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

Year 5 Final Report

to the

New York State Department of Environmental Conservation

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#### **EXECUTIVE SUMMARY**

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. Intensity of pesticide use, reliance on ground water and aquifer characteristics made Genesee County a priority candidate for sampling, as identified by statewide selection protocols developed and refined in prior years. As in prior counties sampled, the primary cooperator was the Genesee County Soil & Water Conservation District (GCSWCD) in conjunction with the Genesee County Department of Health (GCDOH).

Well selection was primarily based on local knowledge of groundwater conditions and vulnerabilities, onsite and aerial image assessment, and the PSUR pesticide database. The GCSWCD and the GCDOH proposed potential sampling sites for Cornell review, and then carried out sampling visits in June 2009, with one site resampled in August 2009. The NYSDEC laboratory conducted broad 93-compound analyses for pesticides. ELISA atrazine and metolachlor assays as well as nitrate were carried out by Cornell personnel.

Agriculture was the primary land use for 32 sampled wells, representing corn/grain cash crops, dairy corn/forage rotation, or vegetables. Primary land uses for remaining wells were woods or scrub regrowth (6 wells, with agriculture as secondary), managed turf (1 well) and mixed (1 well). Woods and scrub combined were the most significant secondary (29 wells) and tertiary land uses (15 wells). Of the 35 wells with known depths, 12 well had depths to 30 ft., 13 wells between 31 and 60 ft. deep, and 10 were greater than 60 ft deep. The likelihood of wells penetrating carbonate strata (7 likely, 4 possible, 29 unlikely) was based on well depth and position relative to carbonate mapping.

DEC laboratory scans for all sites and analytes were nondetects (reporting limits of  $1.0 \mu g/L$  or less) except for metolachlor at one well (site 7), which was confirmed by resampling and in Cornell ELISA testing at levels from 2 to 4 µg/L. ELISA testing also found traces (0.1 µg/L or less) of atrazine in the well 7 resample, as well as a trace  $(\leq 0.1 \text{ µg/L})$  atrazine in another well. Conditions coinciding with the Site 7 metolachlor detections included a nearby upslope storage facility, shallow well casing, adjacent treated cropland, and carbonate strata. Nevertheless, the 9  $\mu$ g/L groundwater standard was not exceeded.

Overall, these findings established that the 40 well samples from Genesee County did not exceed any ambient groundwater standards or guidance values. Aside from site 7, testing resulted in remarkably few detections, with the most consistent finding being elevated nitrate. Three wells had nitrate-N levels between 6 and 10 mgN/L, and four wells exceeded the 10 mg/L drinking water standard with measured concentrations between 12 and 15 mg/L. Shallow well depths did not appear to particularly predispose wells to problems, as only two of 12 wells with depths under 30 ft. had pesticide detections or elevated nitrate (over 6 mgN/L). In contrast, carbonate strata did appear to predispose wells to potential issues: of seven wells likely drawing from carbonate strata, four had pesticide detections or elevated nitrate levels.

# **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) and 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 DEC and others) of the human exposure risk from pesticides in groundwater, and to identify needed changes in pesticide management through product registration, applicator training, consumer advice, and technical assistance.

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

# **1.2 County Overview**

Significant agricultural activity – including intensity of pesticide use – and widespread reliance on ground water made Genesee County a priority candidate for sampling, as identified in the statewide selection protocols developed and refined in prior project years. The county has diverse geomorphic regions (Figure 1.1) and numerous scattered wetlands (Figure 1.2). A band of limestone that gives rise to karst formations (e.g. sinkholes, source holes, and solution channels capable of rapid water and contaminant transport) crosses the county (Figure 1.3), as will be discussed under the site selection process.





Figure 1.1. Geomorphic features in Genesee County. Source: Soil survey data.



Figure 1.2. Genesee County wetlands (green) and water bodies (blue). Source: http://gis.co.genesee.ny.us/OnlineMapping/Default.aspx



Figure 1.3. Generalized location ofsurficial carbonate strata in Genesee County that give rise to karst features: hatched area represents Onondaga limestone formation (across center of county) and the southern limit of the Lockport dolomite formation (across the northern edge of the county).

Agricultural districts encompass much of the county (Figure 1.4), although farmland is somewhat less concentrated in the southern third of the county (Figure 1.5). Of the county's 315,482 acres, 58% was in farmland in 2008, with a total of 551 farms (NYASS 2005). The county ranked fourth in NY state for total agricultural sales (nearly \$178,000,000), with dairy products representing 54% of the total, vegetables 25%, grains and dry beans 8%, cattle and calves 7%, and all others 6% (NYASS 2009). In terms of agricultural receipts, the county ranked first in the state for vegetables, fifth for both dairy products and cattle and calves, and eighth for grain/bean field crops.

