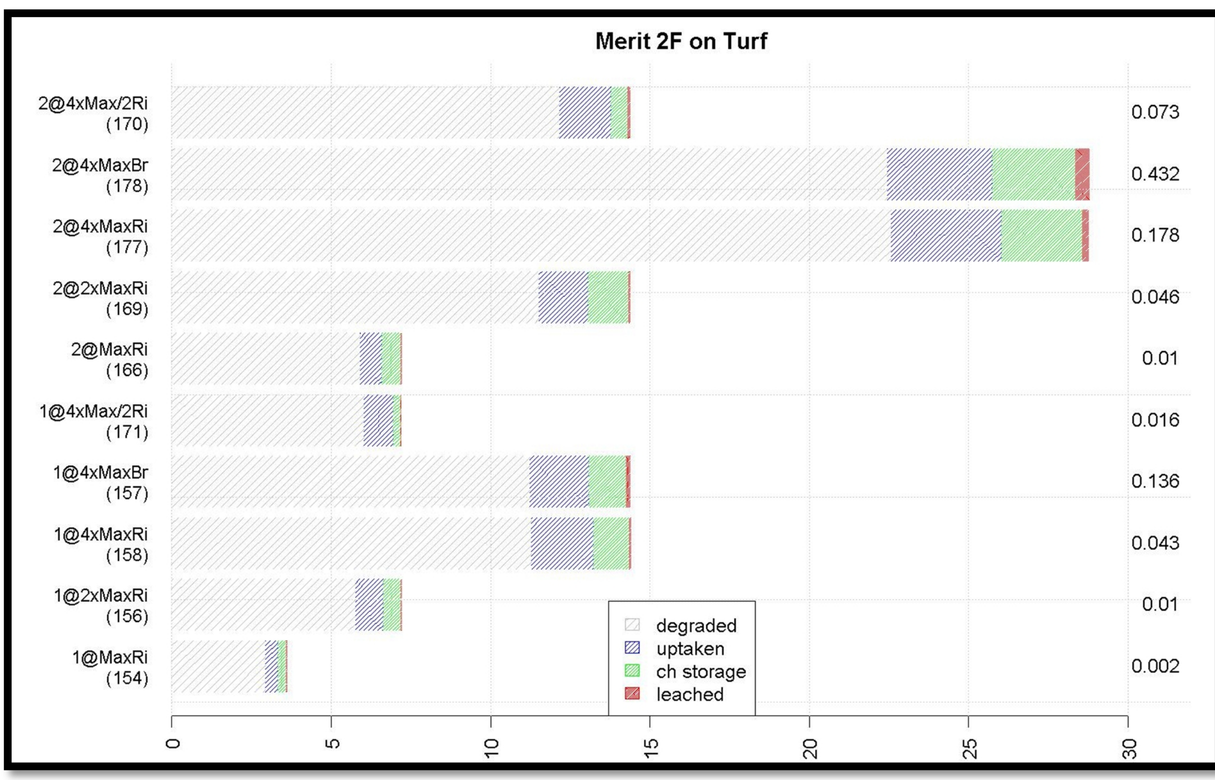


Figure 56: Mass balances for modeled turf cases

Table 25: Fractions leached for LEACHP turf scenarios

Land use	Model	RunID	Input (kg)	Leached (kg)	Leached %
Lawns	2@4xMax/2Ri	170	4x2x1.80=14.4	0.073	0.5
	2@4xMaxBr	178	8x2x1.80=28.8	0.432	1.5
	2@4xMaxRi	177	8x2x1.80=28.8	0.178	0.6
	2@2xMaxRi	169	8x2x0.90=14.4	0.046	0.3
	2@MaxRi	166	8x2x0.45=7.2	0.010	0.1
Golf	1@4xMax/2Ri	171	4x1.80=7.2	0.016	0.2
	1@4xMaxBr	157	8x1.80=14.4	0.136	0.9
	1@4xMaxRi	158	8x1.80=14.4	0.043	0.3
	1@2xMaxRi	156	8x0.90=7.2	0.010	0.1
	1@MaxRi	154	8x0.45=3.6	0.002	<0.1

Figures 57 and 58 for the two sets of five application scenarios demonstrate that peak concentrations at 1.1 m would be very low for Riverhead conditions at the label rate, and still have below 5 µg/L peaks for dual applications at double the label rate.

