# Surveying Upstate NY Well Water for Pesticide Contamination

Year 4 Final Report

to the

New York State Department of Environmental Conservation

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## EXECUTIVE SUMMARY

The New York State Department of Environmental Conservation (NYSDEC) 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. Initial work in this effort included sampling of the shallow aquifer system in Cortland County in cooperation with the Cortland County Soil & Water Conservation District (SWCD), in Schenectady County in cooperation with the county SWCD and Water Quality Coordinating Committee (WQCC), and in Orange County again in cooperation with the SWCD. The effort detailed herein describes work in Cayuga County in cooperation with the Cayuga County SWCD. Significant agricultural activity – including intensity of pesticide use – and reliance on ground water made this a priority candidate for sampling, as identified in the statewide selection protocols developed and refined in prior years

***Cayuga County sampling results*** Well selection was based on a combination of local knowledge of groundwater conditions and vulnerabilities, groundwater modeling, and reviewing the zip code-level Pesticide Sales and Use Reporting (PSUR) pesticide application database. The Cayuga County Soil and Water Conservation District (CCSWCD) assisted in site selection, with landowner contacts, sampling and in-house analyses (ELISA assays for atrazine, metolachlor and alachlor as well as nitrate) carried out by Cornell personnel. Sample collection took place between May 2008 and January 2009.

Wells sampled were characterized for surrounding land uses. Agriculture was the primary land use category for 39 wells and was represented in the mixed category assigned to the 40$^{th}$ well. There were 32 wells for which corn/soybean/wheat/etc. cash crops or corn/forage rotation were the primary land uses. Other crops (small fruits, vegetables on non-muck soils, etc.) were the primary land use near 3 wells, hay/pasture for 2 wells, and muck farms and apple orchards for one well each.
Most wells sampled (34) served single houses with 4 serving barns and 2 as utility wells. Of the 37 wells for which depths were known by landowners, 13 wells were shallow (up to 30 ft.), 14 were between 31 and 99 ft. deep, and 10 wells were 100 ft. or greater.

Detection limits for the 93-compound scan run by DEC laboratory were all at or below 1 µg/L. Well sample analysis found no detectable pesticides or herbicides in any of the 40 samples examined. These nondetects thus established that the 40 well samples from Cayuga County did not exceed any maximum contaminant levels (MCLs) or guidance values for those 15 analytes with such standards.

Enzyme-linked immunosorbent annasy (ELISA) scans at Cornell similarly showed that no maximum contaminant levels (MCLs) or guidance values were exceeded for the three analytes tested (atrazine, alachlor, and metolachlor). In total, twelve wells had quantifiable or trace (falling between the 0.1 µg/L quantitation limit and the 0.05 µg/L trace detection limit) detections, all of which occurred at levels lower than the minimum method detection limits (MDL) of the DEC laboratory tests. Two wells had quantifiable detection of atrazine (0.21 – 0.26 µg/L) and one well had a quantifiable detection of alachlor (0.18 µg/L). In addition, there were five trace detections of atrazine, one of alachlor and six of metolachlor. Three wells had multiple detections/trace detections: two of alachlor+metolachlor, and one of atrazine+metolachlor.

All twelve wells with detections (including trace detections) had either corn/cash crop rotations (CC, 9 wells) or corn/forage rotations (CF, 3 wells) as the primary surrounding land use. No other land use was associated with any detections (assuming that the presence of wooded [W] as secondary or tertiary land uses associated with CC or CF had no contribution). In contrast, there were no detections or trace detections for 20 wells with CC and 5 wells with CF as the primary land uses.

Detections correlated strongly with shallow well depths. All three quantifiable detections and nine trace detections occurred in wells with reported depths of 0 (spring-fed) to 30 feet. Three wells with trace detections had depths of 72 to 85 ft. Of the 13 wells sampled with known depths up to 30 ft, eight had ELISA detections or trace detections.

All nitrate-N concentrations were below 10 mgN/L, the greatest observed value being 9.3 mg/L. Seven sites had concentrations in excess of 5 mgN/L; of these, six were shallow wells with depths of 0 to 30 ft.

The limited resampling of five wells in June 2009 resulted in similar nitrate trends and fewer quantifiable and trace detections for atrazine and metolachlor. The DEC scan of these wells again resulted in nondetects for all analytes.

***State-wide assessment*** Both the statewide assessment and in-county selection protocol modifications using the Groundwater Ubiquity Score (GUS) weightings facilitated identifying regions of markedly greater vulnerability that occur within counties (or that run across multiple counties) and led to siting ongoing work in Genesee and Wayne counties. At the time of writing, sampling in Genesee County (Year 5) is completed, as is the on-site analysis of those samples at Cornell University. Site identification is underway in Wayne County (Year 6), and a candidate site for Year 7 work has been identified.

# 1. INTRODUCTION

## 1.1 Project Background

As summarized in the review of Flury (1996), 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). Targeted groundwater monitoring is essential to determine if pesticide registration and application approaches are sufficiently protective of groundwater resources.

The NYSDEC, 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 NYSDEC 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.

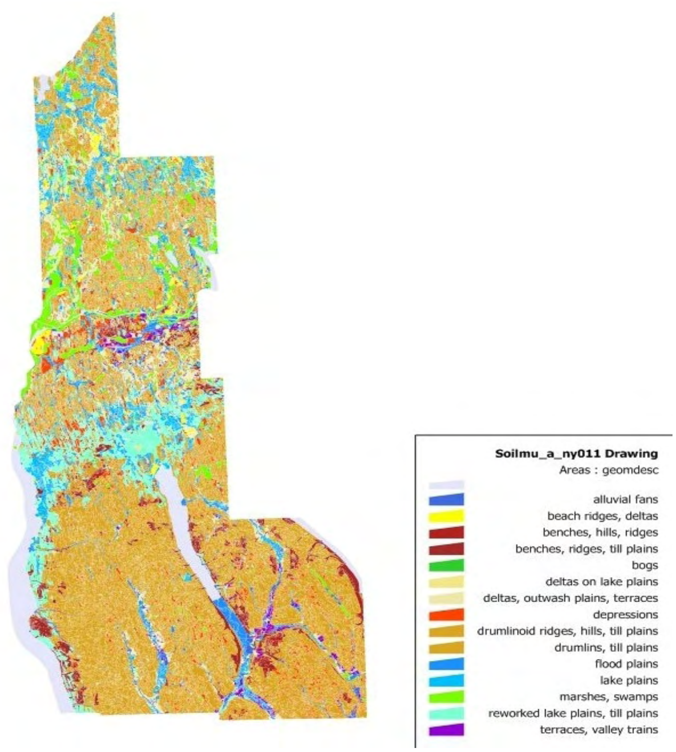

Figure 1.1. Geomorphic features in Cayuga County

## 1.2 Cayuga County Overview

Significant agricultural activity – including intensity of pesticide use – and widespread reliance on ground water made Cayuga County a priority candidate for sampling, as identified in the statewide selection protocols developed and refined in prior project years. The county's north-south extent (beginning at Lake Ontario and stretching into the heart of the Finger Lakes) traverses a number of geomorphic regions (Figure 1.1), leading to a variety of aquifer settings and land use areas (Figure 1.2).

Of the county's 433,628 acres, 54% was in farmland in 2003, with a total of 875 farms (New York Agricultural Statistics Service 2005). As of 2002, the county ranked third in NY for total agricultural sales (over $128,000,000), with dairy products representing 62% of the total, field crops 12%, cattle and calves 8%, vegetables 6%, nursery/greenhouse 4%, and other 8% (NYASS 2005). In terms of agricultural receipts, the county ranked third in the state for dairy, second for field crops and fifth for cattle and calves.

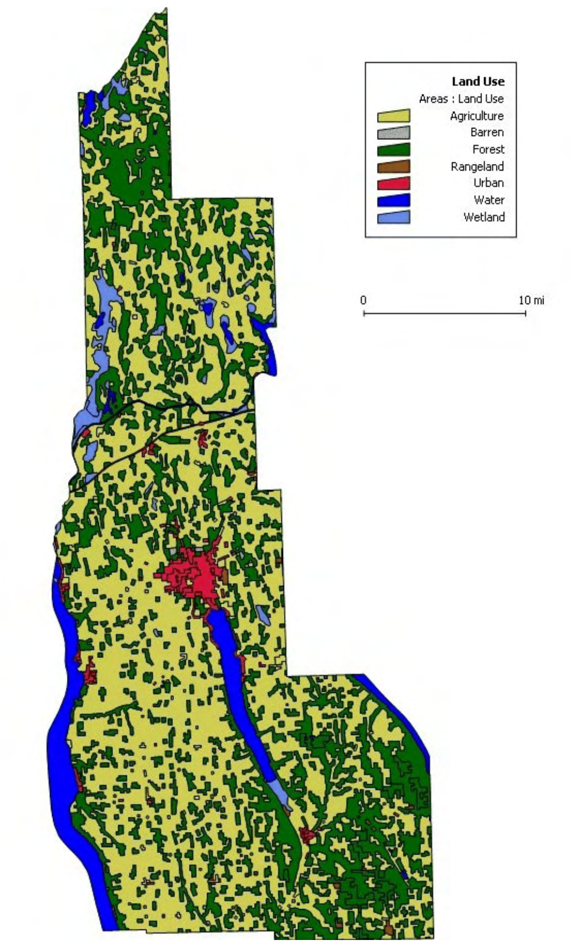


Figure 1.2 Generalized land use pattern in Cayuga County.

Dairy and field crop farming predominate in the southern half of the county, where the terrain is gently rolling between Cayuga, Owasco and Skaneateles Lakes, with a number of large concentrated animal feeding operation (CAFO)-scale farms. Farms are more thinly distributed in the northern half of the county, where the terrain is more strongly influenced by numerous glacial drumlins. There are many small wetlands among the drumlins, with more extensive wertlands in the area where the Seneca River transects the county north of primary urbanized area in and around Auburn (Figure 1.3). Some wetlands in this area are used as muck (organic) soil vegetable farms.

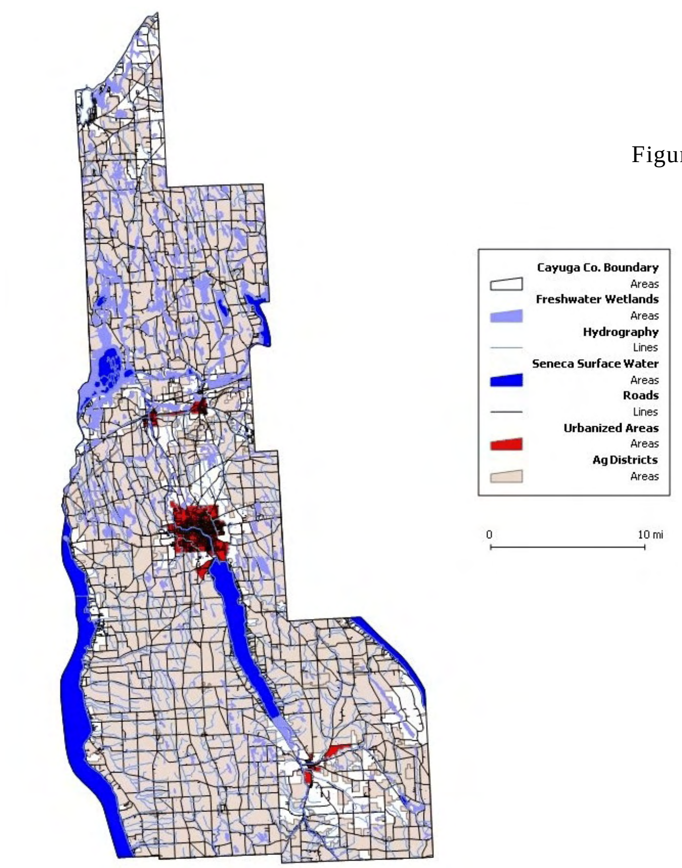


Figure 1.3 Cayuga County overview of wetlands (light blue) and Seneca River/Finger lakes system (dark blue)

## 2. PROJECT COMPONENTS

Four 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. Third is the presentation of *analysis and results* (2.3) of the well sampling carried out in Cayuga County. The final component is the refinement of the GIS-based *statewide assessment of relative groundwater risk* (2.4) used for selection of counties/regions for future research.