Our local cooperators for the project were the Genesee County Soil & Water Conservation District (GCSWCD; George Squires, District Manager) and the Genesee County Health Department (GCDOH; Randy Garney, Public Health Director). Initial contacts with the GCSWCD led to discussion of the project with the county Water Quality Coordinating Committee (WQCC) in April 2008, and formal approval of the GCSWCD cooperation in May 2008.

#### **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 *sampling results* (2.3) of the well sampling carried out in Genesee 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.



Figure 1.4. Agricultural districts (light green) in Genesee County. Source: http://gis.co.genesee.ny.us/OnlineMapping/Default.aspx



Figure 1.5. Strategic farmland (beige) in Genesee County. Source: http://gis.co.genesee.ny.us/OnlineMapping/Default.aspx

# **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 and review process developed for this program involved multiple approaches used in concert: 1) assessing local knowledge about areas of likely vulnerability, 2) examining land use patterns and landscapes using aerial imaging software tools, and 3) examining the NYS Pesticide Sales and Use Reporting (PSUR) database for pesticide and herbicide application trends. This year's work depended most heavily on the first approach, given the complexity of the area. A fourth selection component used in prior years – a potential transport screening model to determine areas of relative vulnerability within the county based on soil type and depth to groundwater – was used only in a *post hoc* manner.

# *2.1.1 Local Knowledge*

This approach involved assessing local knowledge about areas of likely vulnerability, based on prior experience with farming patterns, soil and aquifer characteristics, and reports of nitrate contamination or other well problems. The primary sources in this case were the Genesee County Soil & Water Conservation District (GCSWCD) and the Genesee County Health Department (GCDOH). Also contributing significantly was ongoing research into carbonate formations and hydrology carried out by Dr. Paul Richards (geologist, SUNY Brockport) and James Craft (geologist, NYSDEC Region 8). Meetings were held beginning in April 2008 to learn about their findings to date and to discuss collaboration.

# *2.1.2 Land use and landscape assessments*

The second factor contributing site selection and assessment  $-$  as well as in post-sampling site rechecks – was the visual assessment of land use and landscape topography using aerial imaging, as well as windshield surveys for some sites. Initial site reviews were conducted with monochromatic still photos, but site re-examination used the Google Earth (version 4.2; available at [http://earth.google.com/\)](http://earth.google.com/)) software platform. This approach allows detailed "virtual flyovers" of areas, assessing not only agricultural and other land uses but also the ability to visualize landscape topography.

As can be seen in Figure 2.1 (showing a location randomly chosen from 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 2.1 bottom, same farm site) creates virtual topography, dramatically increasing the available visual information about the juxtaposition between land use(s), landscape position and potential well sites, particularly for shallow wells that may be strongly influenced by local features. The ability to rotate the direction of view, zoom the field of view, change the angle of view, and continuously "fly along" areas of interest makes this a powerful interactive tool for locating and assessing potential sites. In addition to visual relative elevations, the Google Earth platform reports the discrete elevation of any point under the cursor for more precise comparisons.



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

#### *2.1.3 Utilization of the PSUR Database*

#### *Zip-code level data*

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 detailed confidential database, we elected to rely only on the publicly-available zip-code-level PSUR data summaries for determining which pesticides were most heavily used as well as which general regions within Genesee County had the greatest intensities of pesticide use.

Summarized PSUR data was converted to applied mass of active ingredients (AIs) as described in Section 2.4 and plotted using a GIS to reveal application intensity patterns. As can be seen in Figure 2.2 (top), this approach had some utility for targeting, but the intensities of application for all AIs were not too widely distributed and were less than for other areas. However, to better account for the potential 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 Genesee 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.

#### *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 NYSDEC's laboratory pesticide scans with the analysis of one to three active ingredients, using ELISA immunoassays that are one to two orders of magnitude more sensitive. 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 immunoassaytest kits. Table 2.1 summarizes all three considerations for the 25 mostapplied active ingredients in Genesee County. High use intensities and GUS values over 3 for atrazine and metolachlor indicate compounds of greater concern, whereas values of under 1 for compounds indicate much lower concern for potential ground water contamination. Using this data, we elected to perform ELISA tests for metolachlor and atrazine.

#### All active ingredients (kg/km<sup>2</sup>)



GUS x All AI (GUSxkg/km<sup>2</sup>)



Figure 2.2. GIS representations for Genesee County and surrounding areas of 1) top: cumulative active ingredient use intensities (kg  $AI/km<sup>2</sup>$ ) and 2) bottom: cumulative active ingredient weighted for groundwater ubiquity score (kg GUS/km<sup>2</sup>), based on publiclyavailable zip-code level PSUR sales and use summaries for 2000-2005.



Table 2.1. The 25 most-applied pesticide active ingredients in Genesee County (average of 2000-2006 reporting years), relative Groundwater Ubiquity Score (GUS), and availability of ELISA screening test kits.

