Surveying Upstate NY Well Water for Pesticide Contamination

Wayne County Survey Report

to the

New York State Department of Environmental Conservation

Luanne Whitbeck, Project Manager
Bureau of Pesticide Management

June 2013

Tammo Steenhuis, Project Director*
Brian Richards, Project Coordinator**
Steven Pacenka
Sheila Saia
M. Todd Walter
Cornell University, Department of Biological & Environmental Engineering
Riley-Robb Hall, Ithaca NY 14853
* *Email: tss1@cornell.edu phone: 607-255-2489*
** *Email: bkr2@cornell.edu phone: 607-255-2463*

In cooperation with

Lindsey Gerstenslager, District Manager
Henry Kelsey, former District Manager
Scott DeRue, District Technician, Water Quality Specialist
Wayne County Soil & Water Conservation District, Cooperator

Table of Contents

EXECUTIVE SUMMARY

NYS DEC contracted with Cornell University to undertake a survey of selected representative areas in upstate New York to determine the occurrence of pesticide contamination of groundwater by sampling well systems in rural (domestic and farm) and suburban areas. Of particular interest are areas judged most vulnerable, where significant pesticide use (agricultural and otherwise) coincides with shallow aquifers, presenting elevated contamination risks in contrast to areas with low pesticide use and/or less vulnerable groundwater resources. Intensity of pesticide use, reliance on ground water, and aquifer characteristics made Wayne County a priority candidate for sampling, as identified by statewide selection protocols developed and refined in prior years. As in prior counties sampled, the primary cooperator was the Wayne County Soil & Water Conservation District (WCSWCD).

Well selection was primarily based on local knowledge of groundwater conditions and vulnerabilities, onsite and aerial image assessment, and the PSUR pesticide database. Cornell personnel proposed 95 potential sampling sites based on aerial land use and topographic assessments; as sampling progressed another ten sites were identified by the WCSWCD, which carried out sampling visits in December 2009 and January 2010. The NYS DEC laboratory conducted broad multicompound analyses for pesticides and degradation products. ELISA atrazine assays as well as nitrate assays were carried out by Cornell personnel.

The extensive agriculture in Wayne County is reflected in the fact that agriculture was the primary land use category for 37 wells. Of these, there were 21 wells for which orchards was the primary land use, and another 12 for which grain cash crops or corn/forage rotation were the primary land uses. Forage and muck soils were the primary land uses for a total of 4 wells. Woods or scrub regrowth was the primary land use around 4 wells. The most prevalent secondary (20 wells) and tertiary (17 wells) land use was woods or scrub. Agriculture was the second most common secondary (17 wells) and tertiary (11 wells) land use. Suburban areas in the county are primarily served by public water supplies, which resulted in little representation of those land uses in the sampled well array (2 wells). Of the 34 wells for which the depths were known by landowners, two thirds were either shallow (up to 30 ft.) or moderately shallow (31– 60 ft. deep).

NYS DEC pesticide scans found that most analytes were below the detection limits. The only analytes detected by NYS DEC were degradation products of metolachlor (ESA, OA) at five sites and alachlor ESA (at one of those five sites). Of these, the only levels substantially greater than detection limits were 4.4 to 4.6 μg/L of two metolachlor metabolites at one well, and 1.9 μg/L of metolachlor ESA at another. An ELISA scan for atrazine conducted at Cornell University indicated two nonquantifiable trace detections (<0.1 μg/L) at sites where metolachlor degradation products were found. These findings established that the 41 well samples from Wayne County did not exceed any ambient pesticide groundwater standards or guidance values. The detections of metolachlor OA and ESA degradation products (4.4 to 4.6 g/L) have no standard or guidance value against which to compare, although both were lower than the metolachlor standard of 9 μg/L. Similarly, the detection of alachlor ESA (0.1 μg/L) has no standard for comparison. Trace detections of atrazine from tests performed at Cornell were below 0.1 μg/L, well below the 3 μg/L standard.

Of nine wells where corn/grain cash crops was the primary land use, four had pesticide detections and one also had elevated nitrate. Of two muck soil primary land uses, one had pesticide detections (also noting that cash crops was a prominent secondary land use). Of 21 sites with orchards as primary land use, none had pesticide detections, and one had elevated nitrates (and said site again had cash crop corn as the secondary land use). Of the land uses tested, clearly corn/grain cash cropping was the most likely to be associated with detections which consisted of herbicides or their degradation products.

As we have observed in prior counties, not all shallow wells tested had problems, but all detections were clearly associated with shallow wells in close proximity to agricultural land uses.

1. INTRODUCTION

1.1 Project Background

Pesticide transport from agricultural and other sources to groundwater is a well-documented problem, with transport occurring not only through coarse sandy soils but also through preferential flow paths in fine, structured soils. In view of typical application rates and water recharge rates, maximum allowable herbicide contaminant levels can be exceeded if even a small percentage of surface-applied pesticides find their way to groundwater (Steenhuis and Parlange 1990, Boesten 2008, Shipitalo et al. 2000). A nationwide survey in the late 1980's by USEPA found pesticide-related contamination in over 10% of community water systems and over 4% of rural household wells. Aquifer contamination problems in the deep sandy soils of Long Island are well documented. Although substantial advances have been made in vadose zone sampling (Weihermüller et al. 2007) and transport modeling (Kohne et al. 2009) for detecting and predicting potential movement to groundwater, sources of uncertainty remain (e.g. Domange and Gregoire 2006) and targeted groundwater monitoring is essential to determine if pesticide registration and application approaches are sufficiently protective of groundwater resources.

The NYS DEC, the NY State Soil & Water Conservation Committee, and other stakeholders have expressed an interest in a survey of representative areas in upstate New York to determine the occurrence and extent of pesticide contamination of groundwater by sampling rural water systems (domestic and farm), small municipalities and suburban areas. Of particular interest at present are areas where significant pesticide use (agricultural and otherwise) coincides with shallow aquifers, presenting elevated contamination risks in contrast to areas with low pesticide use and/or less vulnerable water resources. The results of this survey can contribute to an assessment (by DEC and others) of the human exposure risk from pesticides in groundwater, and to identify needed changes in pesticide management through product registration, applicator training, consumer advice, and technical assistance.

Cornell University uses a landowner confidentiality approach where public reporting of data involves general but not specifically georeferenced results. Landowners receive confidential reports for their wells, but neither they nor their well(s) are identified in any public reporting. This approach is used in part as an incentive to attract landowner cooperation which would enhance the weight of project findings by maximizing the participation and sampling of sites deemed most vulnerable.

1.2 County Selection and Overview

Significant agricultural activity – including intensity of pesticide use – and widespread reliance on ground water made Wayne County a priority candidate for sampling, as identified in the statewide selection protocols developed and refined in prior project years, and briefly summarized here.

The NY Pesticide Sales and Use Reporting (PSUR) system provides publicly-available data that include a product code, a volume or a weight of product, and a location, either the county name or a 5-digit zip code. The PSUR covers pesticide use by commercial applicators and sales to farmers who apply pesticides themselves. (Farmers are not required to report their own pesticide use.) This report combines the commercial use and sales data.

Use and sales data undergo two conversion steps, with liquid product volume converted to weight using a product density (specific weight), and then product weight is converted into active ingredient weights using a product composition table that contains the weight percentages of each active ingredient. There are some issues with zip codes tabulation areas (ZCTA) and geo-referencing (Grubesic, & Matisziw, 2006) but these are not considered significant in this application. We express results as an intensity of use in kilograms per square kilometer (kg/km^2), convertable to lbs/acre with a factor of 0.0089.

We incorporated the Groundwater Ubiquity Score (GUS) approach (Gustafson, 1989) to better account for the potential for individual pesticides to travel to groundwater. The GUS approach weights pesticide applications using persistence and mobility parameters from the USDA Pesticide Properties Database using an index factor which is greatest for compounds which persist longest in the environment and which are most mobile with water. As can be seen in Figure 1.1,the GUS-weighted pesticide use intensities are greatest in the band of relatively heavily-treated areas spanning the intensive agricultural region of Western and Central New York south of Lake Ontario. This area is highlighted in Figure 1.2, which also overlays shallow carbonate (karst) strata). Based on this mapping and other land use information, we initiated work in Wayne county.

