Surveying Upstate NY Well Water for Pesticide Contamination

Year 3 Final Report

to the

New York State Department of Environmental Conservation

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EXECUTIVE SUMMARY

NYS DEC contracted with Cornell University to undertake a survey of selected representative areas in upstate New York to determine the occurrence of pesticide contamination of groundwater by sampling well systems in rural (domestic and farm) and suburban areas. Of particular interest are areas judged most vulnerable, where significant pesticide use (agricultural and otherwise) coincides with shallow aquifers, presenting elevated contamination risks in contrast to areas with low pesticide use and/or less vulnerable groundwater resources. 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), and in Schenectady County in cooperation with the county SWCD and Water Quality Coordinating Committee (WQCC). The Year 3 effort was focused on Orange County, where diverse land uses and an increasing reliance on ground water combined with pesticide use made this a priority candidate for sampling.

Orange County sampling results Well selection was based on a combination of local knowledge of groundwater conditions and vulnerabilities, groundwater modeling, and reviewing the PSUR pesticide application database. Within this context, the Orange County Soil and Water Conservation District (OCSWCD) took the lead in landowner contacts and sampling. Sample collection took place between June and August 2007.

Wells sampled were characterized for surrounding land uses. Most wells sampled (23) served single houses with 17 serving barns or other agricultural uses. Of the 24 wells for which depths were known by landowners, one well was shallow (<30 ft.), six were between 30 and 100 ft. deep, and 17 wells exceeded 100 ft.

Detection limits for the 93-compound scan run by DEC laboratory were all at or below 1 µg/L except for three analytes at 2 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 Orange County did not exceed any MCLs or guidance values for those 15 analytes with such standards.

ELISA scans at Cornell similarly showed that no MCLs or guidance values were exceeded for the three analytes tested (atrazine, diazinon and metolachlor). Three samples had quantifiable detection of atrazine (two samples) or diazinon (one sample). In addition there were three trace detections (falling between the quantitation limit and the trace detection limit) of atrazine, one of diazinon and five of metolachlor. Nitrate values were low, with mean levels of 0.7 mg/L and a maximum single well value of 5.5 mg/L. There appeared to be no interaction among well detections or trace detections (no multiple detections in any single well) nor with nitrate: of the six wells with nitrate-N over 1 mg/L only one well had a trace or quantifiable detection in the ELISA scans.

State-wide assessment The statewide assessment integrated publicly-available datasets to identify those areas where population dependence on groundwater from hydrologically-vulnerable systems coincides with significant pesticide use as a basis for locating future research. The protocol was improved using finer-resolution zip-code level sales and use data. Using this approach, we identified a band of relatively vulnerable areas spanning the intensive agricultural areas of central and western NY counties south of Lake Ontario. Based on this, we initiated work Genesee County for Year 5 activities. Further developments underway include weighting for mobility and persistence.

1. INTRODUCTION

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. Leaching losses can represent up to 4 to 5% of applied pesticides. 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. Similar contamination problems on the deep sandy soils of Long Island are well documented.

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

Cornell University used a landowner confidentiality approach where public reporting of data involves general but not specifically georeferenced results. Landowners receive confidential reports for their wells, but are not identified in any public reporting. This measure was taken in part as an incentive to attract landowner cooperation which would enhance the weight of project findings by maximizing sampling of sites deemed most vulnerable.

2. PROJECT COMPONENTS

Four project components are reported here. The first is the *site selection process* (Section 2.1) used to identify well sites, including refinement and application of a simple groundwater risk screening model developed in the first year effort, and the application of Pesticide Sale and Use Reporting (PSUR) database information. Second is the *site characterization* (2.2) of the selected sampling sites. Third is the presentation of *sampling results* (2.3) of the well sampling carried out in Orange 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

The Orange County Soil & Water Conservation District (OCSWCD; Kevin Sumner, District Manager) took responsibility for site identification and recruitment in cooperation with Cornell personnel. Site targeting priorities were developed during several joint meetings held in Orange County in early 2007.

Funding constraints dictated that a maximum of 40 well water samples be analyzed in the DEC pesticide laboratory. Because DEC's interest is in targeted sampling of the most vulnerable sites, identification of the best potential sites was important. The site selection process developed for this

program involved three primary approaches: 1) assessing local knowledge about areas of likely vulnerability, 2) using a potential transport screening model to determine relative vulnerability based on soil type and depth to groundwater, and 3) examining the NYS PSUR database for application trends.