### 2.1 Site Selection Process

Program constraints dictated that a maximum of 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 was important. The site selection process developed for this program involved multiple approaches used in concert: 1) assessing local knowledge about areas of likely vulnerability; 2) using a potential transport screening model to determine areas of relative vulnerability within the county based on soil type and depth to groundwater; 3) examining the NYS Pesticide Sales and Use Reporting (PSUR) database for pesticide and herbicide application trends; and 4) examining land use patterns and landscapes using aerial imaging software tools.

#### *2.1.1 Local Knowledge*

This approach involves 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. This process is both iterative and interactive.

The primary source in this case was the Cayuga County Soil & Water Conservation District (CCSWCD; James Hotaling, Executive Director, succeeded upon retirement by Ron Podolak). Initial contact with the CCSWCD led to a presentation the district board in October 2006, which voted formal approval of the district's cooperation. Site targeting priorities were developed during several meetings held in Cayuga County in early 2007, with District Technician Valerie Horning taking the primary role for the CCSWCD.

#### *2.1.2 Groundwater Exposure Assessment Modeling*

The development of the screening model of relative risk based on soil characteristics and groundwater depth was reported in detail in previous reports and is only briefly summarized here. The model (Sinkevich 2004, Sinkevich et al. 2005) was used as a screening tool to identify areas where soils types and shallow groundwater could make groundwater more vulnerable.

Contamination of groundwater is dependent on many factors, many of which cannot be fully known without intensive data collection. However, simplified screening models have been developed to help predict the potential for contaminant transport. The Generalized Preferential Flow Model (GPFM) needs only limited inputs of soil properties and aquifer recharge data to predict potential preferential transport in soils. It is important to note that this is a *relative risk* assessment tool designed to detect areas with greater groundwater vulnerability as an aid in sampling area selection, *not* an attempt to predict actual groundwater pesticide concentrations.

Table 2.1 Screening assessment atrazine parameters.

| **Parameter** | **Value** | **Source** |
|---|---|---|
| $K_{oc}$* Organic Adsorption Coefficient | 160 $cm^3/g$ | DelVecchio & Haith, 1993 |
| $t_{1/2}$ Half-life | 60 days | |
| *H* MCL | 3 µg/L | www.epa.gov/-safewater/mcl.html |
| *M* Application Rate | 1.45 x $10^{-4}$ $g/cm^2$ | www.usda.gov/nass/ |

The GPFM describes solute transport between the land surface and ground water. A conceptualized two-zone soil profile is used, with a near-surface distribution zone and a deeper transmission zone (Jarvis et al., 1991; Steenhuis et al., 1994; Ritsema & Dekker, 1995; Shalit & Steenhuis, 1996; Kim et al., 2005; Steenhuis et al., 1991, 2001). In the distribution zone, water and solutes are funneled into preferential flow paths which transport solutes through the transmission zone, accelerating contaminant transport (Camobreco et al. 1996, Beven & Germann 1982, Darnault et al. 2004, Geohring et al. 1999). The distribution zone depth depends on geomorphology or land use (e.g. plow depth).

We implemented the GPFM in a GIS using spatially-distributed estimates of mean percolation velocity *(v)* and depth to ground water *(x)*. Groundwater depth typically varies throughout the year but soil survey (SURRGO/STATSGO) minimum groundwater depths sufficiently capture the distributed water table depths for our purposes. We used atrazine as a model mobile, slowly-degraded compound and assumed label-based application rates (Table 2.1). The predicted relative concentration of the model compound at the estimated groundwater depth was calculated for each soil type for a three-year duration. Required data consisted of annual recharge to groundwater table (calculated from precipitation, temperature, and evaporation data), soil type and properties, depth to groundwater, and chemical data (degradation and chemical adsorption rate).

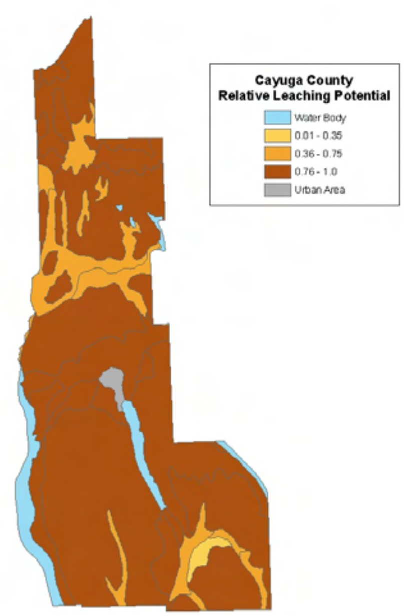


Figure 2.1 Relative groundwater vulnerability as a function of soil characteristics and groundwater depth; dark brown represents greater leaching potential.

A grouped risk classification was then assigned based on the relative risk normalized to the greatest predicted concentration, as mapped in Figure 2.1. It should be reiterated that the figure indicates areas with greater *relative* groundwater vulnerability using the mobility characteristics of a model pesticide, and does not predict actual or potential contamination.

Depth to shallow groundwater proved particularly significant in the model results, as evidenced by the greatest relative risk (red) assigned to the regions of the county where wetlands dominate. However, the majority of the county fell into the moderate vulnerability category. As such, the results of other site selection approaches were given greater weight.

### *2.1.3 Utilization of the PSUR Database*

*Zip-code level data for site selection*

In September 2006 we requested access to the confidential application records of the PSUR database for both Year 3 (Orange County) and 4 (Cayuga County) projects. The Department of Health processed our request quickly, and approval of our request by the Health Research Science Board was granted in January 2007. However, delays in the notification process were substantial: the database group did not receive the authorization to release data until early June 2007, and due to workflow requirements could not generate and release the data report until early August 2007.

Given our experience in prior project years (wherein surrounding land use proved a far better predictor of trace atrazine detections as compared to 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 confidential database, we elected to first rely only on the publicly-available zip-code-level PSUR data summaries for determining which regions within Cayuga County had the greatest intensities of pesticide use.

The summarized data was converted to applied mass of active ingredients (AIs) as described in Section 2.4 and plotted using a GIS (Manifold) to reveal application intensity patterns. As can be seen in Figure 2.2 (top), this approach had some utility for targeting purposes. However, the intensities of application for all AIs did not strongly differ among areas within the county, especially in contrast to some other areas in the figure. To better account for the varying potentials for individual pesticides to travel to groundwater, we incorporated the Groundwater Ubiquity Score (GUS) approach (Gustafson, 1989), which weights pesticides using persistence and mobility parameters from the USDA Pesticide Properties Database (Wauchope et al, 1992; Augustijn-Beckers et al, 1994). The GUS scheme rates active pesticide ingredients using an index which is greatest for compounds which persist longest in the environment and which are most mobile with water. The GUS values for the 25 active ingredients with the greatest use in Cayuga County are shown in Table 2.2, based on the average of 2000-2005 PSUR datasets. A zero GUS value would apply to a pesticide that is immediately degraded and/or immobilized. A GUS value above 2.0 indicates a moderate potential to persist and move to ground water, and a value above 3 indicates a high potential. As can be seen (Figure 2.2 bottom), GUS-weighted application intensities varied significantly in the county, with very high weighted intensities in a number of areas, particularly the southwestern portion of the county. This information was used to focus site selection attention on these areas.

*Additional uses of zip-code level data*

Publicly-available PSUR data summarized at the zip-code level was also used to guide the choice of immunoassay pesticide test kits for more intensive on-site analysis. As detailed below, Cornell supplements NYS DEC's laboratory pesticide scans with the analysis of one to three active ingredients, using greater resolution (one to two orders of magnitude) ELISA immunoassays. The analytes are chosen based on three interacting considerations: (1) extent of use; (2) relative pesticide mobility and persistence (and thus likelihood of reaching ground water); and (3) availability of immunoassay test kits. Table 2.2 summarizes all three considerations for the 25 most-applied active ingredients in Cayuga County. High use intensities and GUS values over 3.0 for atrazine and metolachlor indicate compounds of greater concern, whereas values of under 1.0 for compounds indicate much lower concern for potential ground water contamination. Using this data, we elected to perform ELISA tests for alachlor, metolachlor and atrazine.

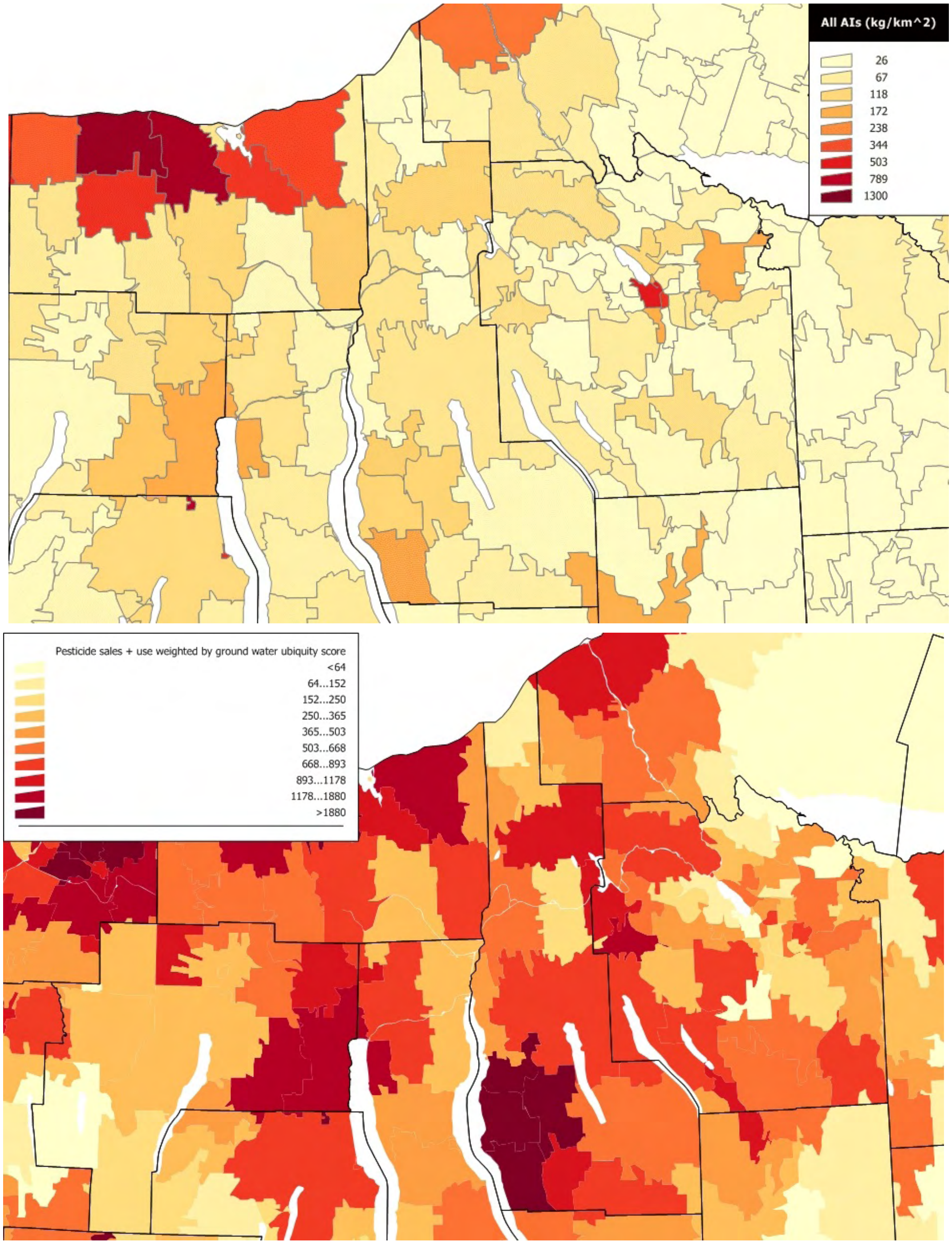


Figure 2.2. GIS representations for Cayuga County and surrounding areas of 1) top: active ingredient use intensities (kg AI $km^2$) and 2) bottom: active ingredient weighted for groundwater ubiquity score (kg GUS $km^2$), based on publicly-available zip-code level PSUR sales and use summaries for 2000-2005.