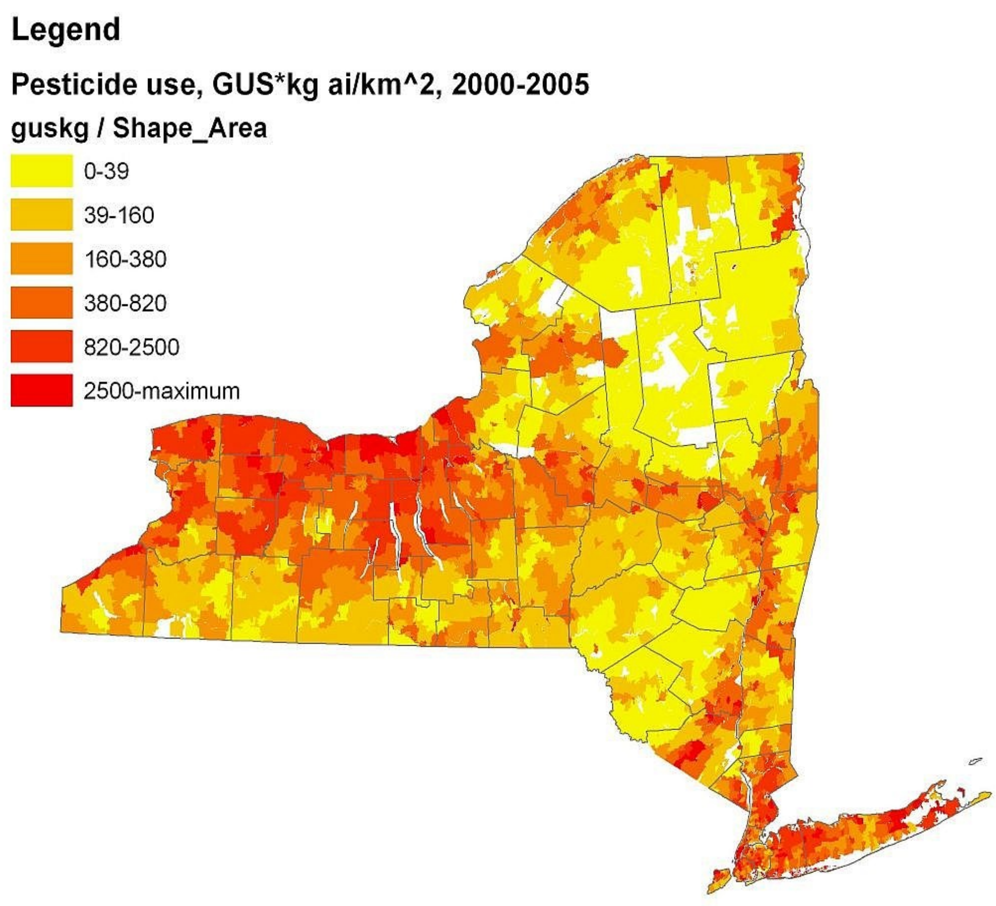

Figure 1.1. Cumulative use intensity of all active ingredients (kg/km^2) weighted for Groundwater Ubiquity Score, based on 2000-2005 PSUR dataset.

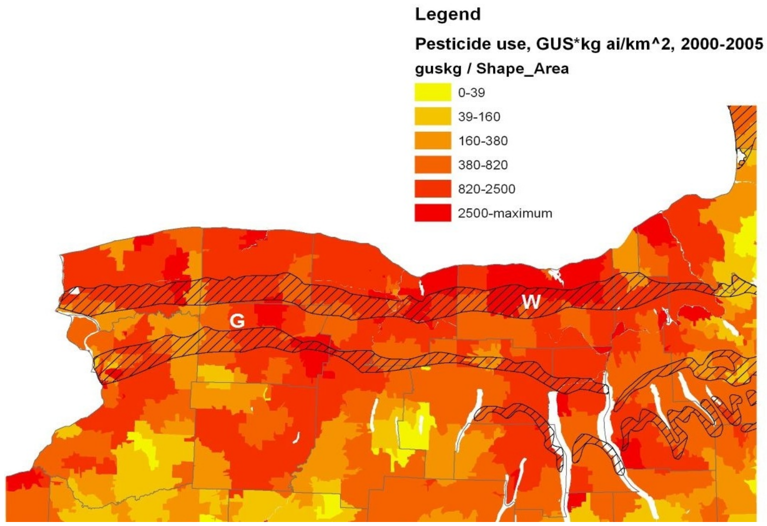

Figure 1.2. GUS-weighted pesticide intensity (as per Fig. 1.1) and shallow carbonate strata (hatched areas). W indicates Wayne county, G indicates Genesee County, site of prior sampling.

Wayne County lies on the shores of Lake Ontario (Figure 1.3) and is part of the state's most intensive agricultural region. The county has diverse geomorphic regions (Figure 1.4). A band of dolomite that can give rise to karst formations (e.g. sinkholes and solution channels capable of rapid water and contaminant transport) crosses the county.

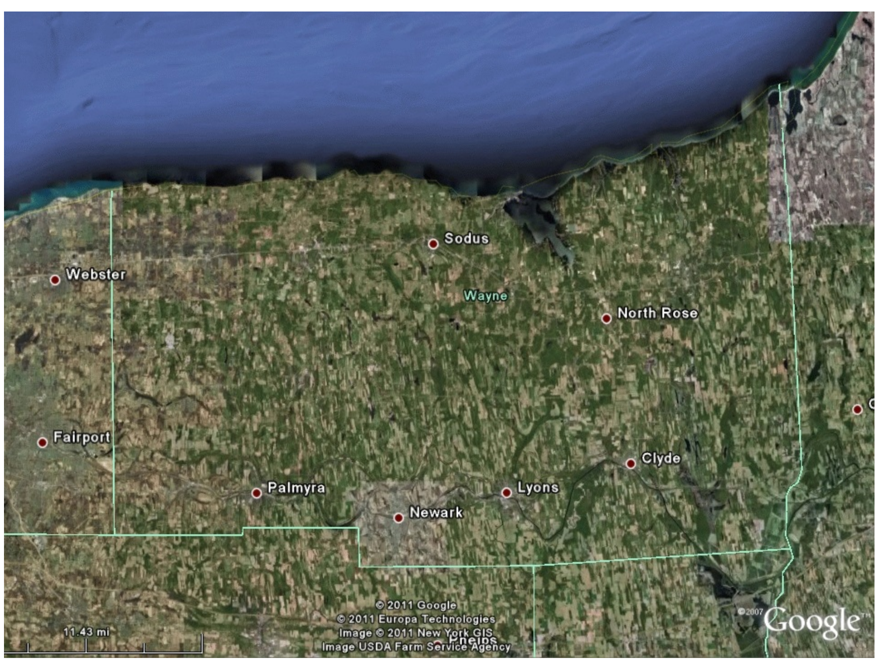

Figure 1.3. Wayne County on the southern shore of Lake Ontario (composite aerial image). Image © 2011 Tele Atlas, used in accordance with permitted terms of use.

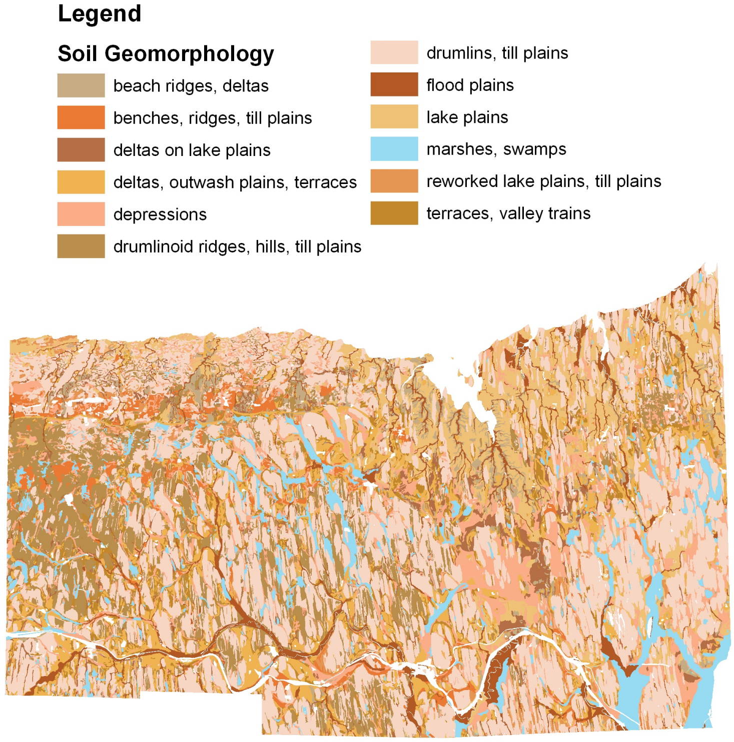

Figure 1.4. Geomorphic features in Wayne County.
Source: Soil survey data.

Figure 1.5. Several of the more than 1.5 million apple trees under cultivation in Wayne County (photo: S. Pacenka).

Apple orchards predominate in Wayne County (Figure 1.5), although significant levels of other agricultural production are also present. Of the county's 386,826 acres, 44% was in farmland in 2008, with a total of 938 farms (NYASS 2009). The county ranked fifth in NY state for total agricultural sales (nearly $169,000,000), with fruits and nuts representing 51% of the total, dairy 15%, grains and dry beans 11%, vegetables 7%, nursery and greenhouse 6%, and all others 10% (NYASS 2009). In terms of agricultural receipts, the county ranked first in the state for fruit and nuts, sixth for nursery and greenhouse, and seventh for grain/bean field crops.

Our local cooperator for the project was the Wayne County Soil & Water Conservation District (WCSWCD; Henry Kelsey, District Manager). Initial contacts with the WCSWCD in mid-2009 led to formal approval of the WCSWCD cooperation in summer 2009.

2. PROJECT COMPONENTS

Three project components are reported here. The first is the *site selection process* (Section 2.1) used to identify well sites. Second is the *site characterization* (2.2) of the selected well sampling sites, and third is the presentation of *sampling results* (2.3) of the well sampling carried out in Wayne County.

2.1 Site Selection Process

Program constraints dictated that a maximum of circa 40 well water samples be submitted for analysis by the DEC laboratory. Because of the interest in targeted sampling of sites judged most vulnerable, identification of potential sites representing vulnerable areas was important. The site selection and review process developed for this program involved multiple approaches used in concert: 1) examining land use patterns and landscapes using aerial imaging software tools, 2) assessing local knowledge about areas of likely vulnerability, and 3) examining the NYS Pesticide Sales and Use Reporting (PSUR) database for pesticide and herbicide application trends.

2.1.1 Land use and landscape assessments

The first factor contributing to site selection and assessment – as well as in post-sampling site rechecks – was the visual assessment of land use and landscape topography using aerial imaging, as well as a subsequent windshield survey for the majority of potential sites. Initial site reviews were conducted with the Google Earth (version 4.2; available at http://earth.google.com/) software platform. This approach allows detailed "virtual flyovers" of areas, assessing not only agricultural and other land uses but also the ability to visualize landscape topography.