2.1.1. Site selection: local knowledge

This approach involves assessing local knowledge about areas of likely vulnerability, a process that is both iterative and interactive. The primary source in this case was the expertise of the Orange County SWCD. Existing mapsets were accessed to exclude areas served by public water supply systems.

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 last year and is only briefly summarized here. The model (Sinkevich 2004, Sinkevich et al. 2005) was used as a screening tool to identify where soils types and shallow groundwater could make groundwater more vulnerable.

Pesticide contamination of groundwater is dependant 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. One of these models is the Generalized Preferential Flow Model (GPFM), which needs only limited inputs – 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, *not* an attempt to predict actual groundwater pesticide concentrations. Results are thus used only to aid in sampling area selection.

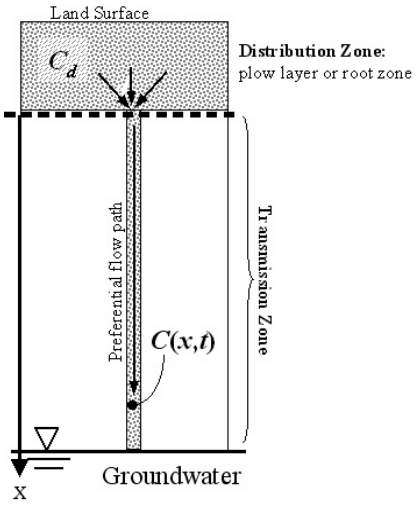

Figure 2.1.1. Schematic diagram of the preferential solute transport process in the vadose zone.

The Generalized Preferential Flow Transport Model

The GPFM describes solute transport between the land surface and the groundwater. Figure 2.1.1 shows the conceptualization of the soil profile used to develop the GPFM, which is divided into two zones: a near surface distribution zone and a deeper transmission zone (Jarvis et al., 1991; Steenhuis et al., 1994; Ritsema and Dekker, 1995; Shalit and 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 transports the solutes through the transmission zone, often accelerating contaminant transport (Camobreco et al. 1996, Beven and Germann 1982, Darnault et al. 2004, Geohring et al. 1999). The thickness of this distribution zone depends on land use or geomorphology, e.g., plow depth in cultivated land. The GPFM has been successfully tested with both lab and field experiments.

To develop a groundwater contamination risk assessment tool, we implemented the GPFM in a GIS using spatially-distributed estimates of average percolation velocity, v, and depth to the groundwater, x. Groundwater depth typically varies throughout the year but for the purposes of risk assessment, the soil survey or SURRGO/STATSGO minimum groundwater depths sufficiently

capture the distributed water table depths for the purposes of pollutant risk assessment.

Model Application

This study used atrazine as a model of a mobile, slowly-degraded model compound, and assumed label-based pesticide application rates. For this study we simulated one complete pesticide pulse. Table 2.1.1 summarizes the atrazine parameters used in this study.

Table 2.1.1. Pesticide parameters for atrazine as the screening assessment model compound.

Parameter	Value	Source
K_{oc}* Pesticide Organic Adsorption Coefficient	160 cm^3/g	DelVecchio and Haith, 1993
$t_{1/2}$ Half-life	60 days	DelVecchio and Haith, 1993
H EPA Drinking Water Standard	3 µg/L	http://www.epa.gov/safewater/mcl.html#mcls
M Application Rate	1.45×10^{-4} g/cm^2	http://www.usda.gov/nass/

* K_{oc} is used in Eq. 2.2.11 to solve for k with Om from STATSGO (see "Soils" section below).

In order to determine a group of possible sampling locations, a relative risk classification was calculated for each soil type in Orange County. The risk classification was found from the predicted relative concentration of a model pesticide at the estimated groundwater depth for each soil type. The data required to do this consisted of annual amount of recharge to groundwater table (calculated from precipitation, temperature, and evaporation data), soil type and properties, depth to groundwater, and specific chemical data (degradation rate and chemical adsorption rate). Once the predicted concentration was determined, a risk classification was assigned. The risk classification was calculated based on the relative risk (i.e. each predicted concentration divided by the highest predicted concentration).The data was imported into a Geographic Information System (GIS) software package and combined with data from land use and municipal water supply. The areas with overlapping agricultural use and that were not supplied by a municipal water system were selected as principal areas of interest. Soil types coded by predicted relative risk are mapped in Figure 2.1.2; this particular map was also largely restricted to agricultural land uses and surrounding areas. It should be remembered that the figure indicates areas with greater relative groundwater vulnerability using the mobility characteristics of a model pesticide, and are not predictions of actual contamination.