*2.1.4 Groundwater Exposure Assessment Modeling* Simplified screening models are used to help predict the potential for contaminant transport. It is important to note that these are *relative risk* assessment tools designed to detect areas with greater groundwater vulnerability as an aid in sampling area selection, and do not attempt to predict actual groundwater pesticide concentrations. The development of the screening model of relative risk based on soil characteristics and groundwater depth was reported in detail in previous reports and elsewhere (Sinkevich 2004, Sinkevich et al. 2005). The model needs only limited inputs of soil properties and aquifer recharge data to predict potential preferential transport between the land surface and ground water.

A conceptualized two-zone soil profile is used, with a near-surface distribution zone overlying the 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 and land use.

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



Figure 2.3 Relative groundwater vulnerability as a function of soil characteristics and groundwater depth: darker shades indicate greater vulnerability.

application rates. The predicted relative concentration of the model compound at the estimated groundwater depth was calculated for each soil type for a 3-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). A grouped risk classification was then assigned based on the relative risk normalized to the greatest predicted concentration, as mapped in Figure 2.3. It should be reiterated that the figure indicates areas with greater *relative* groundwater vulnerability using the mobility characteristics of a model pesticide and based on soil type and depth, and does not prediction actual or potential contamination.

#### *2.1.5 Site identification process*

Site targeting priorities were discussed in a joint meeting held in Genesee County in June 2008 with George Squires and Melanie Roberts of the GCSWCD, David Whitcroft and Jessica Zaremski of the GCDOH, and Paul Richards of SUNY Brockport (an expert in local karst conditions). A potential site list with nearly 80 candidate sites was assembled by GCSWCD with some input from GCDOH and submitted to Cornell in September 2008.

This list (which also included GCDOH-regulated sites such as restaurants and parks) was examined at Cornell and compared with aerial imagery(monochromatic stills, given the low resolution images available on Google Earth at the time) and approved in October 2008. Given the date and the anticipated potential occurrence of rapid surface water/groundwater interaction in the karst areas of the county, we elected to delay sampling until after spring 2009 pesticide applications.

#### *2.1.6 Landowner recruitment and confidentiality guidelines*

Information detailing sample collection and confidentiality/disclosure protocols (discussed below) were distributed. Landowner cooperation was essential, especiallyfor gaining access to sites deemed to have elevated risk of contamination. (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 – could be frustrated if such access is not obtained.) 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:

 $\Box$  In all *public* reporting (published reports to DEC as well as any academic or extension publications), only blurred georeferences – rounded coordinates, dithered maps– are reported.

 $\Box$  Reports indicating pesticide concentrations determined by Cornell and NYSDEC would be compiled and sent to individual landowners.

 $\Box$  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 GCSWCD and GCDOH would be advised to safeguard the health of those consuming water from the well(s) by taking appropriate remedial and/or preventative measures.

 $\Box$  In cases where levels were somewhat elevated but not in excess of drinking water standards, landowners would be encouraged to contact relevant agencies for appropriate remedial and/or preventative measures.

 $\Box$  Cornell will retain landowner contact information and exact well locations, which will be disclosed only to NYSDEC upon reasonable request from NYSDEC.

# **2.2 Site Characterization and Sampling**

Recruitment letters were sent in March 2009, and site visits for sample collection were conducted by GCDOH personnel in June 2009. (It should be noted that the GCDOH contributed the labor for the sampling process given their interest in serving water users in the county.) Based on the results of this round of sampling, site (ID 7) was resampled in August 2009 to confirm analysis findings.

# *2.2.1. Sampled Well Sites*

Table 2.3 presents sampled well information, including well type, depth, likely strata (as discussed below), and prioritized surrounding land use(s)for surrounding and upslope areas judged to be potential well contributing areas, particularly for shallow wells. (It is important to note that these surficial observations are by no means determinative in view of flow complexity of underlying xarbonate strata and abundant anecdotal evidence of "unexpected" flow paths, such as agricultural practices in a valley on one side of a drumlin impacting water quality on the far side of the drumlin due to lateral flow in carbonate strata *under* the drumlin.) Land uses were ranked as primary (i.e. most extensive and dominating general and upslope areas), and, if diverse land uses were present to a significant degree, secondary and tertiary. Land use sources included windshield survey notes in addition to Google Earth imaging (which was at a lower resolution for much of Genesee County). Nevertheless, distinctions among specific cropping systems – particularly corn/grain (cash crops including corn, soybean, wheat, oats etc.) corn/forage (dairy farm feedstocks), and vegetable land uses – often involved judgment calls, including determining the presence of nearby grain silos, livestock facilities, etc. Similarly, designations of farms as CAFO operations (concentrated animal feeding operations) was a judgement based on apparent size.