As can be seen in Figure 2.1 (showing a location randomly chosen from upstate NY and not representing a sampled site), a standard aerial photo image (top) conveys significant land use information. However, Google Earth's incorporation of a topographic elevation model in combination with the ability to change the angle of view (Figure 2.1 bottom, same farm site) creates virtual topography, dramatically increasing the available visual information about the juxtaposition between land use(s), landscape position and potential well sites, particularly for shallow wells that may be strongly influenced by local features. The ability to rotate the direction of view, zoom the field of view, change the angle of view, and continuously "fly along" areas of interest makes this a powerful interactive tool for locating and assessing potential sites. In addition to visual relative

Figure 2.1 Example of GoogleEarth aerial imagery using location chosen at random from upstate New York and not representing a sampled site. *Top:* standard aerial photo image conveys significant land use information. *Bottom:* same farm site with altered angle of view, which allows visualization of strong drumlin topography in relation to farm fields, nonfarm areas, and potential well sites. Image © 2009 Tele Atlas, used in accordance with permitted terms of use.

elevations, the Google Earth platform reports the discrete elevation of any point under the cursor for more precise comparisons.

2.1.2 Local Knowledge

This approach involved assessing local knowledge about areas of likely vulnerability, based on prior experience with farming patterns, soil and aquifer characteristics, and reports of nitrate contamination or other well problems. The primary source in this case was the Wayne County Soil & Water Conservation District (WCSWCD), both for reviewing candidate sites identified with aerial imagery as well as selecting additional sites.

2.1.3 Utilization of the PSUR Database

Given our experience in prior project years (wherein surrounding land use proved a far better predictor of trace atrazine detections as compared to detailed PSUR records for Cortland County), the inherent limitations of the PSUR database (which does not report application sites for farmer-applied pesticides), and the formidable task of analyzing the detailed confidential database, we elected to rely only on the publicly-available zip-code-level PSUR data summaries for determining which pesticides were most heavily used as well as which general regions within Wayne County had the greatest intensities of pesticide use. As can be seen in Figure1.2, GUS-weighted application intensities varied in the county, being greatest in the orchard-dominated northern half. Nevertheless, overall rates were elevated in the county compared to other areas of the state (Figure 1.1).

PSUR data summarized at the zip-code level was also used to guide the choice of immunoassay pesticide test kits for more on-site analysis. Table 2.1 summarizes the 25 most-applied active ingredients in Wayne County. Using this data (and recognizing substantial improvements in DEC laboratory detection limits), we elected to perform ELISA tests only for atrazine.

2.1.4 Site identification process

Site targeting priorities were discussed in a joint meeting held in Wayne County in June 2009. A potential site list with nearly 95 candidate sites was subsequently assembled and prioritized by Cornell personnel using above methods. The list was reviewed by WCSWCD and ten more added. (Consistent with past years, 80-100 sites must be identified to generate ~40 final samples).

2.1.5 Landowner recruitment and confidentiality guidelines

Information detailing sample collection and confidentiality/disclosure protocols (discussed below) were distributed. Landowner cooperation was essential, especially for gaining access to sites deemed to have elevated risk of contamination. (If such access is not obtained, it may be argued that the whole intent of the sampling program – to test the most vulnerable sites as a way of assessing the upper limits of exposure risk – would be frustrated.) Candidate landowners were presented with the protocol (via the landowner handout that appears in the Appendix) that introduced the program and specified the confidentiality/disclosure protocol, with the following provisions:

Table 2.1. The most-applied pesticide active ingredients in Wayne County (average of 2000-2006 reporting years)		
Active Ingredient	**Combined Sales+Use (kg/yr)**	**Available ELISA kit?**
Captan	53,411	
Sulfur	51,830	
Zinc Ion + Manganese Ethylenebisdithiocarbamate	41,374	
Mancozeb	23,966	
Aliphatic Petroleum Hydrocarbons	22,792	
Amsco 140	21,441	
APPA	17,095	
Bensulfoid	16,531	
Sodium Hypochlorite	16,424	
Carbaryl	15,559	
Atrazine	14,488	✓
Carbatene	12,822	
Copper Chloride Hydroxide	8,787	
Arasan	7,333	
Chlorothalonil	7,225	✓
Metolachlor	6,696	✓
Copper Hydroxide	5,909	
Thiophanate-methyl	5,644	
Ziram	5,625	
Pemdimethalin	5,504	
Alachlor	4,457	✓
Cp 70139	4,373	
Chlorpyrifos	4,220	

□ In all *public* reporting (published reports to DEC as well as any academic or extension publications), only blurred georeferences – rounded coordinates, dithered maps– are reported.
□ Reports indicating pesticide concentrations determined by Cornell and NYS DEC would be compiled and sent to individual landowners.
□ In the event that pesticide concentrations exceeding drinking water standards were found, the landowner would be contacted and the well would be resampled twice to confirm the initial findings. If confirmed by resampling, the WCSWCD would be advised to safeguard the health of those consuming water from the well(s) by taking appropriate remedial and/or preventative measures.
□ In cases where levels were somewhat elevated but not in excess of drinking water standards, landowners would be encouraged to contact relevant agencies for appropriate remedial and/or preventative measures.

□ Cornell will retain landowner contact information and exact well locations, which will be disclosed only to NYS DEC upon reasonable request from NYS DEC.

2.2 Site Characterization and Sampling

Recruitment letters were sent in fall 2009, and site visits for sample collection were conducted by WCSWCD personnel in December 2009 and January 2010. This timing of sampling was elected to allow for completion of growing season spray schedules and time for fall groundwater recharge to begin.

2.2.1. Sampled Well Sites

Table 2.3 presents sampled well information, including well type, depth, and prioritized surrounding land use(s)for surrounding and upslope areas judged to be potential well contributing areas, particularly for shallow wells. (It is important to note that these surficial observations are by no means determinative in view of flow complexity of underlying strata.) Land uses were ranked as primary (i.e. most extensive and dominating general and upslope areas), and, if diverse land uses were present to a significant degree, secondary and tertiary. Land use sources included windshield survey notes in addition to Google Earth imaging. Nevertheless, distinctions among specific cropping systems – particularly corn/grain (cash crops including corn, soybean, wheat, oats etc.) corn/forage (dairy farm feedstocks), and vegetable land uses – often involved judgment calls, including determining the presence of nearby features including grain silos, livestock facilities, etc.

Land uses are summarized at the bottom of Table 2.3 in terms of the number of wells linked to each category, and these uses are further aggregated by general land management class in Table 2.4. The extensive agriculture in Wayne County is reflected in the land use categorization, with agriculture as the primary land use category for 37 wells. Of these, there were 21 wells for which orchards (O) was the primary land use, and another 12 for which corn/soybean/wheat/ etc. grain cash crops (CC) or corn/forage rotation (CF) were the primary land uses. Forage (F) and muck soils (M) were the primary land uses around 2 wells each. Woods (W) or scrub regrowth (R, representing abandoned farmland) was the primary land use around 4 wells.

The most prevalent secondary (20 wells) and tertiary (14 wells) land use was woods (W). Scrub regrowth was the tertiary land use around 3 wells. Together these “unmanaged land” classes accounted for 20 wells (secondary) and 17 wells (tertiary). Agriculture (CF, CC, F, M, O, T) was the second most common secondary (17 wells) and tertiary (11 wells) land. Suburban lawn and managed turf appeared only as a secondary land use for 2 wells.

Table 2.3. Well and surrounding area land use characteristics. *NA* indicates well depth/type not available. Land use key and category totals appear at bottom of table.							
ID*	**Well type**	**Depth (ft)**	**Serves**	**Land use ranked by extent**			**Well position relative to land use and topography**
				Primary	**Secondary**	**Tertiary**	
2	drilled	137	barn	CC	O	W	atop large flat drumlin, CF close, orchards N, woods to W
3	NA	NA	NA	O	W		end of drumlin, orchards, wooded
4	dug	12	house	CC	W		drumlin wooded to SE, extensive row crop otherwise
5	drilled	54	house	O	W	M	orchards on drumlin top, muck to SW, wood patches
8	dug	20	house	W	CC	M	CC on and mucklands among drumlins, wooded N and W
9	drilled	NA	Barn	O	W	B	orchards to N, wooded/scrub, suburban E
10A	drilled	47	house	O	W	CC	on flat dome w/orchards, some other crops, woods
10B	drilled	54	barn	O	W	CC	on flat dome w/orchards, some other crops, woods
13	dug	4-6	NA	O	CC	W	flat mostly orchards, wooded; CC to W, mix station to E
14A	dug	20	house	CC	W		nearly flat, dairy but mostly CC, some woods
14B	drilled	40-45	barn	CC	W		nearly flat, dairy but mostly CC, some woods
15	drilled	120	house	CF	W		nearly flat, dairy but mostly CC, some woods
16	dug	20	house+barn	W	O		in large wooded area sourrounded by orchards
22	drilled	80	house	O	W	CF	atop large flat drumlin, organic orchard, wooded/wetland low areas
37	drilled	40	house	CC	O	W	nearly level, field crops, orchards
39	drilled	43	house	CC	O	W	atop gentle rise with CC, orchards, woods
46	dug	12	NA	M	CC	B	muck S, forage W, scrub E, orchards beyond
47	drilled	NA	house	O	W		flat; orchards surrounded by woods, orchards beyond
49	drilled	NA	house	B	O	CF	patchy fields/orchards, mostly scrub/wooded
53	dug	25	house	O	CC	W	flat; orchard, some CC, wetland stream E
54	dug	22	house	CC	O	W	flat; row crops/forage, orchards to N, wood patches
59	dug	33	house	O	F	W	atop low drumlin, woods and forage; small fruits to SE
72	drilled	107-110	house	O	CF	W	atop low drumlin; small fruits, orchard, CF
73	dug	NA	utility	CC	W	CF	small drumlin; CC, ponds, woods
78	dug	shallow	house	CF	CC	W	between low drumlins, F, CF with woods
80	drilled	60	house	F	CC	W	between low drumlins, CF? field crops
81	drilled	190	house	F	W		forage on drumlin top, woods to most sides
83	drilled	45	house	CC	W	B	between low drumlins, CC field crops, wooded tops, some scrub
89	drilled	87	house	W	S	CC	below wooded drumlins with CF; suburban turf E
93	drilled	100	house	O	W		orchards dominate region, woods to N&W
94	dug	NA	house	M	W		wooded drumlin S/SW; mucks NE to SE
95	drilled	52	house	O	W		wooded area below drumlin with orchard
96	dug	20-25	house	O	F	W	in drumlin vale, orchard, some forage and wooded