| Table 2.2. The 25 most-applied pesticide active ingredients in Cayuga County (average of 2000-2005 reporting years), relative Groundwater Ubiquity Score (GUS), and availability of ELISA screening test kits. | | | | | |
|---|---|---|---|---|---|
| **Name** | **Reported Sales (kg/yr)** | **Reported Use (kg/yr)** | **Combined Sales+Use (kg/yr)** | **Groundwater Ubiquity Score** | **Available ELISA kit?** |
| Metolachlor | 9,880 | 13,960 | 23,840 | 3.32 | ✓ |
| Atrazine | 11,394 | 11,918 | 23,312 | 3.56 | ✓ |
| Pendimethalin | 5,604 | 7,477 | 13,081 | 0.59 | |
| Glyphosate-isopropylammonium | 4,105 | 826 | 4,932 | v. low | ✓ |
| Sodium hypochlorite | 0 | 4,924 | 4,924 | | |
| Alachlor | 3,614 | 1,129 | 4,743 | 2.08 | ✓ |
| Glycine, n-(phosphonomethyl) potassium salt | 1,443 | 1,641 | 3,084 | | |
| Glyphosate, isopropylamine salt | 2,028 | 635 | 2,663 | v. low | ✓ |
| Mancozeb | 2,570 | 38 | 2,608 | 1.29 | |
| Cp 70139 Glycine:2-propamine | 1,692 | 348 | 2,040 | | |
| Terbufos | 1,714 | 3 | 1,717 | 0.91 | |
| Chlorothalonil | 519 | 980 | 1,499 | 1.27 | ✓ |
| Pentachloronitrobenzene | 1,252 | 243 | 1,495 | | |
| Glyphosate | 652 | 553 | 1,204 | v. low | ✓ |
| Carbofuran | 1,136 | 38 | 1,174 | 4.52 | |
| Tefluthrin | 1,026 | 28 | 1,054 | | |
| Aliphatic petroleum hydrocarbons | 986 | 65 | 1,051 | | |
| Mesotrione | 326 | 610 | 936 | | |
| Chlorpyrifos | 588 | 148 | 736 | 0.32 | ✓ |
| Coal tar creosote | 0 | 682 | 682 | | |
| Alcoa sodium fluoride | 0 | 664 | 664 | | |
| Banvel k (code nos. 029802 and 030019) | 363 | 247 | 611 | | |
| Sodium n-methyldithiocarbamate | 0 | 601 | 601 | | |
| Dicamba, dimethylamine salt | 333 | 243 | 576 | | |
| Dimethoate | 474 | 74 | 548 | 2.28 | |

### *2.1.4 Land use and landscape assessments*

The fourth approach used in site selection – used for the first time in this manner in our program – was the visual assessment of land use and landscape topography using integrated aerial landscape imaging available through the free Google Earth (version 4.2; available at http://earth.google.com/) software platform. In areas such as Cayuga County where high resolution aerial imaging is available, 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 2.3 (showing a location randomly chosen from within Cayuga County 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 2.3 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 elevations, the Google Earth platform reports the discrete elevation of any point under the cursor for more precise comparisons.

Sites of interest were tagged and documented (using latitude/longitude coordinates), with the portfolio of potential sites saved as an exportable file for sharing within the research group (it should be noted that potential sites were treated within the same confidentiality restrictions as those eventually sampled, thus a map of potential sites is not presented). Site tags were color-coded to indicate site status (i.e. permission requested/no response/permission granted/sampling completed).

It should be noted that this approach was used not only to identify potential sites but also to further evaluate sites suggested as candidates by other approaches.

Once potential sites were identified, their corresponding land parcels were cross-checked with current Cayuga County tax maps (http://71.176.110.94/ORPS/taxmaps/indexpdf.html) to determine the parcel tax identification numbers, which were then compared with the county tax rolls (http://co.cayuga.ny.us/realproperty/2007FinalRolls/) to determine owner names and mailing addresses.

### *2.1.5 Site identification progress*

Based on landowner response rates in prior project years, the site identification process target was to generate at least 80 to 90 potential sites in order to yield the desired 40 sampled sites. Site identification by the CCSWCD began in late 2007, and their initial list of 17 sites included 9 potential sites that Cornell personnel had scouted during initial visits through the county. Additional sites were added by the district, and visual land use/landscape assessments begun at Cornell in early 2008 expanded the contact list to 54 potential sites by the end of March. Landowner contact mailings (shown in the Appendix) yielded 20 positive responses by the end of April, which was sufficient to begin sampling scheduled to begin after post-planting herbicide applications commenced for the 2008 growing season.

While sampling proceeded, potential site selection continued with another round of mailings (late August) and follow-up contacts that yielded the desired 40 landowner permissions (out of 86 finalized sites) by January 2009.

### *2.1.6 Landowner recruitment and confidentiality guidelines*

Information detailing samples 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.)


Figure 2.3 Example of GoogleEarth aerial imagery using location chosen at random from within Cayuga County 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.

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:

- □ In all *public* reporting (published reports to NYSDEC as well as any academic or extension publications), only blurred georeferences – such as rounded coordinates or dithered maps– are reported.
- □ Reports indicating pesticide concentrations determined by Cornell and NYSDEC 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 CCSWCD would be advised. The CCSWCD would notify relevant county agencies (most likely the County Department of Health) 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 (such as referral to a County Health Department or an Agricultural Environmental Management program) for appropriate remedial and/or preventative measures.
- □ Cornell would retain a list of all landowner contact information and exact well locations that will be disclosed only to NYSDEC upon reasonable request from NYSDEC.

## 2.2 Site Characterization and Sampling

Site visits for sample collection began in May 2008 and continued throughout the summer as additional permissions came in. The final 13 samples resulting from the last mailing were collected after the extended university winter break in January 2009. Five sites (12, 24, 25, 30 and 37) were resampled in June 2009 based on detections or trace detections in earlier sample results.

### *2.2.1. Sampled Well Sites*

Table 2.3 (following 2 pages) presents the sampled well information, including well use, type, depth, surrounding land use(s) and sampling date. Land uses were characterized during sampling visits (as well as during site selection and subsequent rechecks via interactive aerial viewing using Google Earth). The well depth, type and facility information is categorized in Table 2.4. Most wells sampled (34) served single households, with 4 serving barns and 2 listed as utility (garage/shop etc.). Of the 37 wells for which the depths were known by landowners, 11 were shallow (up to 30 ft.), 14 were between 31 and 99 ft. deep, and 10 wells exceeded 100 ft. Two were simply existing surface springs. Well types included 23 drilled wells, 3 driven wells, 9 dug wells and, as noted, 2 spring-supplied wells. Of the dug wells, two were artesian, as was one driven well (Table 2.3); two of these artesian wells were classified as flowing (i.e., with the piezometric head reaching the ground surface).

Table 2.4. Summary of sampled well uses, classes of reported well depths, and well types.

| Use | Wells | Depth | Wells | Type | Wells |
|---|---|---|---|---|---|
| | | Spring (0 ft) | 2 | Drilled | 23 |
| House | 34 | Up to 30 ft | 11 | Driven | 3 |
| Barn | 4 | 31-99 ft | 14 | Dug | 9 |
| Utility | 2 | More than 100 ft | 10 | Spring | 2 |
| | | Unknown | 3 | Unknown | 3 |

Table 2.3. Well and surrounding area land use characteristics. *Well use key*: *H*- household, *B*-barn and *U*-utility. *Well type key:D* - drilled, *R* - driven, *G* - dug, *S* - spring; *-A* suffix indicates Artesian, *-FA* suffix flowing artesian. *NA* indicates well depth/type not available. Land use key and category totals appear at bottom of table.

| ID | Well use | Well type | Depth (ft) | Land use ranked by extent | | | Well position relative to land use and topography | Sample date |
|---|---|---|---|---|---|---|---|---|
| | | | | Primary | Secondary | Tertiary | | |
| **1** | H | D | 35 | **CC** | **W** | - | surrounded by corn/soybean fields, distant woods; nearly flat | 05/01/08 |
| **2** | H | D | 300 | **CC** | **W** | - | surrounded by corn/soybean fields, distant woods; nearly flat | 05/01/08 |
| **3** | H | D | 65 | **CC** | - | - | surrounded by corn/soybean/alfalfa/wheat fields; nearly flat | 05/01/08 |
| **4** | H | D | 120 | **CC** | - | **W** | surrounded by corn/soybean/alfalfa/wheat fields; nearly flat | 05/01/08 |
| **5** | H | D | 80 | **CF** | **CC** | **A** | entire upslope landscape is farmland, small orchard near house | 05/01/08 |
| **6** | H | D | 100 | **CC** | - | **W** | flat, surrounded by extensive farm fields, few scattered woodlots | 05/14/08 |
| **7** | H | D | 85 | **CC** | - | **W** | flat, surrounded by extensive farm fields, few scattered woodlots | 05/14/08 |
| **8** | H | G | 12 | **CC** | **W** | - | sandy soil farm fields on all sides; woods beyond; many springs; mapped as karst | 05/14/08 |
| **9** | H | D | 104 | **CC** | **W** | **M** | downslope from large corn/rotation crop field, muck soil on one side, woods all sides | 05/14/08 |
| **10** | H | D | 85 | **CF** | **CC** | **W** | flat, area dominated by corn/rotation crops., few scattered woodlots | 06/02/08 |
| **11** | B | D | 72 | **CF** | **CC** | **W** | flat, area dominated by corn/rotation crops., few scattered woodlots | 06/23/08 |
| **12** | H | G | 25 | **CC** | **W** | - | downslope from flat drumlin top cropped with corn/soy, more distant woods | 06/23/08 |
| **13** | H | D | 58 | **X** | **W** | - | mixed small fruit, hay and crop field, scrub; mostly woods more distant | 06/23/08 |
| **14** | H | D | 176 | **CC** | - | - | surrounded by corn/soybean/alfalfa/wheat fields; nearly flat | 07/16/08 |
| **15** | H | D | 35 | **CC** | - | - | on gently rolling drumlin; well downslope from rotational crop fields | 07/16/08 |
| **16** | H | D | 101 | **H** | **W** | - | on rolling drumlin landscape, downslope from former cornfield | 07/16/08 |
| **17** | H | G | 4 | **A** | **X** | **R** | on low flat drumlin; apple orchards on 2 sides, mixed crop fields and scrub on 2 sides | 07/16/08 |
| **18** | H | *NA* | *NA* | **H** | **CC** | - | down gentle slope from extensive fields: closest hay/pasture; upslope rotation | 09/30/08 |
| **19** | H | D | 80 | **CC** | **W** | - | gently rolling to nearly flat, dominated by corn/rotation crops, scattered large woodlots | 09/30/08 |
| **20** | H | D | 48 | **CC** | **W** | - | gently rolling to nearly flat, dominated by corn/rotation crops, scattered woodlots | 09/23/08 |
| **21** | H | *NA* | *NA* | **CC** | - | **W** | in depression surrounded by extensive corn/rotation fields, distant woods | 09/23/08 |
| **22** | H | *NA* | *NA* | **O** | **CF** | - | downslope from extensive small grain (wheat/oats/barley) fields, some forage/corn | 09/30/08 |
| **23** | H | D | 40 | **CC** | **W** | - | corn/soy/wheat on fields in strong drumlin landscape; woods on steep sides | 09/23/08 |
| **24** | H | D | 15 | **CC** | **W** | - | on low drumlin top surrounded by extensive corn/rotation crop fields, woods beyond | 09/23/08 |
| **25** | H | G | 30 | **CC** | **W** | - | on low drumlin top surrounded by extensive corn/rotation crop fields, woods beyond | 09/23/08 |

continued on following page

Table 2.3, *continued*.