The map served to help identify areas for the initial site search. Sites ultimately selected were located in the elevated vulnerability area of the county, with no sites falling in the predominantly "negligible risk" areas in the northwest corner nor in the southeastern region of the county (areas dominated by yellow in Figure 2.1.2).

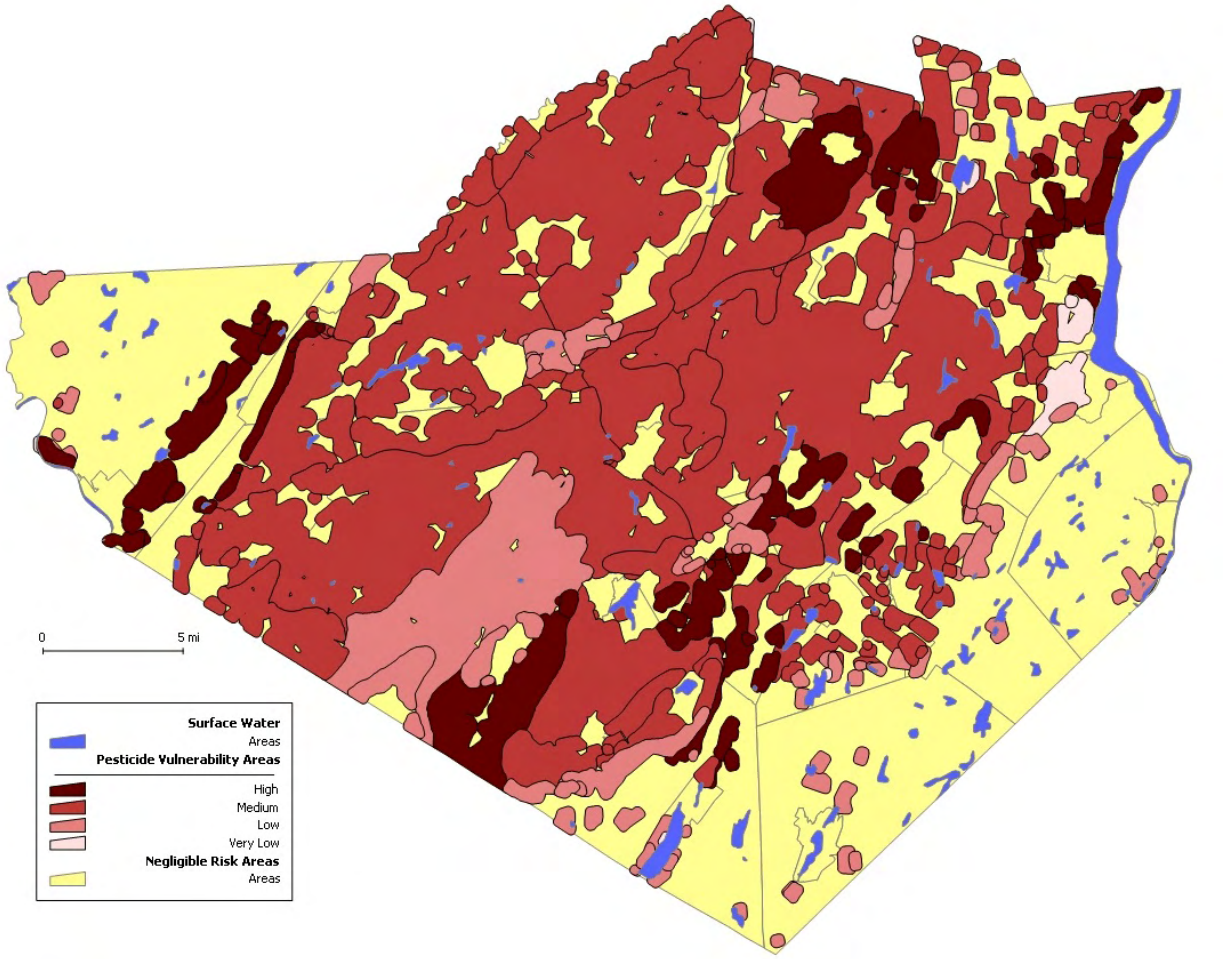

Figure 2.1.2. Relative groundwater vulnerability as a function of soil characteristics using mobility characteristics of a model pesticide (atrazine in agricultural use).