continued on following page

Table 2.3, continued. Well and surrounding area land use characteristics. *Well type key:D* - drilled, *R* - driven, *G* - dug, *S* - spring. *NA* indicates well depth/type not available. Land use key and category totals appear at bottom of table.							
ID*	**Well type**	**Depth (ft)**	**Serves**	**Land use ranked by extent**			**Well position relative to land use and topography**
				Primary	**Secondary**	**Tertiary**	
97	drilled	20-22	barn	O	W	T	orchards of varying size N,E, W; wooded, some turf
98	dug	15	house	O	W	CC	on flat dome w/orchards, some other crops, woods
99	drilled	100	house	O		F	flat, orchards all sides; some pasture to SE; mix station to NE
100	drilled	130	house	O	W		orchards to all sides; wooded to E & W
102	drilled	NA	house	O	F		orchards all sides except forage downhill to N
103	dug	25-30	house	O		W	orchards all sides, woods to SW
104	drilled	50-60	house	O	S	W	orchards 3 sides, mix station E, turf/woods NE
105	dug	27	house	CF	O	W	crops+forage to E & S, orchard to NW, scattered woods

Legend and category totals by ranked land use class				
Category	**Primary**	**Secondary**	**Tertiary**	**Land use category explanation**
CF	3	1	3	corn/forage rotation (typical to dairy farms)
CC	9	6	4	corn/cash crop rotation (minimal forage apparent)
F	2	3	1	forage (alfalfa,. etc.)
O	21	7	0	orchards (primarily apple)
T	0	0	1	row crop fruits (non apples): grapes, berries, etc
M	2	0	2	muck/organic soil/ black dirt vegetables
W	3	20	14	wooded
B	1	0	3	scrub/regrowth on abandoned farmland
S	0	2	0	suburban/turf

Table 2.4. Summarized well land use classes (land use code legend in Table 2.3).

Class	Primary	Secondary	Tertiary
All agricultural (CF, CC, F, M, O, T)	37	17	11
All lawn/residential/managed turf (S)	0	2	0
All unmanaged: woods, scrub (W,B)	4	20	17

Well depth, type, and well use is categorized in Table 2.5. Of the 34 wells for which the depths were known by landowners, 14 were shallow (up to 30 ft.) including one surface spring. 11 wells were between 31 and 60 ft. deep, 4 were between 61 and 100 ft, and only 5 wells exceeded 100 ft. Well types included 24 drilled wells, 15 dug wells, one spring-supplied well and one of unknown construction. Houses were served by 31 wells, barns by 5, one serving both a house and barn, one utility well, and 3for which the usage was unknown or not recorded.

Table 2.5. Summary of classes of reported well depths, well types, and whether water sampling point preceded any treatment processes.

Depth	Wells	Type	Wells	Wells Serving	Wells
Springs	1				
Up to 30 ft	13	Drilled	24	House	31
31-60 ft	11	Dug	15	Barn	5
61-100 ft	4	Spring	1	House+Barn	1
>100 ft	5	Unknown	1	Utility	1
Unknown	7			Unknown	3

2.2.2. Sampling Protocols

The protocol followed during field sampling is summarized here; the *Sampling Protocol* and *Sample Information Log* forms developed and used are shown in the Appendix. The faucet/spigot was allowed to run for several minutes to purge the plumbing lines.

Certified precleaned (Environmental Sampling Supply, PC class) HDPE polyethylene bottles were used for sample collection, with one set collected for samples for submission to DEC and archiving, and another collected for Cornell analysis and archiving. Sample bottle labels specified only a tracking code. Nitrile gloves were used to prevent operator contamination of the water sample. Hand contact with the interior of the cap and bottle was avoided. Bottles and caps were rinsed three times with the sampled water prior to filling. Bottles were filled approximately 90% full to allow subsequent freezing and were placed in an ice chest until returning to the County office. Bottles were frozen within 8 hours of collection and stored frozen except when thawed for analysis. Samples were accumulated and shipped frozen via overnight courier to Cornell. A mid-project change in container standards triggered a thawing and rebottling at Cornell of about half of the samples (making stored bottles more robust during long-term freezing). Samples were stored frozen at Cornell and the bottles designated for DEC were shipped frozen via overnight courier to the NYS DEC laboratory.

2.3 Analysis and Results

Pesticide analysis conducted by DEC determined pesticides, phenoxy acid herbicides and carbamates, as detailed below. Analyses conducted at Cornell University included nitrate-N concentrations as well as ELISA screening for atrazine.

2.3.1 Analytical Protocols

DEC pesticide scans

This section consists of text forwarded by Peter Furdyna of the NYS DEC Pesticides Laboratory, with the analyte list and reporting limits summarized in Table 2.6:

Water samples from the Cornell Shallow Groundwater Monitoring Program were submitted to the NYSDEC Pesticides Laboratory in January 2010. The samples were screened for pesticides and select metabolites, phenoxy acid herbicides and carbamates.

All of the pesticide and herbicide compounds except dithiopyr, and aminomethylphosphonic acid (AMPA), were analyzed by direct injection followed by UPLC/MSMS. Dodine was extracted using the Quechers extraction technique and analyzed by gas chromatography/mass spectrometry (GC/MS). AMPA was analyzed by derivitization using 9-fluorenylmethylchloroformate (9FMOC) followed by UPLC/MSMS.

Quality control consisted of analyzing reagent blanks, method blanks (DI water), matrix spikes, and matrix spike duplicates. All target chemicals were spiked for QC analyses. Spike levels were 1ppb for all target chemicals except for dodine (5ppb), and AMPA (10 ppb). In all 5 sets of samples were spiked in duplicate, with the exception of one pair of spikes which were lost due to a lab accident for Dithiopyr, and AMPA QA(4 sample spike duplicates were ran.)

ELISA and nitrate assays

Water samples were screened at Cornell University for atrazine as well as nitrate. The pesticide methods employed use Enzyme-Linked ImmunoSorbent Assays (ELISA) to detect the analyte and related compounds. In each case we used magnetic particle ELISA kits from Strategic Diagnostics Inc (SDI). Atrazine kits (SDI Kit No. A00071) have quantitation ranges of 0.1 to 5 ppb (μg/L) and trace (nonquantifiable) detection limit of 0.05 μg/L (Table 2.7). The contribution of closely-related compounds present cannot be distinguished by the ELISA tests due to cross-reactivity, and results are reported on an "as primary analyte" basis. Potentially cross-reactive compounds are reported in Table 2.7.

Magnetic particle assays were analyzed on duplicate samples with a dedicated Ohmicron RPA-1 spectrometer and supplied sample tubes. Calibration data is linearized using logarithms and logit functions.

Nitrate was analyzed at Cornell by a colorimetric salicylic acid test to avoid interference from high sulfate. A detection limit of 0.5 mg/L was determined from calibration curve noise. Nitrate was expressed as ppm (mg/L) of nitrate-N.

Table 2.6. Method reporting limits of pesticide/herbicide analyses run by the NYS DEC laboratory. All concentrations are reported as µg/L (ppb). Method codes: *U* - UPLC/MS-MS; *G* - GC/SIM-MS; *H* - HPLC/MS-MS.

Analyte	Reporting Limit	Method Code	Analyte	Reporting Limit	Method Code
Base Neutral Parent Chemicals			***Base Neutral Metabolites & Sulfentrazone***		
Aldicarb	<0.1µg/L	U	3-Hydroxy Carbofuran	<0.1µg/L	U
Atrazine	<0.1µg/L	U	Aldicarb Sulfone	<0.2µg/L	U
Azinphos Methyl	<0.1µg/L	U	Aldicarb Sulfoxide	<0.1µg/L	U
Azoxystrobin	<0.2µg/L	U	De Ethyl Atrazine	<0.1µg/L	U
Carbaryl	<0.1µg/L	U	De Isopropyl Atrazine	<0.1µg/L	U
Carbendazim	<0.1µg/L	U	Hydroxy Atrazine	<0.1µg/L	U
Carbofuran	<0.1µg/L	U	Sulfentrazone	<0.2µg/L	U
Chlorosulfuron	<0.1µg/L	U			
Clethodim	<0.1µg/L	U	***Acid Metabolites & Acid Herbicides***		
Cyprodynil	<0.1µg/L	U	2,4-D	<0.1µg/L	U
Diazinon	<0.1µg/L	U	Alachlor - OA	<0.1µg/L	U
Dimethoate	<0.1µg/L	U	Alachlor - ESA	<0.1µg/L	U
Dithiopyr	<1µg/L	G	Clopyralid	<0.2µg/L	U
Diuron	<0.1µg/L	U	Dicamba	<0.1µg/L	U
Fluazafop-p-butyl	<0.2µg/L	U	MCPA	<0.1µg/L	U
Halofenozide	<0.1µg/L	U	MCPP	<0.1µg/L	U
Imazalil	<0.2µg/L	U	Metolachlor ESA	<0.1µg/L	U
Imidacloprid	<0.1µg/L	U	Metolachlor OA	<0.1µg/L	U
Malathion	<0.2µg/L	U			
Metalaxyl	<0.1µg/L	U	***Special Analytes***		
Methomyl	<0.1µg/L	U	AMPA	<1µg/L	H
Metolachlor	<0.2µg/L	U	Captan	unstable	
Metsulfuron Methyl	<0.1µg/L	U			
Nicosulfuron	<0.1µg/L	U			
Oxamyl	<0.1µg/L	U			
Oxydemeton Methyl	<0.1µg/L	U			
Propamocarb	<0.1µg/L	U			
Propoxur	<0.1µg/L	U			
Prosulfuron	<0.1µg/L	U			
Simazine	<0.1µg/L	U			
Tebuconazole	<0.1µg/L	U			
Tebufenozide	<0.1µg/L	U			
Thiacloprid	<0.1µg/L	U			
Thiamethoxam	<0.1µg/L	U			
Thifensulfuron Methyl	<0.1µg/L	U			
Thiodicarb	<0.1µg/L	U			

Table 2.7. ELISA detection and quantitation limits and potential cross-reactivities of related compounds, reported as concentrations required to generate responses equivalent to primary analytes at the specified LOQ. All concentrations expressed as μg/L.