| ID | Well use | Well type | Depth (ft) | Land use ranked by extent | | | Well position relative to land use and topography | Sample date |
|---|---|---|---|---|---|---|---|---|
| | | | | Primary | Secondary | Tertiary | | |
| **26** | B | G-A | v.shallow | **CC** | **W** | **-** | on gentle slope with extensive corn/rotation and other crops; scattered woodlots | 09/23/08 |
| **27** | H | D | 180 | **CF** | **-** | **W** | downslope from extensive corn/forage rotation fields; deep stream gully parallels fields | 11/19/08 |
| **28** | H | D | 100 | **O** | **W** | **-** | on slope below extensive vegetable/fruit fields; some soy/forage crops; woods | 01/03/09 |
| **29** | H | G-FA | 25 | **CF** | **-** | **W** | extensive flat area dominated by dairy farm fields; few scattered woodlots | 01/03/09 |
| **30** | H | S | 0 | **CF** | **W** | **-** | small dairy farm in rolling vale; fields and wooded lots interspersed | 01/05/09 |
| **31** | U | D | 200 | **CC** | **S** | **-** | nearly flat, area with extensive corn/rotation crops; suburban fringe ~1mi distant | 01/12/09 |
| **32** | H | G | 18 | **CC** | **R** | **-** | on small ridge between 2 streams; extensive corn/soy rotation fields; scattered scrub | 01/12/09 |
| **33** | U | S | 0 | **CC** | **-** | **W** | spring source in flat area surrounded by corn/rotation fields; few scattered woodlots | 01/12/09 |
| **34** | H | D | 90 | **CF** | **-** | **W** | on slope below extensive vegetable/fruit fields; some soy/forage crops, woods | 01/05/09 |
| **35** | H | G | 15 | **CC** | **-** | **W** | atop rolling drumlin, surrounded by extensive corn/soybean fields, scattered woods | 01/08/09 |
| **36** | B | R-FA | 40 | **CF** | **M** | **W** | downhill from large drumlin with extensive corn/forage fields; muck on two sides | 01/08/09 |
| **37** | H | G | 20 | **CC** | **-** | **W** | well is midslope in large vale with corn/soy/forage rotation; scattered woodlots | 01/08/09 |
| **38** | H | R | 100 | **CC** | **-** | **W** | well atop wide flat hill (2 sq mi) with extensive fields; wooded at hill periphery | 01/12/09 |
| **39** | B | D | 75 | **M** | **W** | **CC** | extensive muck fields on 2 sides; woods and corn/rotation crop fields | 01/12/09 |
| **40** | H | R | 25 | **O** | **W** | **-** | at base of low rise, crop fields on all sides, woods past one side. Formerly corn/forage | 01/15/09 |

**Legend and category totals by ranked class**

| Category | Primary | Secondary | Tertiary | Land use category explanation |
|---|---|---|---|---|
| **W** | 0 | **17** | **14** | Woods - forest, woodlots |
| **S** | 0 | **1** | 0 | Suburban turf/lawns, including pockets of development, managed turfgrass |
| **U** | 0 | 0 | 0 | Urban areas with higher density housing or other urban land uses |
| **R** | 0 | **1** | **1** | Scrub/regrowth, typically on abandoned farmland |
| **M** | **1** | **1** | **1** | Muck soil (Black dirt, organic soil) vegetable row crops |
| **H** | **2** | 0 | 0 | Hay/pasture - continuous, with no apparent rotation to field crops |
| **CF** | **8** | **1** | 0 | Corn/forage rotation - corn/alfalfa fields typical of many dairy farms |
| **CC** | **24** | **4** | **1** | Corn/soybean/wheat/alfalfa rotation - typical of cash crop and some dairy farms |
| **X** | **1** | **1** | 0 | Mixed use too tightly integrated to delineate into categories |
| **O** | **3** | 0 | 0 | Other crops (small fruits, non-muck soil vegetable crops, etc.) |
| **A** | **1** | 0 | **1** | Apple orchard |
| **-** | 0 | 14 | **22** | no entry: no secondary and/or tertiary land use sufficiently extensive and close to site |

The prioritized land uses shown in Table 2.3 for surrounding and upslope areas were judged to be more likely (though by no means certain, depending on the complexity of the underlying strata) to serve as potential contributing areas to each well, particularly for shallow wells. Land uses were ranked as primary (i.e. most extensive and dominating general and upslope areas), and, if present to a significant degree, secondary and tertiary. In some cases a primary land use was paired with a tertiary land use which occupied an areal extent judged to be too small to be termed secondary. Land uses are summarized at the bottom of Table 2.3 in terms of the number of wells linked to each category.

The primarily agricultural land uses in Cayuga County (particularly for areas not served by public water supplies) are reflected in the land use categorization in Table 2.3. Agriculture was the primary land use category for 39 wells and was represented in the mixed category assigned to the $40^{th}$ well. There were 32 wells for which corn/soybean/wheat/etc. cash crops (CC) or corn/forage rotation (CF) were the primary land uses. Other crops (small fruits, vegetables on non-muck soils, etc.) were the primary land use near 3 wells, hay/pasture for 2 wells, and muck farms and apple orchards for one well each.

The most prevalent secondary land use (17 wells) was woods, often occurring as scattered woodlots in agricultural regions or wooded hillslopes among the steeper drumlins. In 14 cases no secondary land use was assigned, indicating the dominance of the primary land use. Similarly, the assignment of no tertiary land use in 22 cases indicated the predominance of the assigned primary (i.e. sites 3, 14 and 15) or secondary land uses. Scattered or more distant woods were the most common tertiary assignment (14 cases). Areas of scrub/regrowth were little represented (suggesting relatively little abandoned farmland in the area), being a secondary or tertiary use for only 2 sites. The fact that suburban/urban areas are served by public water supply resulted in almost no representation in the sampled well array.

### *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. Landowners were asked to identify accessible spigots or faucets that were closest to the well and preceding, if possible, any existing water treatment equipment such as softeners or carbon filters. The faucet/spigot was allowed to run for several minutes to purge the plumbing lines.

Certified precleaned (Environmental Sampling Supply, PC class) polyethylene bottles were used for sample collection. Four 250 mL bottles were collected for samples for submission to DEC and archiving, and four 60 or 250 mL bottles were 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 (with several landowners needing reassurance that we were not trying to protect ourselves from their well water). 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. 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 the NYS DEC laboratory.

## 2.3 Analysis and Results

Pesticide analysis conducted by NYSDEC consisted of 93 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, alachlor and metolachlor.

### *2.3.1. Analytical Protocols*

*DEC pesticide scans*

This section consists of text forwarded by Peter Furdyna of the NYSDEC Pesticides Laboratory:

The water samples which were submitted to the NYSDEC Pesticides Laboratory under the group numbers Y4-01 through Y4-40 were screened for pesticides, phenoxy acid herbicides and carbamates. All sample results were non-detect at the laboratory's method detection limit (MDL). The reporting levels were 1 ug/L (ppb) for all compounds except dicamba, diazinon, MCPA, and the sum of aldicarb and methomyl, which had detection limits of 0.44 ppb, 0.7 ppb, 0.44 ppb, and 0.35 ppb respectively. For this project, the MDLs are at the lowest calibration concentration on the calibration curve. One sample Y4-14, exhibited a hit for daminozide at 16 ppb by initial analysis using Ultraperformance Liquid Chromatography/Triple Quadupole Mass Spectrometry (UPLC/MS-MS). When it was subject to confirmation by High Pressure Liquid Chromatography, Time-of-Flight Mass Spectroscopy (HPLC/TOF-MS), it failed to confirm. Spiked matrix of Y4-14 at 1 ppb daminozide was used to support the lack of detection for this chemical. Therefore, sample Y4-14 was reported to be non-detect for daminozide at a reporting level of 1 ppb (i.e. ND < 1 ppb).

All samples submitted to the laboratory were successfully analyzed. The samples were received frozen and maintained in secure frozen storage until the time of analysis/extraction. Once aliquots were taken from the thawed samples for processing, the samples were returned to frozen storage without delay. If additional sample was needed, it was thawed, the aliquot taken, and the sample refrozen.

All of the pesticide and herbicide compounds except trifluralin, benfluralin, dithiopyr, chlorpyrifos were analyzed by direct injection followed by HPLC/MS-MS. The remaining four compounds were extracted using the Quechers extraction technique and analyzed by Gas Chromatography/Mass Spectrometery in the Selected Ion Mode (GC/SIM-MS).

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 5 pbb and 10 ppb. Spike recovery and precision information are as follows:

For HPLC/MSMS direct injection pesticide samples, recoveries ranged from 25.0% to 514%, with relative percent differences (RPD's) ranging from 0.0% to 132.7%. All analytes were spiked at 10 ppb in 4 sets of duplicate. Due to an injection error on the HPLC, duplicate data for one spiked sample is not available for diazinon, methomyl, and aldicarb.

For GC/MS extraction and analysis samples, chemicals were spiked at 5 ppb in 4 sets of duplicate samples. Recoveries ranged from 71.3% to 152.3%, with RPDs ranging from 5.8% to 40.3%.