Table 2.3. Well and surrounding area land use characteristics. Well type key: D - drilled, R - driven, G - dug, S - spring. NA indicates well depth/type







Land uses are summarized at the bottom of Table 2.3 in terms of the number of wells linked to each category, and these uses are further aggregated by general land management class in Table 2.4. The extensive agriculture in Genesee County is reflected in the land use categorization, with agriculture as the primary land use category for 32 wells. Of these, there were 26 wells for which corn/soybean/wheat/ etc. grain cash crops (CG) or corn/forage rotation (CF) were the primary land uses, and another 6 wells where vegetables (V) or vegetables/cash crops (CV) were the primary land use. Woods (W) or scrub regrowth (R, representing abandoned farmland) was the primary land use around 6 wells, typically itself surrounded by farmland as a secondary use. Only one well had residential turf (H) as a primary land use, occurring as a hamlet-sized residential area surrounded by farmland.

The most prevalent secondary (23 wells) and tertiary (9 wells) land use was woods, often occurring as scattered woodlots in agricultural regions or wooded hillslopes among the steeper areas. Scrub regrowth was the secondary and tertiary land use around 6 wells each. Together these "unmanaged land" classes accounted for 29 wells (secondary) and 15 wells (tertiary). Agriculture was the second most common secondary land use (8 wells). Lawn/managed turf was the second most common tertiary land use, including a number of golf courses in the neighborhood of sampled wells.

Well depth, type, carbonate strata and water treatment information is categorized in Table 2.5. Of the 35 wells for which the depths were known by landowners, 12 were shallow (up to 30 ft.) including two surface springs. 13 wells were between 31 and 60 ft. deep, 8 were between 61 and 100 ft, and only two wells exceeded 100 ft (although one of these had a casing that was only circa 20 feet deep). Well types included 31 drilled wells, 7 dug wells (one of which was subsequently deepened by drilling, with the more vulnerable category retained) and, as noted, two spring-supplied wells. The likelihood of wells penetrating karst strata (7 likely, 29 unlikely) was based on the well's depth and position relative to karst mapping of the county. The four wells listed as "possible" reflected cases where well depth exceeded the carbonate strata depth range in a region, but potential carbonate-source water input would depend on how deeply the well was cased.





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 (Table 2.5). Of the wells sampled, 12 had no treatment systems in place. Treatment systems encountered on the remaining 28 wells included softener only (11), chlorination (8), softener+filtration (4), softener + chlorination (1) and one each of reverse-osmosis, carbon filter, hydrogen peroxide, and ion exchange. Of the treated water systems, in 15 cases it was confirmed that sampling occurred upstream of the treatment process , and in 1 case it was known that sampled water could only be sampled after treatment (carbon filter). In 10 cases (sampled from outdoor spigots) it was considered likely that the sampling point preceded any treatment (chlorination and/or softening). As described later, resampling of one site's well found no difference in results due to sampling before vs. after softening for one pesticide and nitrate.

# *2.2.2. Sampling Protocols*

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

Certified precleaned (Environmental Sampling Supply, PC class) polyethylene bottles were used for sample collection, with one set collected for samples for submission to DEC and archiving, and another collected for Cornell analysis and archiving. Sample bottle labels specified only a tracking code. Nitrile gloves were used to prevent operator contamination of the water sample. Hand contact with the interior of the cap and bottle was avoided. Bottles and caps were rinsed three times with the sampled water prior to filling. Bottles were filled approximately 90% full to allow subsequent freezing and were placed in an ice chest until returning to the County office. Bottles were frozen within 8 hours of collection and stored frozen except when thawed for analysis. Samples were accumulated and shipped frozen via overnight courier to Cornell. A mid-project change in container standards triggered a thawing and rebottling at Cornell of about half of the samples (making stored bottles more robust during long-term freezing). Samples were stored frozen at Cornell and the bottles designated for DEC were shipped frozen via overnight courier to the NYSDEC laboratory. The site 7 resamples were brought directly to Cornell and frozen prior to courier shipment to NYSDEC.

# **2.3 Analysis and Results**

Pesticide analysis conducted by DEC determined 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, with the analyte list and reporting limits summarized in Table 2.6:

Water samples from the Cornell Shallow Groundwater Monitoring Program were submitted to the NYSDEC Pesticides Laboratory in July and September 2009. The samples were screened for pesticides, phenoxy acid herbicides and carbamates.

Table 2.6. Method reporting limits (RL) of pesticide/herbicide analyses run by the NYSDEC laboratory. All MDL concentrations are reported as  $\mu$ g/L (ppb). Method codes: *U* - UPLC/MS-MS; *G* - GC/SIM-MS; *H* - HPLC/MS-MS. All UPLC and GC analytes were base/neutral, while HPLC analytes were acid.