Atrazine (SD A00071)	
Limit of Quantitation: 0.1	
Method Detection Limit: 0.05	Cross-reactivity at LOQ:
Atrazine	0.1
Propazine	0.1
Ametryn	0.05
Prometryn	0.09
Prometon	0.31
Desethyl atrazine	0.45
Terbutryn	0.76
Terbutylazine	2.15
Simazine	0.68
Desisopropyl atrazine	30.1
Cyanazine	>10000
6-hydroxy atrazine	20.6

2.3.2 Analysis Results

Results text forwarded by Peter Furdyna of the NYS DEC Pesticides Laboratory:

For UPLC/MSMS direct injection pesticide samples, recoveries ranged from 62% to 226%, with RPD's ranging from 0.1% to 30.2%. For UPLC/MSMS direct injection pesticide metabolites and phenoxy acid herbicides, recoveries ranged from 15% (clopyralid) to 760% (aldicarb sulfone). Review of the data indicated that this was due to matrix effects on the individual analyte responses, as continuing standard responses remained stable throughout the analyses. RPD's for these chemicals ranged from 0.0% to 28.5%. Recoveries for AMPA ranged from 86% to 108%, with RPD's ranging from 3.3% to 21.4%

For Dithiopyr by GC/MS extraction and analysis samples recoveries ranged from 123% to 164%, with RPD's ranging from 2.7% to 37.9%.

In the case of actual target analytes detected in the samples, two samples were run in duplicate. Sample WC-14b had detections for Metolachlor OA (3.3/5.4 ppb, RPD 48.3%), and Metolachlor ESA(3.6/5.6 ppb, RPD 43.5%). Sample WC-54 also had detections for Metolachlor OA (0.1/0.1 ppb, RPD 0.0%), and Metolachlor ESA(1.4/2.3 ppb, RPD 47.7%).

Pesticide analysis results were transmitted from the NYS DEC laboratory in 2012. Detections by NYS DEC and Cornell University are summarized in Table 2.8.

As noted in the prior section, the NYS DEC pesticide scans found that most analytes were below the detection limits specified in Table 2.6. The only analytes detected by NYS DEC were degradation products of metolachlor (at five sites) and alachlor (at one of those five sites). Of these, the only levels substantially greater than detection limits were 4.4 to 4.6 µg/L metolachlor metabolites at site 14b, and 1.9 µg/L of metolachlor ESA at site 54. Both were retested on separate subsamples and reported as the mean of those two analyses.

The ELISA scan conducted at Cornell University for atrazine indicated two nonquantifiable trace detections (<0.1 µg/L) at sites 14b and 54, which coincided with DEC nondetections (<0.1 µg/L) noted above. The site characteristics associated with the detections will be further examined in the discussion section.

Table 2.8. Summary of well water detections by the NYS DEC laboratory (top) and Cornell (bottom). All other sites and analytes were non-detects, indicating concentrations less than the reporting limits cited in Table 2.6. *Trace<0.1* indicates ELISA detection at concentrations lower than the specified Limit of Quantitation (LOQ).

Well ID	**Analytes (reported as µg/L)**		
DEC laboratory results	**Metolachlor OA**	**Metolachlor ESA**	**AlachlorESA**
14b*	4.4	4.6	ND < 0.1
37	ND < 0.1	0.2	ND < 0.1
39	0.2	0.6	0.1
46	0.2	0.2	ND < 0.1
54*	0.1	1.9	ND < 0.1
Cornell ELISA scan	**Atrazine (µg/L)**		
14b	Trace <0.1		
54	Trace <0.1		

* Results for sites 14b and 54 represent the mean of separate analyses on two subsample bottles.

Cornell results for nitrate-N are shown in Table 2.9. Because low levels of nitrate can be masked by elevated sulfate, nitrate is reported with a detection limits of 0.5 mg/L (<0.5 mg/L), depending on the extent of required dilution to eliminate sulfate peak interference. Twenty five wells had quantifiable nitrate (Table 2.9), with 21 wells less than 5 mgN/L, two between 5 and 10 mgN/L (flagged yellow), and two wells exceeding the 10 mg N/L drinking water standard with measured concentrations between 13 and 24 mg/L (flagged orange).

Table 2.9. Well sample nitrate-N analysis (reported as mgNO_3-N/L).

Well	Nitrate-N	Well	Nitrate-N	Well	Nitrate-N
2	<0.5	37	<0.5	89	<0.5
3	1.2	39	1.3	93	<0.5
4	2.4	46	1.3	94	<0.5
5	<0.5	47	0.7	95	<0.5
8	1.7	49	0.9	96	0.7
9	1	53	1	97	6.7
10A	<0.5	54	<0.5	98	1.2
10B	<0.5	59	<0.5	99	0.9
13	13.6	72	0.6	100	0.7
14A	4	73	<0.5	102	0.7
14B	24	78	5.2	103	1.4
15	<0.5	80	4.2	104	0.9
16	0.9	81	<0.5	105	0.7
22	<0.5	83	<0.5		

3. DISCUSSION and ONGOING WORK

3.1 Comparison to Groundwater Standards

In Table 3.1 we compare the maximum allowable groundwater concentrations (NYS DEC 1998; with the addition of a more recent metolachlor standard) with the DEC scan detection limits. The table shows only those analytes shown in Table 2.6 that have an associated groundwater (class GA) standard (or, as in the case of aldicarb sulfone and sulfoxides, guidance levels in the absence of a promulgated standard. The lower atrazine guidance level is also shown). Of the 15 analytes listed, all had DEC scan detection limits that were equal to or lower than the standard, which means that the tests that yielded nondetects ruled out any exceedence of groundwater standards. The detection limits for the scans run in the DEC laboratory were adequate for determining if samples were in exceedence of the fifteen Class GA ambient groundwater standards (MCLs or, in their absence, guidance values) listed. *These results thus established that the well samples from Wayne County did not exceed any ambient groundwater standards or guidance values.* The detections of metolachlor OA and ESA degradation products (4.4 to 4.6 g/L) have no standard or guidance value against which to compare, although both were lower than the metolachlor standard of 9 µg/L. Similarly, the detection of alachlor ESA (0.1 µg/L) has no standard for comparison. Trace detections of atrazine from tests performed at Cornell were below 0.1 µg/L, well below the 3 µg/L standard.

3.2 Comparison to Land Use and Well Characteristics

The extensive agriculture in Wayne County is reflected in the land use categorization, with agriculture as the primary land use category for 37 wells. Of these, there were 21 wells for which orchards (O) was the primary land use, and another 12 for which grain cash crops (CC) or corn/forage rotation (CF) were the primary land uses. Forage (F) and muck soils (M) were the primary land uses for only 4 wells total. Woods (W) or scrub regrowth (R, representing abandoned farmland) was the primary land use around 4 wells.

Table 3.1. Comparison of NYS ambient groundwater (GA) standards with DEC pesticide scan method reporting limits.

Analyte	**NYS Standard (µg/L)**	**DEC Reporting Limit (µg/L)**	**Do DEC results rule out standard exceedence?**
2,4-D	50	0.1	Yes
Aldicarb+Methomyl (sum of both)	0.35	0.1 each	Yes
Aldicarb Sulfone	2*	0.2	Yes
Aldicarb Sulfoxide	4*	0.1	Yes
Atrazine	7.5 (3*)**	0.1	Yes
Azinphos Methyl	4.4	0.1	Yes
Carbaryl	29	0.1	Yes
Carbofuran	15	0.1	Yes
Diazinon	0.7	0.1	Yes
Dicamba	0.44	0.1	Yes
Malathion	7	0.2	Yes
MCPA	0.44	0.1	Yes
Metolachlor	9	0.2	Yes
Oxamyl	50	0.1	Yes
Trifluralin	35	not tested	not tested

*guidance levels rather than actual standards; **guidance value =3 for surface waters for human consumption

The most prevalent secondary (20 wells) and tertiary (17 wells) land use was woods (W) or Scrub (B). Agriculture (CF, CC, F, M, O, T) was the second most common secondary (17 wells) and tertiary (11 wells) land use. Suburban lawn and managed turf appeared only as a secondary land use for 2 wells. Suburban and urban areas are served by public water supplies, which resulted in almost no representation of those land uses in the sampled well array.

It is again important to note that these surficial observations are useful but are by no means determinative of actual well contributing areas, especially in view of flow complexity of underlying carbonate strata in some areas of Wayne County.

Of the 34 wells for which the depths were known by landowners, two thirds were either shallow (up to 30 ft.) or moderately shallow (31– 60 ft. deep), whereas few exceeded 100 ft.

Table 3.2 summarizes well and land use information for all six wells with pesticide detections and/or elevated >10 mg/L) nitrate-N levels. The trace and quantified detections of pesticides at four wells (14b, 37, 39, and 54) had cash crop rotation (CC) as the primary land use. For well 46, CC was the secondary land use with muckland (M) as primary. Orchards were the secondary land use of three sites, and all sites had unmanaged lands (woods or scrub) as the lowest-ranked land use. Site 14b was clearly the most problematic, with the greatest levels of metolachlor degradation products, trace atrazine and the greatest nitrate-N level observed (24 mg/L). Interestingly, nearby site 14A had no detections and only moderate nitrate levels. Site 13 (Orchard primary, CC secondary) had no pesticide detections but a high nitrate level of 13.6 mg/L.