Table 2.5. Method detection limits (MDL) of pesticide/herbicide analyses run by the NYS DEC laboratory. All MDL concentrations are reported as ì g/L (ppb). Method codes: *U* - UPLC/MS-MS; *G* - GC/SIM-MS

| Analyte | MDL | Code | Analyte | MDL | Code |
|---|---|---|---|---|---|
| 2,4-D | 1 | U | Imazalil | 1 | U |
| 3 Hydroxy Carbofuran | 1 | U | Imidacloprid | 1 | U |
| 3,4,5 Trimethacarb | 1 | U | Isoproturon | 1 | U |
| 6-chloro-4-hydroxy-3-phenyl-pyridazin | 1 | U | Isoxaflutole | 1 | U |
| Acephate | 1 | U | Linuron | 1 | U |
| Aldicarb+Methomyl | 0.35 | U | Malathion | 1 | U |
| Aldicarb Sulfone | 1 | U | MCPA | 0.44 | U |
| Aldicarb Sulfoxide | 1 | U | MCPP | 1 | U |
| Amidosulfuron | 1 | U | Metalaxyl | 1 | U |
| Atrazine | 1 | U | Metamitron | 1 | U |
| Azinphos Methyl | 1 | U | Methamidophos | 1 | U |
| Azoxystrobin | 1 | U | Methiocarb | 1 | U |
| Bendiocarb | 1 | U | Metolachlor | 1 | U |
| Benfluralin | 1 | G | Metsulfuron-Methyl | 1 | U |
| Butocarboxim | 1 | U | Monocrotophos | 1 | U |
| Butoxycarboxim | 1 | U | Nicosulfuron (Accent) | 1 | U |
| Carbaryl | 1 | U | Omethoate | 1 | U |
| Carbendazim | 1 | U | Oxamyl | 1 | U |
| Carbofuran | 1 | U | Oxydemeton-Methyl | 1 | U |
| Chlorosulfuron | 1 | U | Pendimethalin | 1 | U |
| Chlorpyrifos | 1 | G | Primicarb | 1 | U |
| Cinosulfuron | 1 | U | Promecarb | 1 | U |
| Clethodim | 1 | U | Propamocarb | 1 | U |
| Clopyralid | 1 | U | Propoxur | 1 | U |
| Cyprodinil | 1 | U | Prosulfuron | 1 | U |
| Daminozid | 1 | U* | Pymetrozine | 1 | U |
| DCPP | 1 | U | Pyridate | 1 | U |
| Demeton-S-Methyl Sulfone | 1 | U | Pyrimethanil | 1 | U |
| Diazinon | 0.7 | U | Quinmorac | 1 | U |
| Dicamba | 0.44 | U | Quizalofop Ethyl | 1 | U |
| Dimethoate | 1 | U | Rimsulfuron | 1 | U |
| Dithiopyr | 1 | G | Spiroxamine | 1 | U |
| Diuron | 1 | U | Tebuconazole (Folicur) | 1 | U |
| Ethiofencarb | 1 | U | Tebufenozide | 1 | U |
| Ethiofencarb-sulfone | 1 | U | Thiacloprid | 1 | U |
| Ethiofencarb-sulfoxide | 1 | U | Thifensulfuron-Methyl (Pinnacle) | 1 | U |
| Fenhexamid | 1 | U | Thiodicarb | 1 | U |
| Fenoxycarb | 1 | U | Thiofanox-sulfone | 1 | U |
| Fenpropimorph | 1 | U | Thiofanox-sulfoxide | 1 | U |
| Flazasulfuron | 1 | U | Triademefon | 1 | U |
| Fluazifop-p-butyl | 1 | U | Triasulfuron | 1 | U |
| Flufenoxuron | 1 | U | Trichlorfon | 1 | U |
| Furathiocarb | 1 | U | Triclopyr | 1 | U |
| Halofenozide | 1 | U | Trifluralin | 1 | G |
| Haloxyfop Ethoxyethyl | 1 | U | Triflusulfuron-Methyl | 1 | U |
| Haloxyfop Methyl | 1 | U | Vamidothion | 1 | U |

*one sample (Well 14) confirmed by HPLC/TOF-MS

*ELISA and nitrate assays*

Water samples were screened at Cornell University for atrazine, alachlor and metolachlor (as the most likely to be detected pesticides, given significant reported use and relative mobility). The five repeat samples collected in June 2009 were tested for atrazine and metolachlor.

The methods employed use Enzyme-Linked ImmunoSorbent Assays (ELISA) to detect the analyte and related compounds. Kits were obtained from Strategic Diagnostics Inc (SDI). Atrazine (SDI Kit No. A00071), alachlor (SDI A00072) and metolachlor (SDI A00080) are magnetic particle ELISA kits with quantitation ranges of 0.1 to 5 ppb (ì g/L) and trace (nonquantifiable) detection limit of 0.05 ì g/L.

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 the results section.

Magnetic particle assays were analyzed on duplicate samples with a Milton-Roy Spectronic 501 using 1 cm path length cuvettes or with the dedicated Ohmicron RPA-1 spectrometer. Calculations transform absorbance data as a fraction of the absorbance ($B/B_0$) produced by the "negative control" (zero standard).

The calibration data is then linearized using logarithms and logit functions. For the test kits used, the form of the regression equation is:

$$\ln(C) = \text{intercept} + \text{slope}\ (\text{logit}\ (B/B_0) \qquad \text{Eq. 2.1}$$

where B = sample absorbance
$B_0$ = absorbance of zero standard (negative control)
C = standard or sample concentration, µg/L (ppb)

ELISA analysis of the initial 40 samples was run in January 2009 (atrazine and alachlor) and October 2009 (metolachlor), and the 5 resampled sites were analyzed in July 2009.

Nitrate, sulfate and chloride were analyzed at Cornell by ion chromatography (Dionex ICS-2000 with anion column), in January 2009 (original samples) or July 2009 (re-samples). Nitrate was expressed as ppm (mg/L) of nitrate-N.

### *2.3.2 Analysis Results*

*DEC analysis*

Pesticide analysis at the NYSDEC laboratory was completed in mid-2009 with final reports transmitted in August 2009. As noted in the prior section, the NYSDEC pesticide screening found that *all analytes were below the detection limits* specified in Table 2.5. NYSDEC analytical results are summarized in Table 2.6.

Table 2.6. Results of analyses run by the NYSDEC laboratory. All concentrations are reported as ì g/L (ppb). *ND* – non-detects, indicating concentration less than the method detection limit.

| **Analyte** | **Conc. (µg/L)** | **Analyte** | **Conc. (µg/L)** |
|---|---|---|---|
| 2,4-D | ND < 1 | Imazalil | ND < 1 |
| 3 Hydroxy Carbofuran | ND < 1 | Imidacloprid | ND < 1 |
| 3,4,5 Trimethacarb | ND < 1 | Isoproturon | ND < 1 |
| 6-chloro-4-hydroxy-3-phenyl-pyridazin | ND < 1 | Isoxaflutole | ND < 1 |
| Acephate | ND < 1 | Linuron | ND < 1 |
| Aldicarb+Methomyl | ND < 0.35 | Malathion | ND < 1 |
| Aldicarb Sulfone | ND < 1 | MCPA | ND < 0.44 |
| Aldicarb Sulfoxide | ND < 1 | MCPP | ND < 1 |
| Amidosulfuron | ND < 1 | Metalaxyl | ND < 1 |
| Atrazine | ND < 1 | Metamitron | ND < 1 |
| Azinphos Methyl | ND < 1 | Methamidophos | ND < 1 |
| Azoxystrobin | ND < 1 | Methiocarb | ND < 1 |
| Bendiocarb | ND < 1 | Metolachlor | ND < 1 |
| Benfluralin | ND < 1 | Metsulfuron-Methyl | ND < 1 |
| Butocarboxim | ND < 1 | Monocrotophos | ND < 1 |
| Butoxycarboxim | ND < 1 | Nicosulfuron (Accent) | ND < 1 |
| Carbaryl | ND < 1 | Omethoate | ND < 1 |
| Carbendazim | ND < 1 | Oxamyl | ND < 1 |
| Carbofuran | ND < 1 | Oxydemeton-Methyl | ND < 1 |
| Chlorosulfuron | ND < 1 | Pendimethalin | ND < 1 |
| Chlorpyrifos | ND < 1 | Primicarb | ND < 1 |
| Cinosulfuron | ND < 1 | Promecarb | ND < 1 |
| Clethodim | ND < 1 | Propamocarb | ND < 1 |
| Clopyralid | ND < 1 | Propoxur | ND < 1 |
| Cyprodinil | ND < 1 | Prosulfuron | ND < 1 |
| Daminozid | ND < 1 | Pymetrozine | ND < 1 |
| DCPP | ND < 1 | Pyridate | ND < 1 |
| Demeton-S-Methyl Sulfone | ND < 1 | Pyrimethanil | ND < 1 |
| Diazinon | ND < 0.7 | Quinmorac | ND < 1 |
| Dicamba | ND < 0.44 | Quizalofop Ethyl | ND < 1 |
| Dimethoate | ND < 1 | Rimsulfuron | ND < 1 |
| Dithiopyr | ND < 1 | Spiroxamine | ND < 1 |
| Diuron | ND < 1 | Tebuconazole (Folicur) | ND < 1 |
| Ethiofencarb | ND < 1 | Tebufenozide | ND < 1 |
| Ethiofencarb-sulfone | ND < 1 | Thiacloprid | ND < 1 |
| Ethiofencarb-sulfoxide | ND < 1 | Thifensulfuron-Methyl | ND < 1 |
| Fenhexamid | ND < 1 | Thiodicarb | ND < 1 |
| Fenoxycarb | ND < 1 | Thiofanox-sulfone | ND < 1 |
| Fenpropimorph | ND < 1 | Thiofanox-sulfoxide | ND < 1 |
| Flazasulfuron | ND < 1 | Triadimefon | ND < 1 |
| Fluazifop-p-butyl | ND < 1 | Triasulfuron | ND < 1 |
| Flufenoxuron | ND < 1 | Trichlorfon | ND < 1 |
| Furathiocarb | ND < 1 | Triclopyr | ND < 1 |
| Halofenozide | ND < 1 | Trifluralin | ND < 1 |
| Haloxyfop Ethoxyethyl | ND < 1 | Triflusulfuron-Methyl | ND < 1 |
| Haloxyfop Methyl | ND < 1 | Vamidothion | ND < 1 |

| Table 2.7. Comparison of NYS ambient groundwater (GA) standards with NYSDEC pesticide scan method detection limits. | | | |
|---|---|---|---|
| **Analyte** | **NYS Standard (µg/L)** | **DEC Scan Detection Limit (µg/L)** | **Does DEC nondetection rule out MCL exceedence?** |
| 2,4-D | 50 | 1 | Yes |
| Aldicarb+Methomyl (sum of both) | 0.35 | 0.35 | Yes |
| Aldicarb Sulfone | 2* | 1 | Yes |
| Aldicarb Sulfoxide | 4* | 1 | Yes |
| Atrazine | 7.5 (3*)** | 1 | Yes |
| Azinphos Methyl | 4.4 | 1 | Yes |
| Carbaryl | 29 | 1 | Yes |
| Carbofuran | 15 | 1 | Yes |
| Diazinon | 0.7 | 0.7 | Yes |
| Dicamba | 0.44 | 0.44 | Yes |
| Malathion | 7 | 1 | Yes |
| MCPA | 0.44 | 0.44 | Yes |
| Metolachlor | 9 | 1 | Yes |
| Oxamyl | 50 | 1 | Yes |
| Trifluralin | 35 | 1 | Yes |

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

In Table 2.7 we compare the maximum allowable MCLs (NYSDEC 1998, with the addition of a more recent metolachlor standard) with the NYSDEC scan detection limits. The table shows only those analytes shown in Tables 2.2.4/2.2.5 that have an associated groundwater (class GA) MCL 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 NYSDEC scan detection limits that were equal to or lower than the MCL, which means that the tests that yieded nondetects ruled out MCL exceedence.

*Cornell analyses*

The three ELISA scans conducted at Cornell University for atrazine, diazinon and metolachlor indicated three quantifiable detections (Table 2.8): 0.21 and 0.26 µg/L atrazine at sites 24 and 25, and 0.18 µg/L alachlor at site 8. These were all at levels well below the 1.0 µg/L detection limits of the corresponding DEC scans. In addition, there were twelve nonquantifiable trace detections found, with analyte responses greater than the 0.1 µg/L method detection limit (MDL) but less than the 0.5 µg/L minimum limit of quantitation (LOQ). Trace detections included five atrazine (wells 15, 26, 30, 33 and 37), one alachlor (well 12) and six metolachlor (wells 7, 8, 10, 11, 12, and 15). As can be seen in Table 2.8, of the twelve wells that had ELISA detections, there were three cases of multiple analyte detection: wells 8, 12 (both alachlor/metolachlor), and 15 (atrazine/metolachlor).