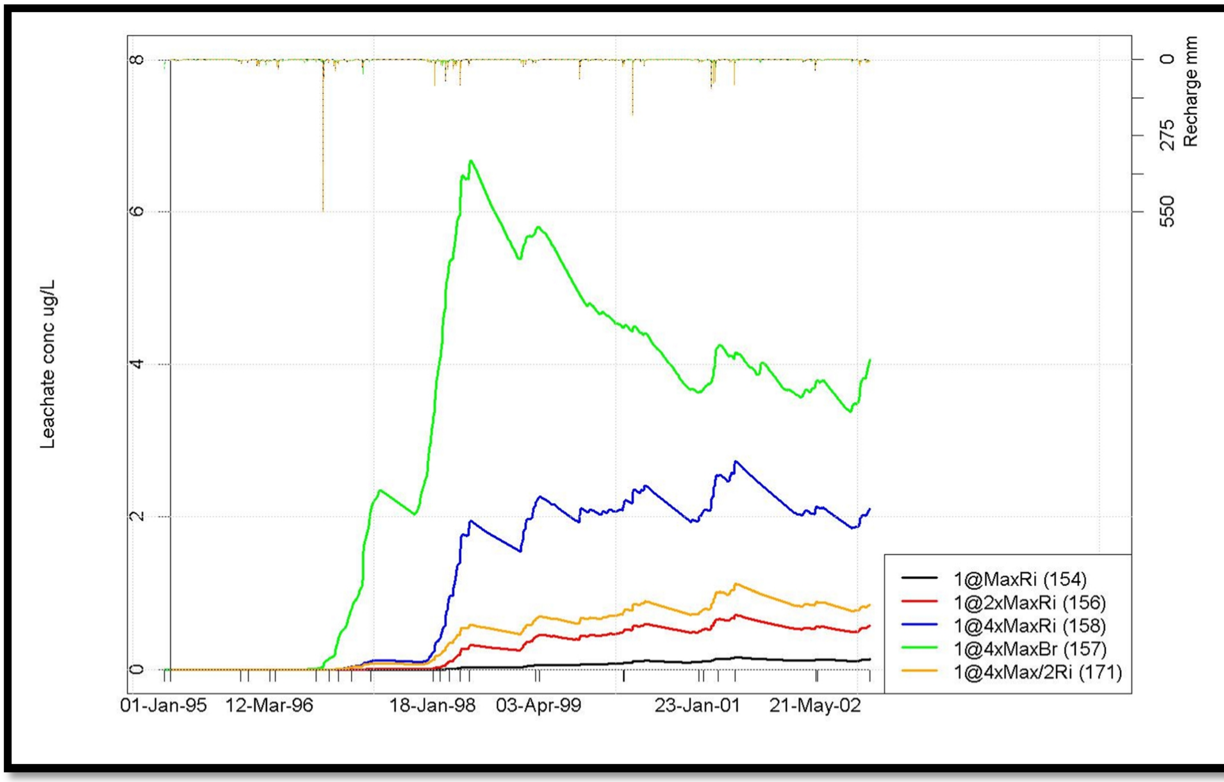


Figure 57: LEACHP concentrations for annual applications to turf

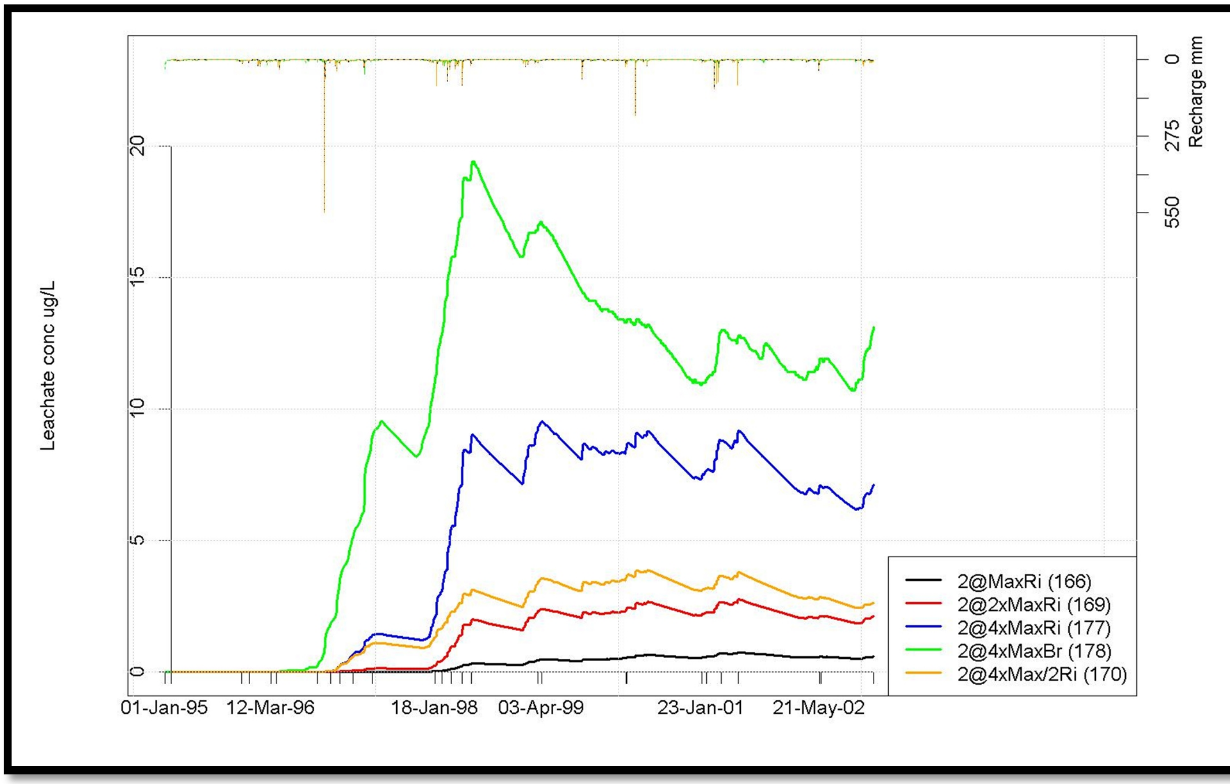


Figure 58: LEACHP concentrations for semi-annual applications to turf

Figure 59 repeats the single and dual at-label rates with observed data from the CC-1 well at the Riverhead golf course discussed in Section 3.5. The very deep 28 m water table at that site provides a several-year opportunity for dispersion to smooth out peaks and degradation to reduce average concentrations, thus the simulated concentration at 1.1 should be several times higher than the observed concentrations in wells for the two series to be consistent. A once pear year application would yield a simulated peak concentration at 1.1 somewhat below the observed values at CC-1, too low to be consistent. The semi-annual applications yield averages in recharge around 0.6 after the initial ramp-up and are more consistent with the observed data.