Based on primary land uses, of nine wells where CC [corn/grain cash crops] was primary, four had pesticide detections and one also had elevated nitrate. Of 2 Mucks primary land uses, one had pesticide detections (also noting that CC was a prominent secondary land use). Of 21 sites with Orchards as primary, none had pesticide detections, and one had elevated nitrates (and that site again had CC as the secondary land use). Of the land uses tested, clearly the CC cash crop was the most likely to be associated with detections, which consisted of herbicides or their degradation products. In contrast, Orchard pesticide use is predominantly short-lived fungicides.

The range of well depths for wells with detections and/or elevated nitrate in Table 3.2 is from 4 to 45 feet. As we have observed in prior counties, not all shallow wells tested had problems, but all detections were clearly associated with shallow wells in close proximity to agricultural land uses. As noted, Well 14b (which served a barn) was clearly the most problematic, yet only nitrate exceeded any relevant standards.

Table 3.2. Well characteristics (depth,type) and analytical results for all wells with quantified or trace pesticide detections and/or elevated nitrate-N levels; ND indicates not detected.
Well type key:D - drilled, *G* - dug, *S* - spring.
Land use key: CC - corn/grain cash crop rotation; *O* - orchards (apple); *B* - scrub/regrowth; *M* -muckland vegetables; *W* - wooded.

Well characteristics			**Land use assessments**			**NO_3-N**	**Pesticide detections (µg/L)**			
No.	**Depth (ft)**	**Type**	**1°**	**2°**	**3°**	**(mg/L)**	**Metolachlor OA**	**Metolachlor ESA**	**Alachlor ESA**	**Atrazine**
13	4-6	S	O	CC	W	13.6	ND < 0.1	ND < 0.1	ND < 0.1	ND
14b	40-45	D	CC	W	-	24	4.4	4.6	ND < 0.1	trace<0.1
37	40	D	CC	O	W	<0.5	ND < 0.1	0.2	ND < 0.1	ND
39	42	D	CC	O	W	1.3	0.2	0.6	0.1	ND
46	12	G	M	CC	B	1.3	0.2	0.2	ND < 0.1	ND
54	22	G	CC	O	W	<0.5	0.1	1.9	ND < 0.1	trace <0.1

As per the confidentiality protocols, owners were advised regarding the nitrate levels exceeding drinking water standards as well as notable (within standards) levels of pesticide residues, and have been put in contact with the Wayne County SWCD to investigate potential remedial measures. Owners of wells with nitrate above 6 mgN/L were provided with a fact sheet about health effects of nitrate.

3.3 County-Level Studies To Date

The patterns of pesticide detections for the county-level studies (Cortland, Schenectady, Orange, Cayuga, Genesee, and Wayne Counties) are shown in Figures 3.1 and 3.2. It should be remembered that due to equipment upgrades and later refinement of screening protocols, the detection capability of the NYS DEC laboratory improved markedly over time. During the initial Cortland County study, only the Cornell-run ELISA atrazine tests were capable of quantitation at concentrations equal to or below the relevant groundwater standards. For Schenectady County and onward, the DEC laboratory was able to confirm non-exceedence of groundwater standards, whereas Cornell-run

ELISA tests could report quantified concentrations below groundwater standards as well as non-quantifiable trace detections. Most recently, the DEC results reported here for Wayne County represent detection limits comparable to ELISA levels and add the capability to detect degradation products. It is also important to note that, given varying use patterns and ELISA kit availability, ELISA analyses varied from county to county.

Those *provisos* notwithstanding, the detection patterns provide a useful overview of program detections to date. Atrazine has been the most detected pesticide (Figure 3.1), yet at levels not exceeding 0.3 µg/L, which is one tenth of the drinking water standard. Most detections were nonquantified traces (less than 0.1 µg/L), particularly in Cortland County.

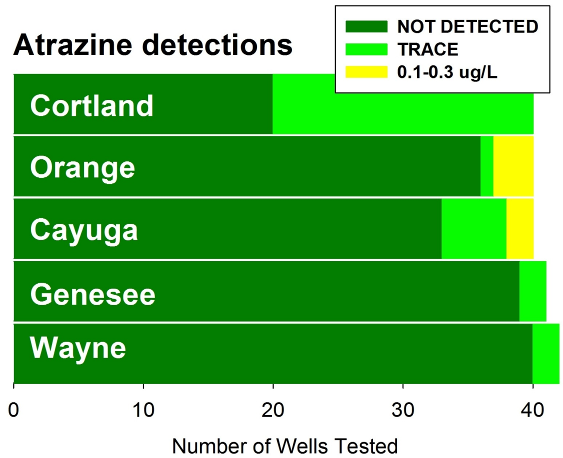

Figure 3.1. Summary of atrazine detections. Trace levels were nonquantified detections below 0.1 µg/L.

Metolachlor (or its degradation products in the case of Wayne County) was the second most commonly-detected pesticide (Figure 3.2 top). Only traces were detected in Orange and Cayuga Counties, while Genesee had a single detection of 4.6 µg/L that was confirmed in subsequent resampling of the well. This detection was below the 9 µg/L drinking water standard, and involved a special case where a well had only a shallow casing and was near pesticide mixing areas. The detections shown in Figure 3.2 for Wayne County are for metolachlor ESA and OA degradation products, as reported above.

Infrequent detections (Figure 3.2 bottom) were alachlor (one trace and one quantified in Cayuga County, one degradation product (ESA) in Wayne County), diazinon (one quantfied in Orange County), and imidacloprid (one trace in Schenectady County).

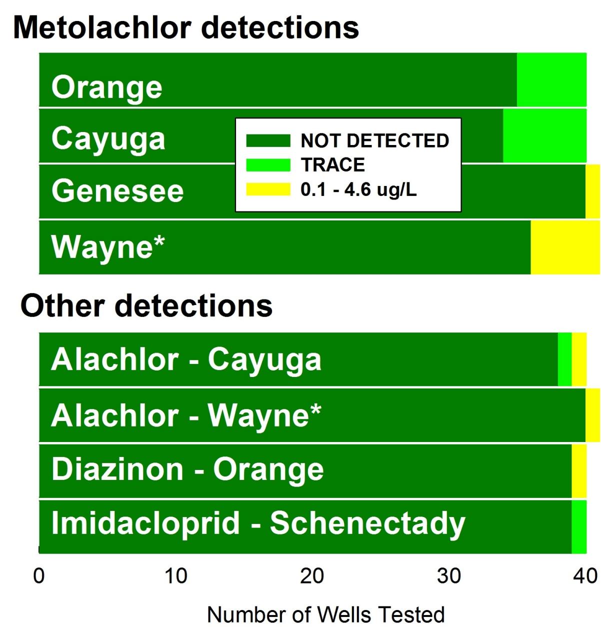

Figure 3.2 Summary of metolachlor (top) and other pesticide (bottom) detections. Trace levels were nonquantified detections below 0.1 µg/L. *Wayne County detections were for degradation products only (metolachlor ESA and OA, and alachlor ESA).

Limited resampling of wells to confirm these results has been carried out. In Cayuga County, five wells (which in the first round had two quantified and three trace detections) were resampled in 2009. The resampled wells yielded one quantified and one trace detection of atrazine, and no detection of metolachlor. In Cortland County, a resampling of seven wells which had trace atrazine in the first round yielded one trace and no other detections of atrazine based on the 0.1 µg/L quantitation limit. No resamplings to date have indicated any increases in the rate of detections.

It is interesting to note that the limited range of pesticide detections took place in the context of a number of wells being susceptible to problems with nitrate (Figure 3.3). Detections of nitrate-N in the range of 6 to 10 mg/L were flagged as being of concern (yellow in Figure 3.3) and were particularly noted in Cortland, Cayuga and Genesee County. Detections of nitrate-N in excess of the 10 mg/L drinking water standard (red in Figure 3.3) were found in three wells in Cortland County, in four wells in Genesee County, and in two wells in Wayne County as noted above.

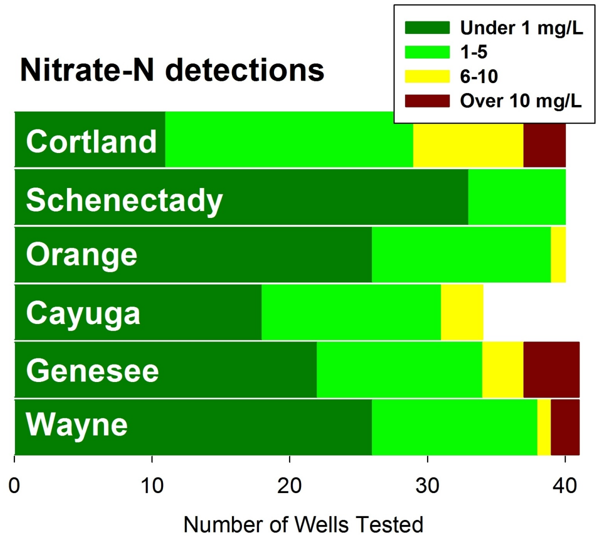

Figure 3.3. Summary of nitrate-N detections. Red indicates levels in excess of the 10 mg/L drinking water standard.

3.4 Outreach and Ongoing Work

Outreach of the results of the county-based sampling programs has been carried out on a number of fronts. Publications have included two refereed publications and a newsletter article:

Sinkevich M.G., M.T. Walter, A. J. Lembo, B. K. Richards, N. Peranginangin, S. A. Aburime, and T.S. Steenhuis. 2005. A GIS-based ground water contamination risk assessment tool for pesticides. *Ground Water Monitoring & Remediation* 25:82-91.