Cornell results for well nitrate-N, chloride and sulfate analyses are shown in Table 2.9. Ion chromatograph nitrate analyses were complicated by high levels of sulfate in some samples which caused the sulfate peak to adversely affect the subsequent nitrate peak.

Table 2.8. ELISA analytical results and reported cross-reactivities. “Trace” indicates detection at concentrations lower than the specified Limit of Quantitation (LOQ) but greater than the Method Detection Limit (MDL). Cross-reactivites of related compounds are reported as concentrations required to generate responses equivalent to primary analytes at the specified LOQ. All concentrations expressed as µg/L.

| Well No. | Well Depth (ft) | Atrazine | Alachlor | Metolachlor |
|---|---|---|---|---|
| | | *LOQ:* 0.1 | 0.1 | 0.1 |
| | | *MDL:* 0.05 | 0.05 | 0.05 |
| 1 | 35 | nd | nd | nd |
| 2 | 300 | nd | nd | nd |
| 3 | 65 | nd | nd | nd |
| 4 | 120 | nd | nd | nd |
| 5 | 80 | nd | nd | nd |
| 6 | 100 | nd | nd | nd |
| 7 | 85 | nd | nd | trace <0.1 |
| 8 | 12 | nd | 0.18 | trace <0.1 |
| 9 | 104 | nd | nd | nd |
| 10 | 85 | nd | nd | trace <0.1 |
| 11 | 72 | nd | nd | trace <0.1 |
| 12 | 25 | nd | trace <0.1 | trace <0.1 |
| 13 | 58 | nd | nd | nd |
| 14 | 176 | nd | nd | nd |
| 15 | 35 | trace <0.1 | nd | trace <0.1 |
| 16 | 101 | nd | nd | nd |
| 17 | 4 | nd | nd | nd |
| 18 | *NA* | nd | nd | nd |
| 19 | 80 | nd | nd | nd |
| 20 | 48 | nd | nd | nd |
| 21 | *NA* | nd | nd | nd |
| 22 | *NA* | nd | nd | nd |
| 23 | 40 | nd | nd | nd |
| 24 | 15 | 0.21 | nd | nd |
| 25 | 30 | 0.26 | nd | nd |
| 26 | v.shallow | trace <0.1 | nd | nd |
| 27 | 180 | nd | nd | nd |
| 28 | 100 | nd | nd | nd |
| 29 | 25 | nd | nd | nd |
| 30 | 0 | trace <0.1 | nd | nd |
| 31 | 200 | nd | nd | nd |
| 32 | 18 | nd | nd | nd |
| 33 | 0 | trace <0.1 | nd | nd |
| 34 | 90 | nd | nd | nd |
| 35 | 15 | nd | nd | nd |
| 36 | 40 | nd | nd | nd |
| 37 | 20 | trace <0.1 | nd | nd |
| 38 | 100 | nd | nd | nd |
| 39 | 75 | nd | nd | nd |
| 40 | 25 | nd | nd | nd |

**Cross-reactivity at specified response level**

| **Atrazine (SD A00071)** | 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 |

| **Alachlor (SD A00072)** | at LOQ |
|---|---|
| Alachlor | 0.1 |
| Alachlor ESA | 0.3 |
| Metolachlor | 7.99 |
| Butachlor | 13.3 |
| Propoachlor | >10,000 |

| **Metolachlor (SD A00080)** | at LOQ |
|---|---|
| Metolachlor | 0.1 |
| Acetochlor | 0.77 |
| Metalaxyl | 0.66 |
| Butachlor | 6.12 |
| Propoachlor | 294 |
| Alachlor | 9.9 |

Nitrate concentrations (Table 2.9) were below the 10 mg N/L drinking water standard, with an observed maximum concentration of 9.3 mg N/L (site 25). Seven sites had concentrations in excess of 5 mg N/L; of these sites, six had shallow well depths (0 to 30 ft), with the seventh site having a well depth of 90 ft. Mean nitrate values for the sample set were not computed given the uncertainty of 10 measurements due to interference caused by large sulfate concentrations (in some cases exceeding 500 mg/L). This area is known to have high sulfate in ground water due to the dissolution of natural gypsum deposits. High sulfate (in one case over 1000 mg $SO_4$/L) interfered with the detection of low nitrate. Examination of individual ion chromatograph peaks using 10-fold dilutions, however, determined that high sulfate was not masking nitrate values over 1 mg N/L, in all likelihood. Thus the samples with high sulfate overlapping into the nitrate peak region are reported as “interference, less than 1 mg/L nitrate-N”.

Table 2.9. Well sample nitrate-N , chloride and sulfate analysis (mg/L).

| Well | Depth | Nitrate-N | Chloride | Sulfate |
|---|---|---|---|---|
| 1 | 35 | 0.5 | 294 | 75 |
| 2 | 300 | <0.5 | <10 | 15 |
| 3 | 65 | 3.5 | 58 | 78 |
| 4 | 120 | interference <1 | <10 | >150 |
| 5 | 80 | interference <1 | 97 | >500 |
| 6 | 100 | interference <1 | 30 | >150 |
| 7 | 85 | <0.5 | 51 | >150 |
| 8 | 12 | 5.6 | 59 | 51 |
| 9 | 104 | interference <1 | 351 | >150 |
| 10 | 85 | interference <1 | 99 | >500 |
| 11 | 72 | interference <1 | 43 | >500 |
| 12 | 25 | 3.7 | <10 | 57 |
| 13 | 58 | 1.0 | <10 | 15 |
| 14 | 176 | <0.5 | 37 | 48 |
| 15 | 35 | 4.4 | 42 | 90 |
| 16 | 101 | interference <1 | 18 | >150 |
| 17 | 4 | 3.2 | 45 | 12 |
| 18 | *NA* | 0.5 | 50 | 60 |
| 19 | 80 | <0.5 | <10 | 42 |
| 20 | 48 | 0.3 | 27 | 72 |
| 21 | *NA* | <0.5 | 15 | 51 |
| 22 | *NA* | 0.4 | <10 | 27 |
| 23 | 40 | 0.5 | <10 | 93 |
| 24 | 15 | 5.3 | 25 | 24 |
| 25 | 30 | 9.3 | 16 | 27 |
| 26 | v.shallow | 8.2 | 72 | 48 |
| 27 | 180 | <0.5 | <10 | <3 |
| 28 | 100 | 5.3 | 18 | 21 |
| 29 | 25 | 1.5 | 45 | 81 |
| 30 | 0 | 5.5 | <10 | 15 |
| 31 | 200 | interference <1 | 53 | >150 |
| 32 | 18 | interference <1 | <10 | >150 |
| 33 | 0 | 4.7 | 45 | >150 |
| 34 | 90 | 5.5 | 16 | 21 |
| 35 | 15 | 3.4 | 10 | 48 |
| 36 | 40 | <0.5 | 193 | 45 |
| 37 | 20 | 3.3 | <10 | 15 |
| 38 | 100 | <0.5 | 15 | 39 |
| 39 | 75 | <0.5 | 232 | 27 |
| 40 | 25 | interference <1 | 16 | >500 |

### *2.3.3. Resampling results*

As noted previously, five wells (12, 24, 25, 30 and 37) were resampled in June 2009 based on detections or trace detections in earlier sample results. Reanalyses included nitriate-N and ELISA scans for atrazine and metolachlor at Cornell as well as submission to NYSDEC for full analysis. As shown in Table 2.10, nitrate testing yielded similar results. ELISA analysis showed fewer detections following the resampling: one quantifiable detection and one trace detection for atrazine (vs. two each for the original sampling) and no detection for metolachlor.

Table 2.10. Well characteristics and analytical results for resampled wells with quantified or trace ELISA detections; *nd* indicates not detected. NYSDEC scans with same analytes and detection levels as Table 2.5. *Well type key:D* - drilled, *G* - dug, *S* - spring.

| **Well characteristics** | | | **DEC Scan (all 93 analytes)** | **$NO_3$-N (mg/L)** | | **Atrazine (µg/L)** | | **Metolachlor (µg/L)** | |
|---|---|---|---|---|---|---|---|---|---|
| **No.** | **Depth (ft)** | **Type** | | **Initial** | **Resample** | **Initial** | **Resample** | **Initial** | **Resample** |
| 12 | 25 | G | nd | 3.7 | 3 | nd | nd | trace <0.1 | nd |
| 24 | 15 | D | nd | 5.3 | 3 | 0.21 | 0.12 | nd | nd |
| 25 | 30 | G | nd | 9.3 | 9 | 0.26 | trace <0.1 | nd | nd |
| 30 | 0 | S | nd | 5.5 | 4 | trace <0.1 | nd | nd | nd |
| 37 | 20 | G | nd | 3.3 | 2 | trace <0.1 | nd | nd | nd |

## 2.4. Statewide Assessment of Relative Groundwater Exposure

One continuing task begun in the first year effort was the development of a protocol to guide the identification and prioritization for screening vulnerable upstate aquifers. This framework followed a GIS-based protocol which overlays vulnerable aquifers, population dependence on groundwater and several indices of pesticide use. These components were overlaid using a GIS to determine the NYS counties with the most population potentially exposed to pesticide residues via groundwater used as drinking water. Cortland, Schenectady and Orange counties emerged from the first year screening process as the primary counties to sample based on the screening criteria used. This original protocol is summarized in prior reports.

However, as indicated previously, the initial selection protocol aggregated data at the county level in the final step in a manner that did not adequately discriminate pesticide applications within areas of counties served by large municipal water systems which, by virtue of having existing monitoring programs in place, are not the focus of this inquiry. The final aggregation also served to mask elevated vulnerability areas within counties that also had low vulnerability areas elsewhere that, when combined, yielded a more moderate average score. The following section thus describes a modified process that eliminates the final county-level aggregation, thus producing assessment maps that present data at the finer resolution of zip-code levels.

### *2.4.1. Zip-code level resolution pesticide use mapping*

The Pesticide Sales and Use Reporting (PSUR) system provides publicly-available data that is summarized by zip code area and county. Data include a product code, a volume or a weight of product, and a location, either the county name or a 5-digit zip code. This report includes 2000-2005 data.

The PSUR covers pesticide use by commercial applicators and sales to farmers who apply pesticides themselves. (Farmers, however, are not required to report their own pesticide uses.) This report combines the commercial use and sales-to-farmers data. One limitation is that, in some cases, the sales data may reflect the zip code of the seller rather than the zip code of ultimate application.

Use and sales data include amounts of each product, reported in either gallons or pounds. These data must undergo two conversion steps. First, liquid product volume is converted to weight using a density (specific weight). Second, product weight is converted into active ingredient weights using a product composition table that contains the weight percentages of each active ingredient in each product. Specific weights and active ingredient percentages used here are preliminary databases from 2007. Improved data of both types are now available from the Cornell Pesticide Management Education Program.

Figure 2.4 shows how these data are synthesized to yield tables and maps of various active ingredient weights. Note that the maps and tables in this report express data in kilograms or kg per square kilometer. [To obtain a common label rates (i.e. pounds of active ingredient per acre per year), multiply kilograms per kilometer squared by 0.01 hectares/km$^2$, by 2.205 lbs/kg, and by 0.4049 hectares/ acre, yielding a conversion factor of 0.0089 lbs/acre per kg /km$^2$.]