All of the pesticide and herbicide compounds except trifluralin, benfluralin, dithiopyr, chlorpyrifos were analyzed by direct injection followed by UPLC/MSMS or HPLC/MSMS. The remaining four compounds were extracted using the Quechers extraction technique and analyzed by gas chromatography/mass spectrometry (GC/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, 6ppb and 10 ppb.

Spike recovery and precision information are as follows:

For HPLC/MSMS and UPLC/MSMS direct injection pesticide samples, recoveries ranged from 28% to 155%, with RPD's ranging from 0.1% to 50.6%. Pyridate recovered at or near 0% for three of the spiked sets of samples. Trichlorfon did not recover in four sets of spiked samples. It can be concluded that there are matrix effects as the other spiked samples recovered these two compounds within an acceptable range. One duplicate set of spike samples (Sample ID CC25) had 0% recovery for the following analytes: vamidothion, ethiofencarb, flufenoxuron, aldicarb, acephate, butocarboxim, clethodim, methiocarb, fenhexamid, and halofenozide. All other spiked samples had recoveries within an acceptable range for these compounds. All analytes were spiked at 10 ppb in 6 sets of duplicate.

For GC/MS extraction and analysis samples, analytes were spiked at 5 ppb or 6 ppb in 6 sets of duplicate samples. Recoveries ranged from 101.3% to 236.7%, with RPD's ranging from 1.8% to 23.1%.

#### *ELISA and nitrate assays*

Water samples were screened at Cornell University for atrazine and metolachlor (as the most likely to be detected pesticides, given reported use and relative mobility) as well as nitrate. The repeat sample collected at site 7 in August 2009 was tested for atrazine, metolachlor and nitrate.

The pesticide methods employed use Enzyme-Linked ImmunoSorbent Assays (ELISA) to detect the analyte and related compounds. In each case we used magnetic particle ELISA kits from Strategic Diagnostics Inc (SDI). Atrazine (SDI Kit No. A00071) and metolachlor (SDI A00080) have quantitation ranges of 0.1 to 5 ppb ( $\mu$ g/L) and trace (nonquantifiable) detection limit of 0.05  $\mu$ g/L (Table 2.7). The contribution of closely-related compounds present cannot be distinguished by the ELISA tests due to cross-reactivity, and results are reported on an "as primary analyte" basis. Potentially cross-reactive compounds are reported in Table 2.7.

Magnetic particle assays were analyzed on duplicate samples with a dedicated Ohmicron RPA-1 spectrometer and supplied sample tubes. Calibration data is linearized using logarithms and logit functions. ELISA metolachlor analysis of the initial 40 samples was run in July 2009, with the resample run in October 2009. All atrazine tests were run in August 2009.

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

Table 2.8. ELISA detection and quantitation limits and potential cross-reactivities of related compounds, reported as concentrations required to generate responses equivalent to primary analytes at the specified LOQ. All concentrations expressed as  $\mu$ g/L.



#### *2.3.2 Analysis Results*

#### *DEC analysis*

Results text forwarded by Peter Furdyna of the NYSDEC Pesticides Laboratory:

All samples submitted to the laboratory were successfully analyzed. All sample results were non-detect at the laboratory's method detection limit (MDL) except for GC07, GC79, and GC80 [GC79 and 80 being the site GC07 resamples, before and after the softener] which had detected amounts of metolachlor at 3.7, 2.0, and 2.0  $\mu$ g/L, respectively. The reporting levels were 1  $\mu$ g/L (ppb) for all compounds except dicamba, diazinon, MCPA, and the sum of aldicarb and methomyl, which had detection limits of 0.44, 0.7, 0.44, and 0.35 ppb (µg/L) respectively. For this project, the MDLs are at the lowest calibration concentration on the calibration curve.

Pesticide analysis results were transmitted from the NYSDEC laboratory in October 2009. As noted in the prior section, the NYSDEC pesticide scans found that, *except for one analyte in one well, all analytes were below the detection limits* specified in Table 2.6. The sole DEC analytical results indicating detections are summarized in Table 2.7.



#### *Cornell analyses*

The sets of ELISA scans conducted at Cornell University for atrazine and metolachlor indicated a single quantifiable detection (Table 2.8) of 2.0  $\mu$ g/L metolachlor at site 4, as well as a trace (<0.1)  $\mu$ g/L) of atrazine at site 24. The resamples from site 4 (which were not reanalyzed for metolachlor, given the reasonable agreement between our initial ELISA test and the DEC laboratory result) detected atrazine at or below the 0.1 µg/L quantitation limit. The site characteristics associated with the detections at site 4 will be further examined in the discussion section.