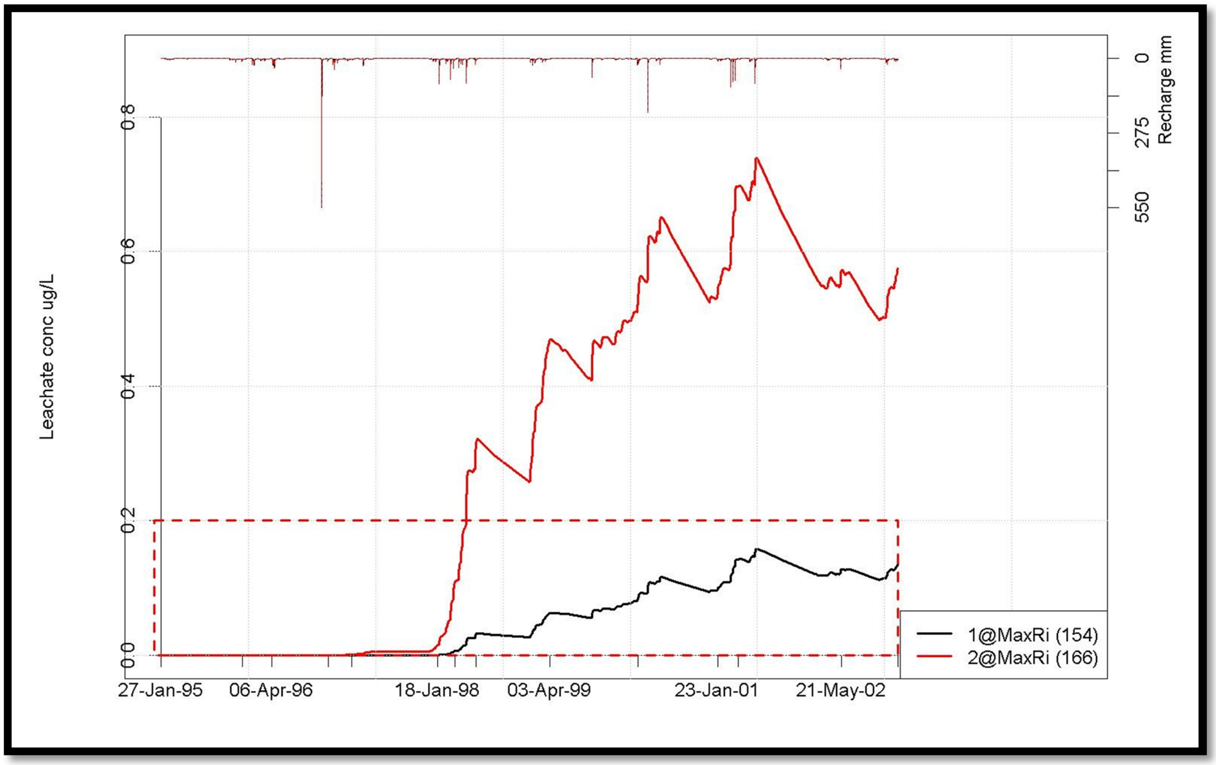


Figure 59: LEACHP turf simulation results with CC-1 observed data

Figure 59 Caption: Observed data represented by the dashed box are portrayed to apply to the entire simulated period rather than the monitored period of 2005-2009.

The main lesson of the turf application of LEACHP is that, as for potatoes, available data for modeling lead to simulation results that have comparable magnitudes to observed values in monitor wells. Concentrations from turf should be expected to be lower from surface applied products in turf grass than furrow-applied products in potatoes, which the LEACHP model represents well.

5.6 Vineyards (Sinkevich)

A well near an Oregon Road vineyard covered in Section 3.6 had concentrations ranging from 0.10 to 0.33 μg/L between 2004 and 2009. Vineyards could be represented using LEACHP working forward from labeled rates, but again with a deep water table (20 m in this case) LEACHP's output concentrations for 1.1m could be much higher and arrive several years earlier than would be observed at the water table. It was decided to use the Sinkevich model in this case analogously to the greenhouse applications in Chapter 4.

Figure 60 applies the Sinkevich model to this case. Emission rates from 7 g/ha to 30 g/ha three times per year for eight years, combined with transmission zone degradation rates of 0.3 to 0.6/yr, yield concentrations at 20 m that have the same magnitude appearing in the monitor well, a bit above the detection limit 0.2.

Note that by back-calculating in this fashion the emission rate is effectively net after photodegradation, rather than the gross amount applied according to a label. In a glass greenhouse there is not an opportunity for photodegradation of fugitive emission through the building floor. An outdoor foliar application is highly subject to photodegradation.