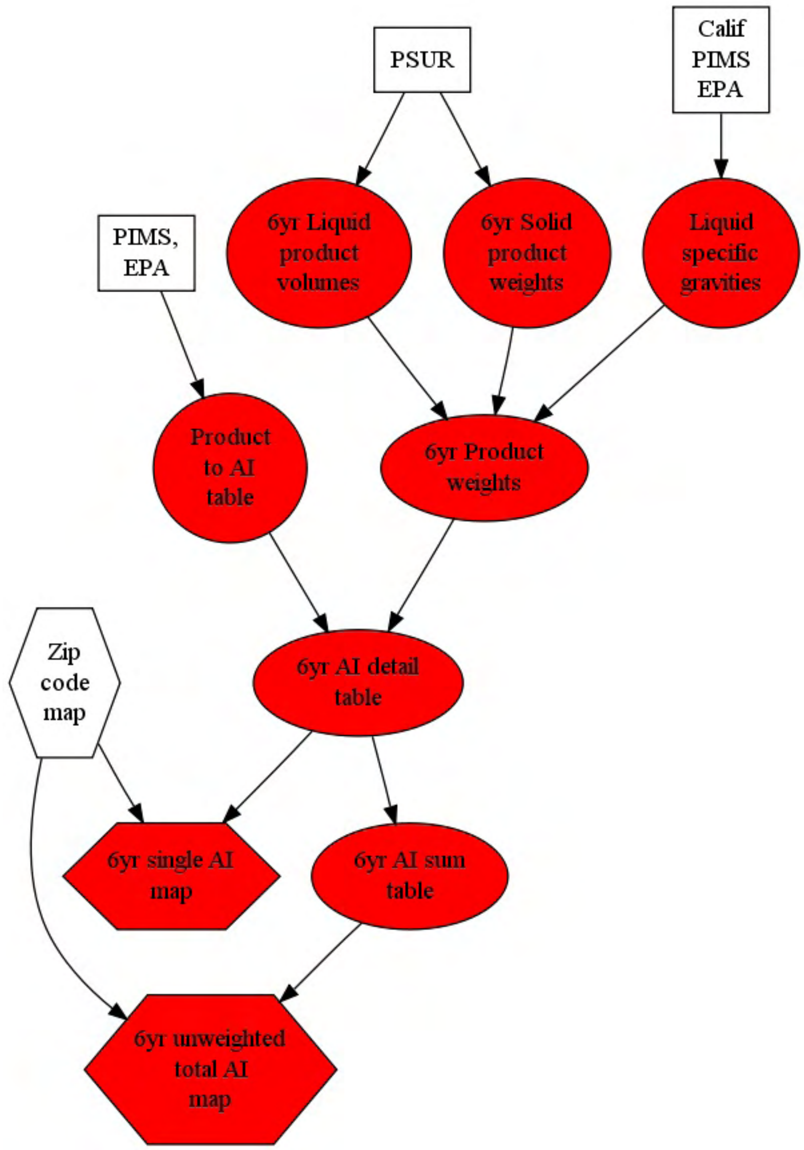


Figure 2.4. Schematic of procedure used to synthesize cumulative active ingredient data

Figure 2.5 maps the use intensity of all active ingredient weights for all of New York. The density color index is skewed by heavy use rates in New York City, southern Westchester County, Long Island, and the counties adjacent to Lake Ontario. (Previously-shown Figure 2.2 (top) focuses on Cayuga County and vicinity).

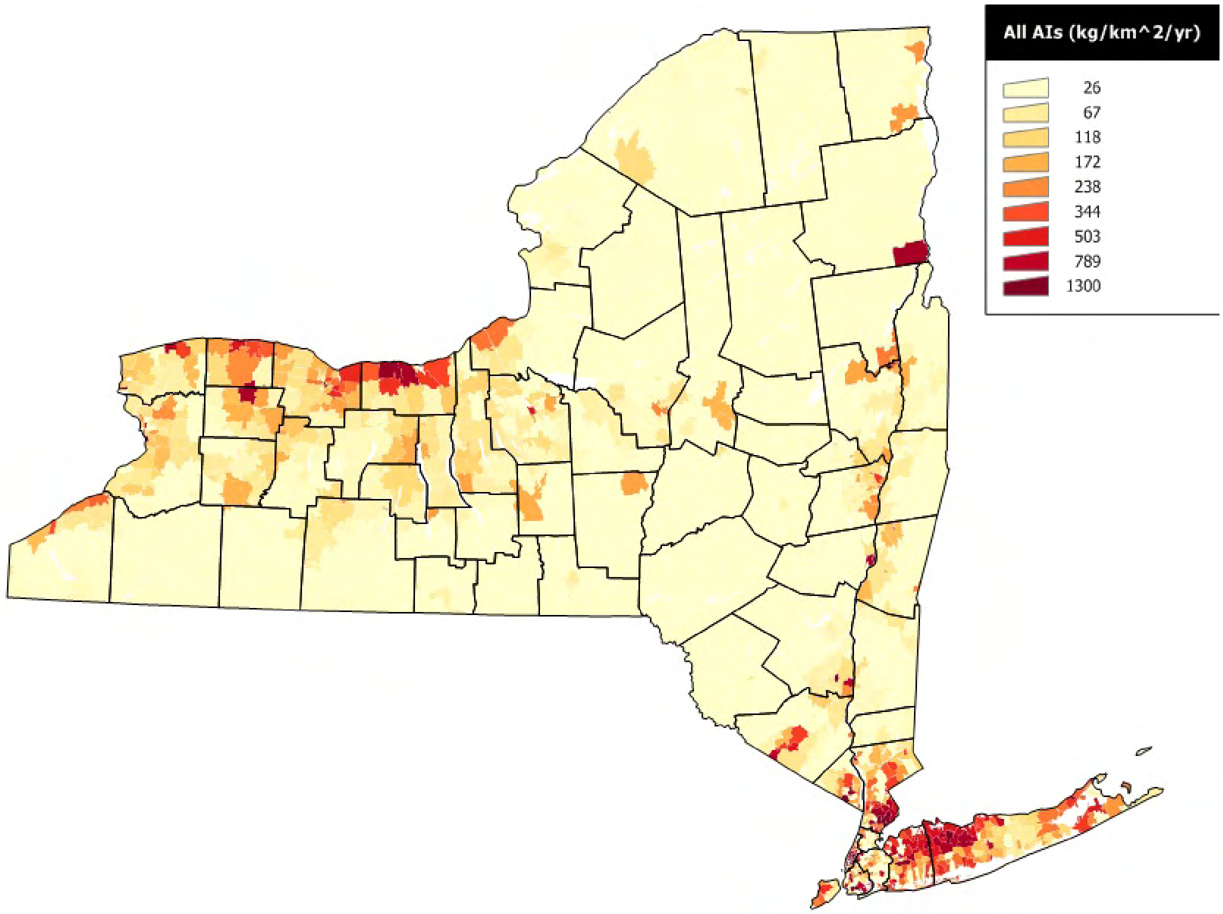

Figure 2.5. Summary of the use intensity of all active ingredients (kg/$km^2$) in New York, 2000-2005.

As stated previously, 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 which is greatest for compounds which persist longest in the environment and which are most mobile with water. As can be seen in Figure 2.6, the use of GUS-weighted application intensities changes the statewide pattern markedly. GUS-weighted scores for Cayuga County and surroundings were shown in Figure 2.2( bottom).

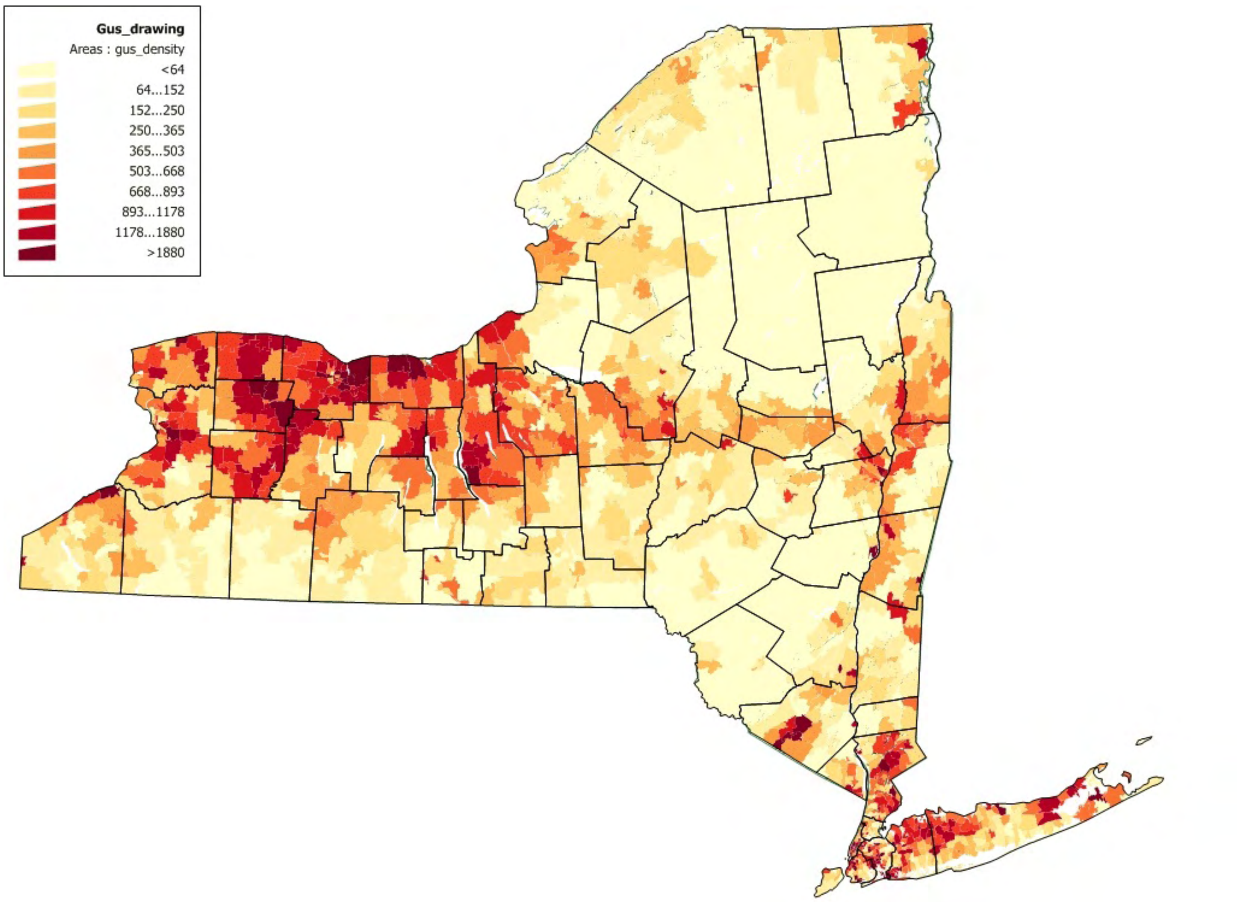


Figure 2.6. Use intensity of all active ingredients (kg/km$^2$) weighted for Groundwater Ubiquity Score, based on 2000-2005 PSUR dataset.

### *2.4.2. Implications for future testing*

This GUS-weighted approach highlights the band of relatively heavily-treated areas spanning the intensive agricultural region of Western and Central New York south of Lake Ontario. High usage of relatively mobile/persistent compounds is also notable in urban/suburban areas in the region (notably Rochester and associated outlying areas in Monroe County) but where municipal water is widely used. Based on this mapping and other land use information, we initiated work Genesee County for Year 5 activities and are beginning work in Wayne county for Year 6 activities (tagged G and W in Figure 2.7, respectively). Vulnerable aquifers in that region include substantial karst formations with close connections between groundwater and surface flow.