Table 2.8. ELISA analytical results. *Trace<0.1* indicates detection at concentrations lower than the

Cornell results for nitrate-N are shown in Table 2.9. Because low levels of nitrate can be masked by elevated sulfate, nitrate is reported with a detection limits of 1 or 2 mg/L (<1 or <2 mg/L), depending on the extent of required dilution to eliminate sulfate peak interference. Eleven wells had quantifiable nitrate (Table 2.9), with four wells less than 5 mgN/L, three between 5 and 10 mgN/L, and four wells exceeding the 10 mg N/L drinking water standard. These four wells had measured concentrations between 12 and 15 mg/L. Resampling at site 7 led to a similar high result. Mean nitrate values for the sample set were not computed given the variable detection limits due to sulfate concentrations.





#### **2.4. Statewide Assessment of Relative Groundwater Exposure**

One continuing task has been refinement of a protocol to guide the identification and prioritization for screening vulnerable upstate aquifers. This framework followed a GIS-based protocol which overlaid vulnerable aquifers, population dependence on groundwater and several indices of pesticide use 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. As indicated previously, this 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. Aggregation also masked elevated vulnerability areas within counties that also had low vulnerability areas elsewhere that, when combined, yielded a more moderate average score. This section describes a modified process that does not use county-level aggregation, producing assessment maps at the finer resolution of zip-code levels. In addition, the assessment uses Groundwater Ubiquity score weighting to better reflect the use intensity of compounds that are more mobile and persistent in the environment.

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

The Pesticide Sales and Use Reporting (PSUR) system provides publicly-available data that include a product code, a volume or a weight of product, and a location, either the county name or a 5-digit zip code. This report employs 2000-2005 data. The PSUR covers pesticide use by commercial applicators and sales to farmers who apply pesticides themselves. (Farmers are not required to report their own pesticide use.) This report combines the commercial use and sales data. 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; we here assume that the two are the same.

Use and sales data undergo two conversion steps, with liquid product volume converted to weight using a product density (specific weight), and then product weight is converted into active ingredient weights using a product composition table that contains the weight percentages of each active ingredient.

Figure 2.4 shows how these data are synthesized to yield tables and maps of various active ingredient weights. There are some issues with zip codes tabulation areas (ZCTA) and geo-referencing (Grubesic, & Matisziw, 2006) but these are not considered significant in this application. We express results in kilograms per square kilometer, convertable to lbs/acre with a factor of 0.0089.

Figure 2.5 maps the use intensity of all active ingredient weights for all index is skewed by heavy use rates in New York City, southern



of New York. The density color Figure 2.4. Schematic of procedure used to synthesize cumulative active ingredient data

Westchester County, Long Island, and the counties adjacent to Lake Ontario. (Previously-shown Figure 2.2 (top) focuses on Genesee County.) 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. As can be seen in Figure 2.6, the use of GUSweighted application intensities changes the statewide pattern, most notably intensifying mapped intensities in the Western and Central New York agricultural belt. GUS-weighted mapping for Genesee County was shown in Figure 2.2 (bottom).



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



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

#### *2.4.2 Implications for future testing*

The 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 and 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 in Wayne county for Year 6 activities (labeled W in Figure 2.7), which also includes potential carbonate formations



with close connections between  $_{\text{Figure 2.7. GUS-weighted~pesticide}$  intensity (as per Fig. 2.6) groundwater and surface flow, and and shallow carbonate strata (hatched areas). planned more detailed ongoing studies

in the karst area of Genesee County (G in Figure 2.7) in continued collaboration with Dr. Paul Richards (SUNY Brockport) and in communication with the GCSWCD.

# **3. DISCUSSION and ONGOING WORK**

The extensive agriculture in Genesee County is reflected in the land use categorization, with agriculture as the primaryland use category for 32 wells, representing corn/soybean/grain cash crops (CG), dairy corn/forage rotation (CF), vegetables (V) or vegetables/cash crops (CV) as primaryland uses. Unmanaged lands (Woods (W) or scrub regrowth (R) representing abandoned farmland) was the primary land use around 6 wells, along with one well with managed turf as the primary land use and another with closely mixed land uses. Woods and scrub combined were the most significant secondary (29 wells) and tertiary land uses (15 wells). Agriculture was the secondary land use for 8 wells. Lawn plus managed turf together were the second most common tertiary land use, including a number of golf courses in the neighborhood of sampled wells. Suburban and urban areas are served by public water supplies, which resulted in almost no representation of those land uses in the sampled well array. It is again important to note that these surficial observations are by no means determinative, especially in view of flow complexity of underlying carbonate strata. Abundant anecdotal evidence of "unexpected" flow paths exists for the karst-dominated areas of Genesee County, including contaminants flowing between adjacent valleys under an intervening drumlin.