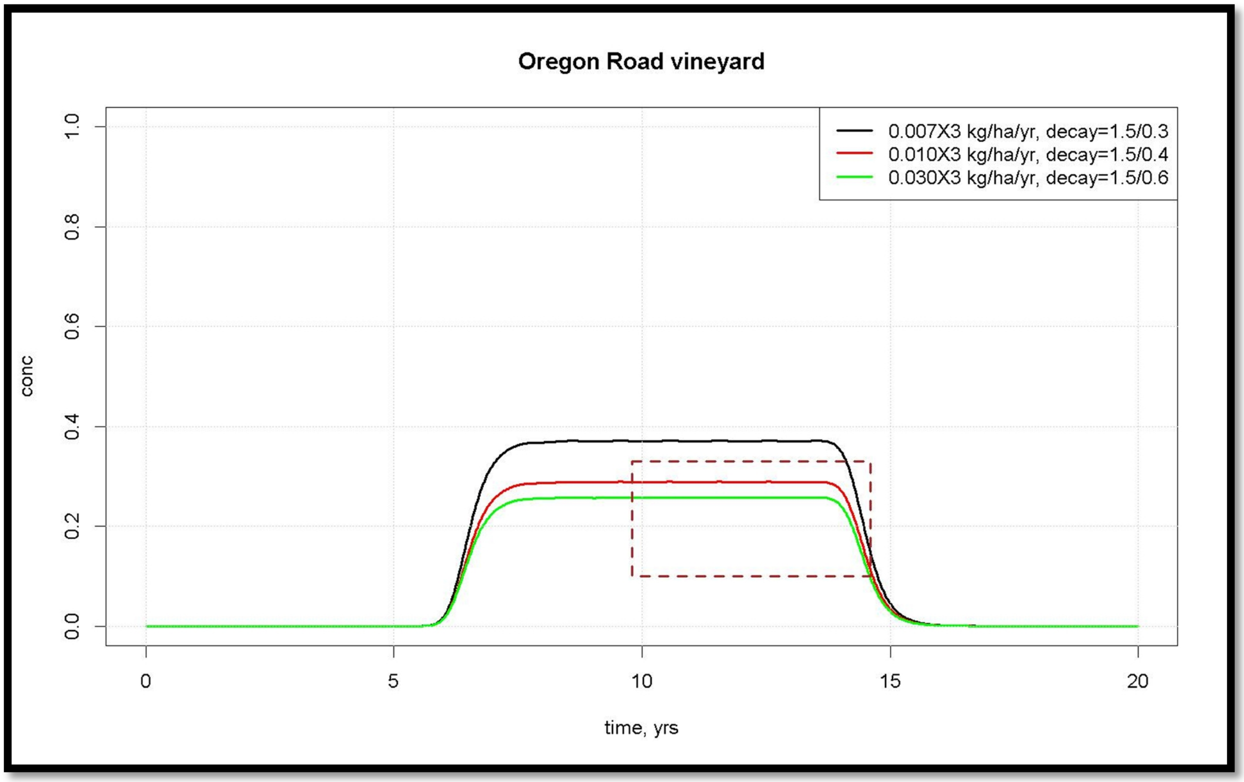


Figure 60: Oregon Road vineyard simulation with Sinkevich Model

Figure 60 Caption: Model:

```
slineit2S( x=2000, M=rep(0.007,24), M2=rep(0.01,24),
M3=rep(0.03,24), tv=c(0.33,0.66,1.0, 1.33,1.66,2.0,
2.33,2.66,3.0, 3.33,3.66,4.0, 4.33,4.66,5.0, 5.33,5.66,6.0,
6.33,6.66,7.0, 7.33,7.66,8.0), cmax=1, decay=1.5,
decaystar=c(0.3,0.4,0.6), tmax=20, R=48, rho=1.31, rhoT=1.66,
Af=0.25, dthick=5, koc=220, fom=0.03, fomT=0.001, tinc=0.02,
main="Oregon Road vineyard",
cap=c("0.007X3 kg/ha/yr, decay=1.5/0.3",
"0.010X3 kg/ha/yr, decay=1.5/0.4",
"0.030X3 kg/ha/yr, decay=1.5/0.6"), legendPos="topright",
obsRect=c(9.8,0.1,14.6,0.33), obsCol="brown",
plotfile="sink-oregon-4" )
```

The main lesson from the vineyard application of the Sinkevich model is essentially the same as for greenhouses: it does not take high effective loading rates at the surface to reach the detection limit magnitude in deep wells. Much higher effective emission rates from vineyards (or any other routine use) would be necessary to reach the 250x higher applicable drinking water guideline at 50.

5.7 Summary of Area Source Interpretations

LEACHP yielded realistic concentration predictions for both aldicarb and imidacloprid on Long Island potatoes, and possibly also for imidacloprid used on turf though this is not as well monitored. This is without calibration, using literature-based data for near-surface degradation rates.

The LEACHP results suggests that this model should continue to be used as an advance screening tool for Long Island field usage rates and timings. However, LEACHP and Sinkevich are only applicable to chemicals that are relative weakly sorbing and non-volatile.

Note that LEACHP's omission of processes like photodegradation, volatilization, and effects of plant surfaces after foliar application makes the model biased toward higher levels of pesticide that reach soil. The simulated application rates of surface-applied chemicals could be reduced to reflect these effects.

Soil and hydrological conditions are different enough between the Riverhead and Bridgehampton areas that it may be helpful to include both scenarios in DEC's standard recommendations.

LEACHP was used diagnostically in this work, rather than as a predictive tool. LEACHP has limited value as a forecasting model for Long Island mainly because the water table is much deeper than 1m in most areas. However, the peak and average concentrations resulting at 1-meter depth will decline by the time a deeper water table is reached by advancing recharge. In a regulatory setting such conservatively high values are acceptable, as long as they do not tip the economy/environment balance too far away from the economic aspects. Many other conservative factors are assumed in DEC's use of LEACHP such as: annual use of the same chemical at maximum label rates (unless the label forces gap years); deactivating plant uptake; and no surface loss processes.