Richards, B. K., S. Pacenka, A. E. Salvucci, S. M. Saia, L. F. Whitbeck, P. M. Furdyna, T.S. Steenhuis. 2012. Surveying Upstate NY Well Water for Pesticide Contamination: Cayuga and Orange Counties. *Ground Water Monitoring & Remediation* 32:73-82. *DOI: 10.1111/j.1745-6592.2011.01366.x*.

Richards, B. K., S. Pacenka, A. E. Salvucci, S. M. Saia, L. F. Whitbeck, P. M. Furdyna, T.S. Steenhuis. 2011. Well water needs to be monitored. *New York State Vegetable Growers News* 3(1) Jan/Feb 2011.

A third refereed publication (Genesee County karst-based sampling) is in preparation in collaboration with Paul Richards of SUNY Brockport.

Other outreach vehicles have included presentations at the 2011 New York Empire Farm Days, the 2012 Northeast Pesticides Certification and Training Workshop (American Association of Pesticide Safety Educators), and for Cornell pesticide applicators meetings in 2008 and 2013.

Ongoing work related to the county-based studies consists of time series resampling of a limited number of wells. This is designed to increase confidence in the single-sampling results of prior studies. Five wells which had detections in the original study were sampled in November 2011 and March, April, and June 2012 in Orange County. Analysis of those samples for pesticides and degradation products is still pending in the DEC laboratory. A similar round of sampling for Cortland County is planned for 2013.

4. ACKNOWLEDGMENTS

The authors would like to acknowledge the collegial advice and support of Luanne Whitbeck, DEC project manager, Robert Warfield and Will Smith in the Cornell PMEP program, and Peter Furdyna of the NYS DEC laboratory. Dr. Shree K. Giri performed nitrate and atrazine analyses at Cornell.

5. REFERENCES

Al-Rajab Abdul Jabbar, Amellal Samira, Schiavon Michel. 2008. Sorption and leaching of 14C-glyphosate in agricultural soils. *Agronomy for Sustainable Development* 28(3)419-428.

Augustijn-Beckers, P. W. M., A. G. Hornsby, and R. D. Wauchope. 1994. The SCS/ARS/CES pesticide properties database for environmental decision making II. Additional compounds. *Reviews of Environ. Contamin. Toxicol.* 137:1-82.

Badawi, Nora, Stig Ronhede, Stefan Olsson, Birthe B. Kragelund, Anders H. Johnsen, Ole Stig Jacobsen, Jens Aamand. 2009. Metabolites of the phenylurea herbicides chlorotoluron, diuron, isoproturon and linuron produced by the soil fungus Morrierella sp. *Environmental Pollution* 157(10) 2806-2812.

Beven, K., and P. Germann. 1982. Macropores and water flow in soils. *Water Resources Research* 18:1311-1325.

Camobreco, V. J., B. K. Richards, T. S. Steenhuis, J. H. Peverly and M. B. McBride. 1996. Movement of heavy metals through undisturbed and homogenized soil columns. *Soil Science* 161(11): 740-750.

Darnault, C.J.D, T.S. Steenhuis, P. Garnier, Y.-J Kim, M.B. Jenkins, W.C. Chiorse, P.C. Baveye, J.-Y Parlange. 2004. Preferential flow and transport of Cryptosporidium parvum oocysts through the vadose zone: Experiments and modeling. *Vadose Zone* 3: 262- 270.

Dictor MC, Baran N, Gautier A, Mouvet C. 2008. Acetochlor mineralization and fate of its two major metabolites in two soils under laboratory conditions. *Chemosphere* 71(4):663-70.

Domange, N., and C. Gregoire. 2006. Bias highlighting in the acquisition of pesticide concentration in soil solution. International Journal of Environmental Analytical Chemistry 86(1-2) 91-108. doi: 10.1080/03067310500247447.

Eckhardt, David A.V., Kari K. Hetcher, Patrick J. Phillips, and Todd S. Miller. 2000. Pesticides and Their Metabolites in Community Water-Supply Wells of Central and Western New York, August 1999. U.S. Geological Survey Water-Resources Investigations Report 00-4128.

Eckhardt, David A.V., William M. Kappel, William F. Coon, and Patrick J. Phillips. 1999. Herbicides and their Metabolites in Cayuga Lake and its Tributaries, New York. U.S. Geological Survey Water-Resources Investigations Report 99-4018.

Fava L, Orrú MA, Businelli D, Scardala S, Funari E. 2006.Leaching potential of some phenylureas and their main metabolites through laboratory studies. *Environ Sci Pollut Res* 13(6):386-91.

Flury, M. 1996. Experimental evidence of transport of pesticides through field soils - a review. Journal of Environmental Quality 25:25-45.

Geohring, L.D., P.E. Wright, T.S. Steenhuis, M.F. Walter. 1999. Subsurface drain water quality impacts from manure applications. NABEC Paper No. 9905, Presented at NE Agricultural/Biological Engineering Conference, Lancaster, PA. 18 pp.

Gustafson, D.I. 1989. Groundwater ubiquity score: A simple method for assessing pesticide leachability. Environmental Toxicology and Chemistry 8:339-357.

Grubesic, T.H. and T. C. Matisziw. 2006. On the use of ZIP codes and ZIP code tabulation areas (ZCTAs) for the spatial analysis of epidemiological data. *International Journal of Health Geographics* 5:58. doi:10.1186/1476-072X-5-58

Hernández, Félix; José M. Marín; Óscar J. Pozo; Juan V. Sancho; Francisco J. López; Ignacio Morell. 2008. Pesticide residues and transformation products in groundwater from a Spanish agricultural region on the Mediterranean Coast *International Journal of Environmental Analytical Chemistry,* 88(6) 409-424.

Huntscha S, Singer H, Canonica S, Schwarzenbach RP, Fennert K. 2008. Input dynamics and fate in surface water of the herbicide metolachlor and of its highly mobile transformation product metolachlor ESA. *Environ Sci Technol.*42(15):5507-13.

Jarvis, N.J., P.E. Jansson, P.E. Dik, I. Messing. 1991. Modeling water and solute transport in macroporous soil: 1. Model description and sensitivity analysis. *Soil Sci*. 42:59-70.

Kim, Y-J, C.J.G. Darnault, N.O. Bailey, J.-Y. Parlange, and T.S. Steenhuis. 2005. Equation for describing solute transport in field soils with preferential flow paths. *Soil Science Society of America Journal* 69:291-300.

Kohne, J. M., S. Kohne, J. Simunek, 2009. A review of model applications for structured soils: b) Pesticide transport. Journal of Contaminant Hydrology 104(1-4) 36-60.

Lodgsdon, S.D. Determination of preferential flow model parameters. *Soil Science Society of America Journal* 66(4): 1095-1103.

New York State Department of Health (NYS DOH). November 1999. New York State Source Water Assessment Program Plan. Bureau of Public Water Supply Protection, Troy, NY. 128pp.

NYASS (New York Agricultural Statistics Service), 2009. Wayne County farm Statistics. Source: http://www.nass.usda.gov/Statistics_by_State/New_York/County_Profiles/Wayne.pdf .

NYSDEC (1998) Division of Water Technical and Operational Guidance Series (1.1.1) *Ambient Water Quality Standards and Guidance Values and Groundwater Effluent Limitations.* Reissued 1998.

Parlange, J.-Y., T.S. Steenhuis, R.J. Glass, T.L. Richard, N.B. Pickering, W.J. Waltman, N.O. Bailey, M.S. Andreini, J.A. Throop. 1988. The flow of pesticides through preferential paths in soils. *New York's Food & Life Science Quarterly* 18: 20-23.

Peterson, G.W., J.M. Harmlett, S. Harrison, S.R. Messier, B.M. Evans, G.M. Baumer, M.C. Anderson. 1996. GIS Pesticide Vulnerability Assessment Procedure for Pennsylvania Public Water Systems. Penn State Environmental Resources Research Inst., University Park, PA.

Phillips, Patrick J., David A. Eckhardt, Melissa A. Smith, and Larry Rosenmann. 2000. Pesticides and their Metabolites in Selected Surface-Water Public Supplies in New York State, 1999. U.S. Geological Survey Water-Resources Investigations Report 00-4119.

Phillips, Patrick J. and Robert W. Bode. 2002. Concentrations of pesticides and pesticide degradates in the Croton River Watershed in southeastern New York, July-September 2000. U.S. Geological Survey Water-Resources Investigations Report 02-4063.

Richards, B. K., S. Pacenka, A. E. Salvucci, S. M. Saia, L. F. Whitbeck, P. M. Furdyna, T.S. Steenhuis. 2012. Surveying Upstate NY Well Water for Pesticide Contamination: Cayuga and Orange Counties. *Ground Water Monitoring & Remediation* 32:73-82. *DOI: 10.1111/j.1745-6592.2011.01366.x*.

Richards, B. K., S. Pacenka, A. E. Salvucci, S. M. Saia, L. F. Whitbeck, P. M. Furdyna, T.S. Steenhuis. 2011. Well water needs to be monitored. *New York State Vegetable Growers News* 3(1) Jan/Feb 2011.

Ritsema, C.J. and L.W. Dekker. 1995. Distribution flow – A general process in the top layer of water repellent soils. *Water Resources Research* 31: 1187-1200.

Scribner, Elisabeth A., E.M. Thurman, and Lisa R. Zimmerman. 1999. Analysis of Selected Herbicide Metabolites in Surface and Ground Water of the United States. U.S. Geological Survey Water-Resources Investigations Report 99-4018B.

Shalit, G. and T.S. Steenhuis. 1996. A simple mixing layer model predicting solute flow to drainage lines under preferential flow. *Journal of Hydrology* 183(1-2): 139-150.