Of the 35 wells for which the depths were known by landowners, well depths fell in three main classes: 12 up to 30 ft. (including two surface springs), 13 wells between 31 and 60 ft. deep, and 10 greater than 60 ft deep. Wells were primarily drilled, along with 7 dug wells and two surface springsupplied wells. The likelihood of wells penetrating carbonate strata (7 likely, 29 unlikely) was based on the well's depth and position relative to carbonate indicated as topmost on the State's 1:250,000 geologymap. The four wells listed as "possible" reflected cases where the well could be too shallow

or too deep to terminate in the Onondaga limestone, but potential carbonate-source water input would depend on how deeply the well was cased (as well as geology map precision and accuracy).

InTable 3.1we compare the maximum allowable groundwater concentrations (NYSDEC 1998; with the addition of a more recent metolachlor standard) with the DEC scan detection limits. The table shows only those analytes shown in Table 2.6 that have an associated groundwater (class GA) standard (or, as in the case of aldicarb sulfone and sulfoxides, guidance levels in the absence of a promulgated standard. The lower atrazine guidance level is also shown). Of the 15 analytes listed, all had DEC scan detection limits that were equal to or lower than the standard, which means that the tests that yielded nondetects ruled out any exceedence of groundwater standards. Aside from a single detection of metolachlor in one well, well testing 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 DEC laboratory were adequate for determining if samples were in exceedence of the fifteen Class GA ambient groundwater standards (MCLs or, in their absence, guidance values) listed. These nondetects thus established that the 40 well samples from Genesee County did not exceed any ambient groundwater standards or guidance values, the standard for metolachlor being 9 µg/L.



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

ELISA scans performed at Cornell had lower detection limits, and similarly showed that no MCLs or guidance values were exceeded for the two analytes tested (atrazine and metolachlor). As summarized in Table 3.2, one well had a trace detection of atrazine in the initial round (well 40) as well as both trace and near-trace (0.1 µg/L) detections for the well 7 resampling, all of which occurred at levels lower than the reporting limits of the DEC laboratory tests. The one quantifiable detection for metolachlor (initial 2 µg/L; 3.0-3.2 µg/L when resampled) was consistent with DEC results for the well.



Table 3.2. Well characteristics (depth, likely in carbonate strata, type) and analytical results for wells with quantified or trace ELISA detections or elevated nitrate-N levels; nd indicates not detected. *Well type key:D* - drilled, *G* - dug. *Land use key: CF* - corn/forage dairy rotation; *CG* - corn/grain cash crop rotation; *CV* - corn/vegetables; *H* - residential/housing/hamlet; *R* - scrub/regrowth; *T* - managed turf; *V* -

The detection of metolachlor at site 7 by both DEC and Cornell ELISA tests occurred at levels an order of magnitude greater than any other detections in the study's five counties to date. These detections were reconfirmed by testing of repeated samples by DEC (Table 2.7) and Cornell (Table 2.8), and included subsequent trace atrazine detection at Cornell in addition to reconfirmation of high nitrate levels. More detailed examination of the site during resampling revealed a number of factors that may contribute to the presence of pesticides in the well water. The wellhead is immediately adjacent to surrounding fields in a slight depression relative to, and is downhill and at most 100 feet from the farmstead where pesticides have been stored. A nearby source is consistent with the drilled well being cased only about 20 ft from the soil surface until bedrock was encountered. This means that the well is in effect shallow *in terms of susceptibility to infiltration via carbonate interflow and/or from surface percolation flowing around the well casing.* A distant source could also be involved. With the borehole drawing from the full thickness of the Onondaga Limestone, any deep lateral flow zones could bring water quickly from a distance. As per the confidentiality protocols, owners were advised regarding the nitrate levels exceeding drinking water standards as well as notable (within standards) levels of pesticide residues, and have been put in contact with the Genesee County SWCD and DOH to investigate potential remedial measures. Owners of wells with nitrate above 6 mgN/L were provided with a fact sheet about health effects of nitrate, following GC DOH protocol.

Table 3.2 summarizes well and land use information for the eight wells with pesticide detections and/or elevated (in excess of 6 mg/L) nitrate-N levels. The trace ELISA and quantified (ELISA & DEC) detections at wells 7 and 40 had vegetable/corn/cash crop rotation (CV) as the primary land use, with unmanaged lands (woods) as the secondary land use. (Conversely, there were no detections or trace detections for 3 other wells that had CV as the primary land use.) Elevated nitrate levels observed for 7 of 8 wells in the table were all associated with agricultural primary land uses, while 25 wells with agriculture primary land uses did not show elevated nitrates.

Assuming that the effective well depth (in terms of vulnerability due to the lack of deep casing) may have been as little as 20 feet, the range of well depths represented in Table 3.2 is 20 to 58 feet. Very shallow depths did not appear to particularly predispose a well to problems, as only two of 12

shallow wells (including 2 springs, but not counting site 4) appear in Table 3.1. In contrast, the occurrence of carbonate strata did appear to predispose wells to potential issues, with four of seven wells with likely karst influence appearing in Table 3.2.