Given that imidacloprid potentially can be used over most of Long Island, it would be instructive to model imidacloprid in recharge over the whole area, just as nitrogen has been modeled (Porter, 1978; Lloyd, 2014). This would provide a different perspective than modeling a few land uses individually with LEACHP. In particular it would weigh the distinctive effects of the differing categories of imidacloprid use, according to the relative scales of different types of users in terms of kg/ha intensity multiplied by the treated outdoor area (in hectare), or g/m^2 multiplied by the treated indoor area (in square meters).

LEACHP is only useful for large area, non-point sources. The data show these cases to be inconsequential in the case of imidacloprid. Much more important for higher concentrations, albeit in small areas, are the concentrated point sources to which LEACHP does not apply and which can't readily be modeled in advance. The usage regulations applicable to concentrated point sources are also very different from those for the broad use sources for which the rates and timings that are specified on labels are well evaluated by LEACHP. Technology mandates, complete recordkeeping enable investigation of problem cases and the prominent sanctioning of bad actors to deter others. Californians submit monthly pesticide use reports to their county agriculture commissioner (California Deptartment of Pesticide Regulation, 2016). Similar measures here for problem prevention might be (California Deptartment of Pesticide Regulation, 2016)more useful than changes in labels and field usage rates.

6. Conclusions

SCDHS' large set of monitoring well data up to 2010 was valuable at whole-county and site specific levels. It would be even more beneficial to pesticide assessment if other SCDHS data sets (notably samples from private wells) were similarly organized, to correct for the inherent biases in targeted monitor well sampling. The accessibility of these data to anyone other than SCDHS itself is quite limited. It is important for at least NYS DEC to be able to incorporate these data and their later successors into ongoing assessments.

From the greenhouse cases examined in detail, with water tables ranging from shallow to deep and with notably different concentration results, and from other greenhouse sites where there were no detections at 0.1µg/L or above at all, it is apparent that the routine emissions from greenhouses are at most inconsequential. The highest observed well concentrations (e.g. above 30 µg/L) are from misuse incidents or probable accidents, which affect relatively small areas.

The Sinkevich model employed uses a minimal parameter set necessary to represent a sorbing, degrading chemical entering the soil surface. It is helpful to have a tool available complementing the LEACHP model to represent the entire vadose zone thickness as Long Island has many areas where the depth of the water table is over 10 meters. Major assumptions about parameter values require that wide error margins be associated with all calculated concentrations. The key assumed parameter values include: organic carbon content below the surface soil, moisture content below the surface, and degradation rate of imidacloprid below the surface.

There appears to be no direct way to quantify actual emissions from the greenhouses through their floors. Monitor well data imply that there are recurring pesticide emissions from some of Long Island's conventional greenhouses. Data from monitor wells in areas with shallow water tables can be used together with the Sinkevich model to make indirect estimates of greenhouse emissions. Improved knowledge of a pesticide's deeper vadose zone degradation rate and records of specific application times and rates are important to narrow down the range of uncertainty.

LEACHP yielded realistic concentration predictions for both aldicarb and imidacloprid on Long Island potatoes, and possibly also for imidacloprid used on turf, although this is not as well monitored. This is modeled without calibration, using literature-based data for near-surface degradation rates. The LEACHP results suggest that this model should continue to be used as an advance screening tool for Long Island area pesticide application rates and timings. However, LEACHP and Sinkevich are only applicable to chemicals that are relative weakly sorbing and non-volatile.

LEACHP has an environmentally conservative value as a forecasting model for Long Island mainly because the water table is much deeper than 1m in most areas, and certain aspects of direction from NYS DEC's as to how registrants use LEACHP. These aspects will tend to bias the analysis of groundwater protection against economic aspects, i.e. over-predicting concentrations that would appear at drinking water wells. A diagnostic application of LEACHP as used in this work does yield less biased results because plant uptake was activated, and site specific soil, and actual weather series data were used.

On the other hand, LEACHP was not useful on Long Island in understanding the outlier imidacloprid cases with the highest detects, which are, associated with ephemeral concentrated sources.

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