Shipitalo, M.J., W.A. Dick, and W.M. Edwards. 2000. Conservation tillage and macropore factors that affect water movement and the fate of chemicals. *Soil & Tillage Research* 53:167-183

Simonsen, L, IS Fomsgaard, B Svensmark, NH Spliid. 2008. Fate and availability of glyphosate and AMPA in agricultural soil. *J Environ Sci Health B* 43: 365-75.

Sinkevich M.G., M.T. Walter, A. J. Lembo, B. K. Richards, N. Peranginangin, S. A. Aburime, and T.S. Steenhuis. 2005. A GIS-based ground water contamination risk assessment tool for pesticides. *Ground Water Monitoring & Remediation* 25:82-91.

Sinkevich M.G. 2004. A GIS Interpretation of a Hazard Index for Pesticide Contamination in Groundwater. Unpublished Masters Thesis. Cornell University. Ithaca, NY.

Steenhuis, T. S., J. Boll, G. Shalit, J.S. Selker, and I.A. Merwin. 1994. A simple equation for predicting preferential flow solute concentrations. *Journal of Environmental Quality* 23(5): 1058-1064.

Steenhuis, T.S., and J.-Y. Parlange. 1991. Preferential flow in structured and sandy soils. *Proceedings of the National ASAE Symposium on Preferential Flow*. Chicago, 1991. 12-21.

Steenhuis, T.S., J.-Y. Parlange, and M.S. Andreini. 1990. A numerical model for preferential solute movement in structured soils. *Geoderma* 46:193-208.

Steenhuis, T.S. and L.M. Naylor. 1987. A screening method for preliminary assessment of risk to groundwater from land-applied chemicals. *Journal of Contaminant Hydrology* 1: 395-406.

Steenhuis, T.S., S. Pacenka, and K.S. Porter. 1987. MOUSE: A management model for evaluating groundwater contamination from diffuse surface sources aided by computer graphics. *Applied Agricultural Research* 2(4): 277-289.

Steenhuis, T.S., Y.J. Kim, J.-Y. Parlange, M.S. Akhtar, B.K. Richards, K.-J.S. Kung, T.J. Gish, L.W. Dekker, C.J. Ritsema, and S.A. Aburime. 2001. An equation for describing solute transport in field soils with preferential flow paths. p. 137-140. In D.D. Bosch, K.W. King (eds.) *Preferential Flow, Water Movement and Chemical Transport in the Environment*. Proc. ASAE 2nd Int. Symp., Honolulu, HI. Jan. 3-5, 2001. ASAE, St. Joseph, MI.

Steenhuis, T.S. and W.H. van der Molen. 1986. The Thornthwaite-Mather procedure as a simple engineering method to predict recharge. *Journal of Hydrology.* 84 (3-4): 221-229.

Wauchope, R. D., T. M. Buttler, A. G. Hornsby, P. M. Augustijn-Beckers, and J. P. Burt. 1992. The SCS/ARS/CES pesticide properties database for environmental decision making. *Reviews of Environ. Contamin. Toxicol.* 123:1-155.

Weihermüller, L., J. Siemens, M. Deurer, S. Knoblauch, H. Rupp, A. Göttlein and T. Pütz. 2007. In situ soil water extraction: a review. *J Environ Qual* 36:1735-1748 (2007). doi: 10.2134/jeq2007.0218

6. APPENDICES

The following forms used in the study are appended:

6.1 Landowner Information Handout
6.2 Sampling Protocol
6.3 Well Sampling Log

Cornell University
College of Agriculture and Life Sciences

Wayne County
Soil & Water
Conservation District

Research Project:
Surveying Wayne County Drinking Water Wells for Pesticide Residues

What is this about? Researchers from Cornell University's Department of Biological & Environmental Engineering are carrying out a voluntary and confidential sampling of a limited number of drinking water wells in selected areas of Wayne County, in cooperation with the Wayne County Soil & Water Conservation District (SWCD). Sampling and analysis results will be confidential and without cost to landowners.

Why? Groundwater in some areas of New York State – notably Long Island – has been monitored for pesticides after it was discovered in the 1970's that wells on Long Island had been contaminated by intensive agricultural and suburban pesticide use on sandy soils that allowed the pesticides to leach downward into the groundwater. Soil and aquifer conditions in upstate New York are different, and it has long been assumed that there is a much lower likelihood of groundwater becoming contaminated in the same way. However, little actual sampling of upstate wells has been carried out to confirm this. The New York Department of Environmental Conservation (DEC) is funding this research to confirm the quality of upstate drinking water. DEC has asked Cornell to carry out a limited, voluntary and confidential sampling of drinking water wells in selected areas of upstate NY. Wayne County was chosen because of its range of soil and water characteristics and land uses. *The goal is to get an accurate "snapshot" of well water quality in areas of the county for research purposes and is not a "hunt" for potentially contaminated wells.*

Where? Potential sampling areas have been selected based on several factors, including likely pesticide use (agricultural or suburban), relatively shallow groundwater levels, soils that allow leaching, degree of hillslope, etc. as well as the number of people depending on groundwater wells. While pesticide contamination of groundwater is unlikely, wells in these situations are more vulnerable than those in areas where pesticides are rarely used and/or where the soil resists pesticide leaching. We are trying to sample a variety of settings and well types, but due to program constraints can only test a limited number of wells.

How? Samples will be collected from the landowners sink or outdoor faucet by Cornell or District personnel using a standard sampling procedure, as shown below. We would also like to learn any relevant information about the well (depth, age, type of well, softeners or other water treatment, if well ever goes dry, etc.).

Sampling procedure:

1) We will use certified precleaned sample containers coded with a tracking number.

2) Allow faucet/spigot to run for 5 to 10 minutes to fully purge plumbing lines. If possible, sample at the closest accessible valve to well (i.e. before storage tank) and prior to any existing treatment (such as softeners or filters).
3) Rinse and dump each sample bottle three times with the water being sampled.
4) Fill sample bottles 90% full, cap tightly and place bottles in ice chest.
5) Return samples to laboratory for preservation and analysis.

What happens to the samples? Each well sample will be analyzed at Cornell for nitrate, which is sometimes found when agricultural pesticides are also present in groundwater. We will also analyze for several pesticides at Cornell, depending on the likely pesticide use in the area. One set of samples – identified only by a code number – will be shipped to the NY DEC lab for a scan that measures for a wide range pesticides/herbicides). Because of program limitations, we can submit only 40 samples to DEC for full analysis.

What will happen with the information about my well? Several things will happen with the data, but first you should understand that information about individual wells is *not* for public disclosure. What will happen?

1) We will prepare and send you a confidential report indicating lab results determined by Cornell and NYS DEC. Note that the DEC analysis may take a long time to be completed. In the event that traces of pesticides are found, we will also include for comparison the safe drinking water concentration limits for those pesticides.
2) In the very unlikely event that pesticide concentrations exceeding safe drinking water levels are found, we would contact you in order to resample the well twice to confirm the initial findings. If resampling confirms that levels are too high, we would advise both you and the county SWCD. The SWCD would notify relevant county agencies – most likely the Department of Health – to help you safeguard the health of people consuming water from the well(s) by taking appropriate remedial and/or preventative measures.
3) In cases where levels are somewhat elevated but not in excess of drinking water standards, landowners will be encouraged by the SWCD to contact relevant agencies (such as DOH or Agricultural Environmental Management) to take measures that could prevent levels from going any higher.
4) Any published reports about this study will summarize data on a general basis for the county. The location and concentrations of particular well(s)/land cannot be determined from the report. No landowner identities or addresses will be published.
5) Cornell is required to retain a confidential list of all landowner contact information and well locations that will be disclosed only to the NY DEC only upon reasonable request from DEC.

6.2 Sampling Protocol

☐ Fill out SAMPLE INFORMATION LOG SHEET; assign coding number(s) to sample(s).

☐ Label new, certified precleaned polyethylene sample containers. Sample bottle labels will specify ***only*** the tracking code; only the SAMPLE INFORMATION LOG SHEET will link the sampling code to the sampling location, date and comments. The coding format will be ## (two digit number beginning with 01) followed by replicate (A/B/C/etc.). Two bottles will be for DEC submission; and two bottles will be for Cornell analysis and archiving.

☐ If the sampling point is faucet or a spigot, allow faucet/spigot to run for 10 minutes to fully purge plumbing lines; sample at the closest accessible valve to well (i.e. before storage tank) or directly from shallow well and prior to any existing treatment (such as softeners or carbon filters).

☐ Use nitrile gloves to minimize potential contamination. Avoid contact with interior of cap or bottle; do not place cap on ground during filling.

☐ Rinse each sample bottle three times with the water being sampled.

☐ Fill replicate sample bottles approximately 90% full to allow freezing and cap tightly.

☐ Place bottles in ice chest.

☐ Return samples to laboratory and freeze immediately

6.3 Well Sampling Log

Surveying Upstate NY Well Water for Pesticide Contamination
Department of Biological & Environmental Engineering, Cornell University
Wayne County Soil & Water Conservation District

SAMPLE Code: WC____
DATE: / /
INITIALS:___________

SAMPLE INFORMATION LOG SHEET

LOCATION INFORMATION IS CONFIDENTIAL AND IS NOT TO BE DISCLOSED

Contact information

Name ____

Address ____

Phone ______________________________ Email ___________________________________

Well information

Depth: ❑____________ ft. ❑ unknown Type: ❑ drilled ❑ driven ❑ dug ❑ unknown

Age: ❑____________ y. ❑ unknown Wellhead visible? ❑ yes ❑ no

Location (★ on map)____

____

____

GPS: N ° W ° Elev ft.

Water system information

Pump type: ❑ submersible ❑ jet/shallow ❑ unknown Tank?:_____________________________

Treatment: ❑ none ❑ softener ❑ filter ❑ other____

Point of sampling:____

____

____

Area information (surrounding topography & land use) **Map** ✎ ***N***

____

____

____

____

____

____