The results from Genesee County are of broader interest. The metolachlor detections at Site 7 could be attributed to the juxtaposition of familiar causes of pesticide problems in wells: an upslope pesticide facility, shallow casing, adjacent treated cropland, and carbonate strata. Even with all these vulnerability factors, the groundwater standard of 9  $\mu$ g/L meant that groundwater standards were not exceeded. Aside from site 7, the testing resulted in remarkably few detections, with the most consistent finding in Table 3.2 being elevated nitrate as well as a single other site (40) with trace levels of atrazine. Although confidentiality restrictions prevent us from mapping the pattern of wells appearing in Table 3.2, a general description finds that detections (of pesticides and/or elevated nitrate) in wells likely associated with carbonate strata occurred in the eastern part of the county, while most sites in non-carbonate strata were in the northern third of the county along with one in the south east.

Both the statewide assessment and in-county selection protocol modifications using the Groundwater Ubiquity Score weightings facilitated identifying regions of greater vulnerability that occur within or across multiple counties, and led to this work in Genesee County as well as ongoing work in Wayne County. At the time of writing, Wayne County (Year 6) analysis is nearly complete, and a more intensive work on the karst region in Genesee county is underway.

#### **4. ACKNOWLEDGMENTS**

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#### **6. APPENDICES**

The following forms used in the study are appended:

- 6.1 Landowner Information Handout
- 6.2 Sampling Protocol
- 6.3 Well Sampling Log



**Cornell University** College of Agriculture and Life Sciences

 **Genesee County Soil & Water Conservation District**

# **Research Project:**

# **Surveying Genesee 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 Genesee County, in cooperation with the Genesee County Soil & Water Conservation District (SWCD). Sampling and analysis results will be confidential and without cost to landowners.

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

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

**How?** Samples will be collected from the landowners sink or outdoor faucet by Cornell 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) We will use certified precleaned sample containers coded with a tracking number.

2) Allow faucet/spigot to run for 5 to 10 minutes to fully purge plumbing lines. If possible, sample at the closest accessible valve to well (i.e. before storage tank) and prior to any existing treatment (such as softeners or filters).

- 3) Rinse and dump each sample bottle three times with the water being sampled.
- 4) Fill sample bottles 50% full, cap tightly and place bottles in ice chest.
- 5) Return samples to laboratory for preservation and analysis.

**What happens to the samples?** Each well sample will be analyzed at Cornell for nitrate, which is sometimes found when agricultural pesticides are also present in groundwater. We will also analyze for several pesticides at Cornell, depending on the likely pesticide use in the area. One set of samples – identified only by a code number – will be shipped to the NY DEC lab for a scan that measures for over 90 pesticides/herbicides). Because of program limitations, we can submit only 40 samples to DEC for full analysis.

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

1) We will prepare and send you a confidential report indicating lab results determined by Cornell and NYSDEC. Note that the DEC analysis may take a long time to be completed. In the event that traces of pesticides are found, we will also include for comparison the safe drinking water concentration limits for those pesticides.

2) In the very unlikely event that pesticide concentrations exceeding safe drinking water levels are found, we would contact you in order to resample the well twice to confirm the initial findings. If resampling confirms that levels are too high, we would advise both you and the county SWCD. The SWCD would notify relevant county agencies – most likely the Department of Health – to help you safeguard the health of people consuming water from the well(s) by taking appropriate remedial and/or preventative measures.

3) In cases where levels are somewhat elevated but not in excess of drinking water standards, landowners will be encouraged by the SWCD to contact relevant agencies (such as DOH or Agricultural Environmental Management) to take measures that could prevent levels from going any higher.

4) Any published reports about this study will summarize data on a general basis for the county. The location and concentrations of particular well(s)/land cannot be determined from the report. No landowner identities or addresses will be published.

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

**If you have any questions** contact Brian Richards of the Department of Biological & Environmental Engineering (607-255-2463; bkr2@cornell.edu) or George Squires of the Genesee County SWCD (585-343-2362; George. Squires@ny.nacdnet.net).

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

 $\Box$  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 bottles will be for DEC submission; and four bottles will be for Cornell analysis and archiving.

 $\Box$  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).

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

 $\Box$  Rinse each sample bottle three times with the water being sampled. Discard rinsate into rinse pail.

 $\Box$  Fill replicate sample bottles approximately 90% full to allow freezing and cap tightly.

 $\square$  Place bottles in ice chest.

 $\Box$  Return samples to laboratory and freeze immediately



 $\mathbb{R}^2$ 

# **SAMPLE INFORMATION LOG SHEET**

LOCATION INFORMATION IS CONFIDENTIAL AND IS NOT TO BE DISCLOSED