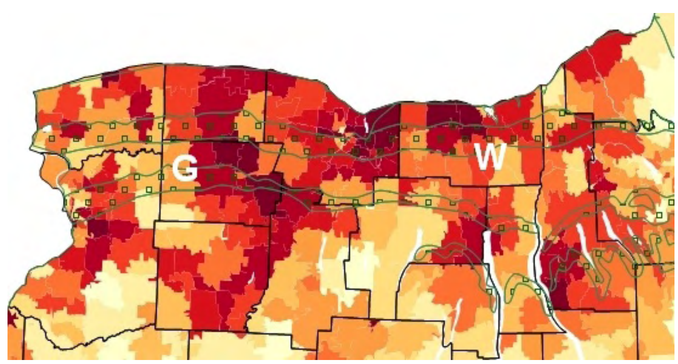


Figure 2.7. GUS-weighted pesticide intensity (legend Fig. 2.6) and shallow carbonate strata (green pattern).

## 3. DISCUSSION and ONGOING WORK

The extensive agriculture in Cayuga County was well reflected in the sample set land use categorization. Agriculture dominated primary land uses, with 32 wells for which cash crops (CC) or corn/forage rotation (CF) were the primary land uses. Other crops were the primary land use near 7 additional wells, and agriculture was part of the mixed land use around the remaining well. The most prevalent secondary land use was woods, often occurring as scattered woodlots in agricultural regions or wooded hillslopes among the steeper drumlins. In 14 cases no secondary land use was assigned, indicating the dominance of the primary land use. Similarly, the assignment of no tertiary land use in 22 cases indicated the predominance of the assigned primary or secondary land uses. Scattered or more distant woods were the most common tertiary assignment (14 cases). Suburban/urban areas are served by public water supply, which resulted in almost no representation of those land uses in the sampled well array.

Well testing results by the DEC laboratory found no detectable pesticides or herbicides in any of the 40 samples examined. The detection limits for the scans run in the NYSDEC 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 in Table 2.8. These nondetects thus established that the 40 well samples from Cayuga County did not exceed any ambient groundwater MCLs or guidance values.

ELISA scans performed at Cornell had much lower detection limits, and similarly showed that no MCLs or guidance values were exceeded for the three analytes tested (atrazine, alachlor and metolachlor). As summarized in Table 3.1, two wells had quantifiable detection of atrazine (0.21 – 0.26 µg/L) with five additional nonquantifiable trace detections (falling between the quantitation limit and the trace detection limit). There was one quantifiable detection for alachlor (0.18 µg/L) and another trace detection. There were six trace detections for metolachlor. All of these detections occurred at levels lower than the MDLs of the NYSDEC laboratory tests. These coincided with nitrate levels between 5 and 9 mg/L. Of the twelve wells that had ELISA detections, there were three cases of multiple analyte detection: wells 8, 12 (alachlor+metolachlor), and 15 (atrazine+metolachlor). All three cases coincided with nitrate levels between 4 and 6 mg/L.

Table 3.1. Well characteristics and analytical results for wells with quantified or trace ELISA detections; nd indicates not detected. *Well type key:D* - drilled, *G* - dug, *S* - spring; *-A* suffix indicates artesian well. Land use key: *CC* - corn/cash crop rotation; *CF* - corn/forage rotation; *W* - wooded.

| **Well characteristics** | | | **Land use assessment** | | | **$NO_3$-N** | **ELISA detections (µg/L)** | | |
|---|---|---|---|---|---|---|---|---|---|
| **No.** | **Depth (ft)** | **Type** | **1°** | **2°** | **3°** | **(mg/L)** | **Atrazine** | **Alachlor** | **Metolachlor** |
| 7 | 85 | D | CC | - | W | <0.1 | nd | nd | trace <0.1 |
| 8 | 12 | G | CC | W | - | 5.6 | nd | 0.18 | trace <0.1 |
| 10 | 85 | D | CF | CC | W | <1 | nd | nd | trace <0.1 |
| 11 | 72 | D | CF | CC | W | <1 | nd | nd | trace <0.1 |
| 12 | 25 | G | CC | W | - | 3.7 | nd | trace <0.1 | trace <0.1 |
| 15 | 35 | D | CC | - | - | 4.4 | trace <0.1 | nd | trace <0.1 |
| 24 | 15 | D | CC | W | - | 5.3 | 0.21 | nd | nd |
| 25 | 30 | G | CC | W | - | 9.3 | 0.26 | nd | nd |
| 26 | v.shallow | G-A | CC | W | - | 8.2 | trace <0.1 | nd | nd |
| 30 | 0 | S | CF | W | - | 5.5 | trace <0.1 | nd | nd |
| 33 | 0 | S | CC | - | W | 4.7 | trace <0.1 | nd | nd |
| 37 | 20 | G | CC | - | W | 3.3 | trace <0.1 | nd | nd |

All three quantifiable detections had corn/cash crop rotation (CC) as the primary land use, and all twelve wells with detections (including trace detections) had either CC (9 wells) or corn/forage (CF, 3 wells) as the primary land use. No other land use was associated with any detections (assuming that the presence of wooded [W] as secondary or tertiary land uses associated with CC or CF had no contribution). In contrast, there were no detections or trace detections for 15 wells with CC and 5 wells with CF as the primary land uses.

Detections correlated strongly with shallow well depths. Three wells with trace detections had depths of 72 to 85 ft. (wells 7, 10 and 11), whereas all three quantifiable detections and the remaining nine trace detections and occurred in wells with reported depths of 0 (spring-fed) to 30 feet. In fact, of the 13 wells with known depths up to 30 ft, eight had ELISA detections or trace detections. While all nitrate-N concentrations were below the 10 mg N/L, seven sites had concentrations in excess of 5 mgN/L; of these sites, six had shallow well depths (0 to 30 ft), with the seventh site having a well depth of 90 ft.

The limited resampling of five wells in June 2009 resulted in similar nitrate trends and fewer quantifiable and trace detections for atrazine and metolachlor. DEC scan results again indicated nondetects for all analytes.

Both the statewide assessment and in-county selection protocol modifications using GUS weightings facilitated identifying regions of markedly greater vulnerability that occur within counties (or that run across multiple counties). GUS-weighting led to siting ongoing work in Genesee and Wayne counties. At the time of writing, sampling in Genesee County (Year 5) is completed, as is the on-site analysis of those samples at Cornell University. Site identification is underway in Wayne County (Year 6).

## 4. ACKNOWLEDGMENTS

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## 5. REFERENCES

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.

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.

DelVecchio, G.M. and D.A. Haith. 1993. Probabilistic screening of ground-water contaminants. *ASCE Journal of Environmental Engineering* 119: 287-299.

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.

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.

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.

New York Agricultural Statistics Service, 2005. Cayuga County farm Statistics. Source: http://www.nass.usda.gov/Statistics_by_State/New_York/County_Profiles/Cayuga.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.

Parker, J.C., and M.Th. van Genuchten. 1984. Determining transport parameters from laboratory and field tracer experiments. Bulletin 84-3. Virginia Ag. Exp. Station, Blacksburg, VA.

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.

Peranginangin, N. 2003. A simple model for predicting the fate of preferentially moving pesticides in a structured soil. Unpublished Doctoral Thesis. Cornell University. Ithaca, NY.

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.

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.

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.

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.

United States Department of Commerce, Weather Bureau. 1961. *Rainfall frequency atlas of the US for durations from 30 minutes to 24 hours and return periods from 1 to 100 years*. Washington, D.C. Technical Paper #40.

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

A) Landowner Information Handout

B) Sampling Protocol

C) Well Sampling Log

D) Landowner Reporting Form

## A) Landowner information handout

Cornell University
College of Agriculture and Life Sciences

**Cayuga County Soil & Water Conservation District**

**Research Project:**

**Surveying Cayuga 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 Cayuga County, in cooperation with the Cayuga County Soil & Water Conservation District (SWCD) and the NY Water Resources Institute. Sampling and analysis 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, relatively little 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. Cayuga County was chosen because of the 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 University 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) Personnel will use certified sample containers coded with a tracking number.
2) Allow faucet/spigot to run for 5-10 minutes to purge plumbing lines. Sample at the closest accessible valve to well and prior to any treatment (i.e. softeners or filters).
3) Rinse each sample bottle three times with the water being sampled.
4) Fill sample bottles and return them to laboratory for preservation and analysis.

**What happens to the samples?** Each well sample will be analyzed at Cornell for nitrate, which is sometimes present in groundwater. We will also analyze for one to three pesticides at Cornell, depending on known or likely pesticide use in the area. One set of samples – *identified only by a code number* – will be shipped to NY DEC for a complete pesticide scan. 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 work with you to notify relevant county agencies – most likely the Department of Health – to help 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 specific well(s) cannot be determined from the report, and no landowner identities or addresses will be included.

5) Cornell is required to retain a confidential list of all landowner contact information and well locations that will be disclosed only to the DEC and only upon reasonable request from DEC.

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**If you have any questions** please contact Brian Richards of the Department of Biological & Environmental Engineering (607-255-2463; bkr2@cornell.edu) or Valerie Horning of the Cayuga County SWCD (315-252-4171; vhorning@cayugaswcd.org).

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## B) 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.). Four large bottles will be for DEC submission; and four small 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. Discard rinsate into rinse pail.

☐ 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

## C) Well Sampling Log

**Surveying Upstate NY Well Water for Pesticide Contamination**

Department of Biological & Environmental Engineering, Cornell University

Cayuga County Soil & Water Conservation District

SAMPLE Code: Y4-____
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***

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## D) Example Well Owner Report

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**Research Project: Surveying Cayuga County Drinking Water Wells for Pesticide Residues**

Dear _________ ,

You are receiving this mailing because you participated in the voluntary testing of drinking water wells in selected areas of Cayuga County carried out by Cornell University's Department of Biological & Environmental Engineering, in cooperation with the Cayuga County Soil & Water Conservation District. This is a research project sponsored by the NY Department of Environmental Conservation (DEC). These results are confidential and are provided without cost to landowners.

We tested a sample from your well (our sample code number ___ taken on __/__/__) for nitrate, chloride, and three pesticides, namely alachlor, metolachlor, and atrazine. An earlier letter transmitted our results for nitrate, atrazine, and alachlor. This letter transmits the results of our additional test for metolachlor, and DEC's results for 93 pesticides and herbicides. The DEC only knows the sample via the code number, and does not know about your participation.

**DEC's analysis of the sample from your well detected none of the 93 pesticides/herbicides being tested.** Analysts do not report results as "zero" concentration because all chemical tests have a lower limit below which they simply cannot detect. The lower detection limits for most tests used here were 1 microgram per liter (also commonly referred to as "parts per billion"). Several compounds had even lower detection limits of between 0.35 to 0.7 micrograms per liter. Results for your well were reported to us as "*not detected*" for all 93 compounds.

Fifteen of these 93 compounds tested have maximum "Ambient Ground Water Quality Standards and Guidance Values" established by New York State. These values are all at least as strict as New York's drinking water quality criteria. For these compounds, the "not detected" results confirm that none of these were present at or above the groundwater limits. This was true for all samples tested in the county.

The metolachlor result at Cornell, from a test more sensitive than DEC's, was: "nd" micrograms per liter. This means: less than the detection limit of 0.1.

Additional details about the tests and substances are available on request.