2.1.3. Utilization of the PSUR Database

In September 2006 we requested access to the confidential application records of the PSUR database. 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 PMEP group did not receive the authorization to release until early June 2007, and due to workflow requirements could not generate and release the data report until early August 2007. The request-to-data access time lag was thus 11 months, longer than the 8-9 process experienced in the second year of the program. Unfortunately, by this time both site selection and sampling were nearly complete.

However, publicly-available PSUR data summarized at the zip-code level was subsequently used to guide the choice of pesticides 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) likelihood of the pesticide reaching ground water, and (3) availability of immunoassay test kits. Immunoassay results

are for screening only, to be confirmed with supplemental methods if they reveal concentrations of concern.

For extent of use, Table 2.1.2 summarizes the 25 most-applied pesticide active ingredients in Orange County, based on the average of 2000-2005 datasets. Figure 2.1.3 shows maps of sales and use of these three compounds by zip code. Note that each map uses a unique scale for application density. All maps of individual AI's have application intensities that are two to three orders of magnitude less than the scales in the all-active-ingredients maps shown later which can reach 1300 kg/km^2.

To better account for the potential of individual pesticides to travel to groundwater, the table includes a Groundwater Ubiquity Score (GUS) (Gustafson, 1989). The GUS is computed 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. A zero GUS value would apply to a pesticide that is degraded and/or immobilized immediately. A GUS value above 2.0 indicates a moderate potential to move to ground water, and a value above 3 indicates a high potential. In Orange County, GUS values over 3.0 for atrazine and metolachlor indicate compounds of more concern, whereas values of under 1.0 for chlorpyrifos and pendimethalin indicate compounds of much lower concern for ground water.

The third consideration was the availability of test kits. ELISA kits are increasingly available for commonly used pesticides that are of concern in water and food. We chose to perform immunoassay tests for metolachlor (SDI), atrazine (SDI), and diazinon (Abraxis). Two suppliers – Strategic Diagnostics (SDI) and Abraxis – were considered and used for Orange County samples.

Table 2.1.2. The 25 most-applied pesticide active ingredients in Orange County, average of 2000-2005 reporting years, relative Groundwater Ubiquity Score (GUS) and availability of ELISA screening/test kits by supplier. Highlights indicate active indgredients chosen for additional ELISA testing.

Name	Reported Sales (kg/yr)	Reported Use (kg/yr)	Combined Sales+Use (kg/yr)	GUS (index)	Available ELISA Kit?
Mancozeb	21,000	300	21,200	1.29	no
Chlorothalonil	7,600	1,800	9,400	1.27	SDI
Chlorpyrifos	7,900	100	8,000	0.32	SDI
Copper Sulfate Pentahydrate	100	7,700	7,800	n/a	no
Pendimethalin	5,600	800	6,300	0.59	no
Maneb	6,100	200	6,200	1.29	no
Aliphatic petroleum hydrocarbons	2,600	3,200	5,800	n/a	no
Acetamide, 2-chloro-n-(2,4-dimethyl-3-thienyl)-n-(2-methoxy-1-methylethyl)-	4,000	200	4,100	n/a	no
Aatram, Component of (With 080803)	3,500	0	3,500	n/a	no
Captan	3,400	0	3,400	0.68	no
Metolachlor	***2,300***	***900***	***3,100***	***3.32***	***SDI, Abraxis***
Dithane (Mancozeb) M-45 technical premix	2,900	0	2,900	n/a	no
Atrazine	***1,600***	***1,000***	***2,700***	***3.56***	***SDI, Abraxis***
Zinc Ion and Manganese Ethylenebisdithiocarbamate, coordination product	1,900	0	2,000	n/a	no
Oxamyl	2,000	0	2,000	1.57	no
Karate	100	1,900	2,000	n/a	no
Iprodione	1,600	300	1,900	1.32	no
Dimethylamine 2,4-dichlorophenoxyacetate	700	1,100	1,800	n/a	no
Sulfur	1,800	0	1,800	n/a	no
Glyphosate-isopropylammonium	700	900	1,700	n/a	Abraxis
Diazinon	***1,100***	***600***	***1,700***	***1.6***	***Abraxis***
Glycine, N-(Phosphonomethyl)- potassium salt	1,400	300	1,700	n/a	no
CP 70139	1,500	100	1,700	n/a	no
Hexahydro-1,3,5-tris(2-hydroxyethyl)-s-triazine	0	1,600	1,600	n/a	no
Acephate	1,600	0	1,600	1.76	no

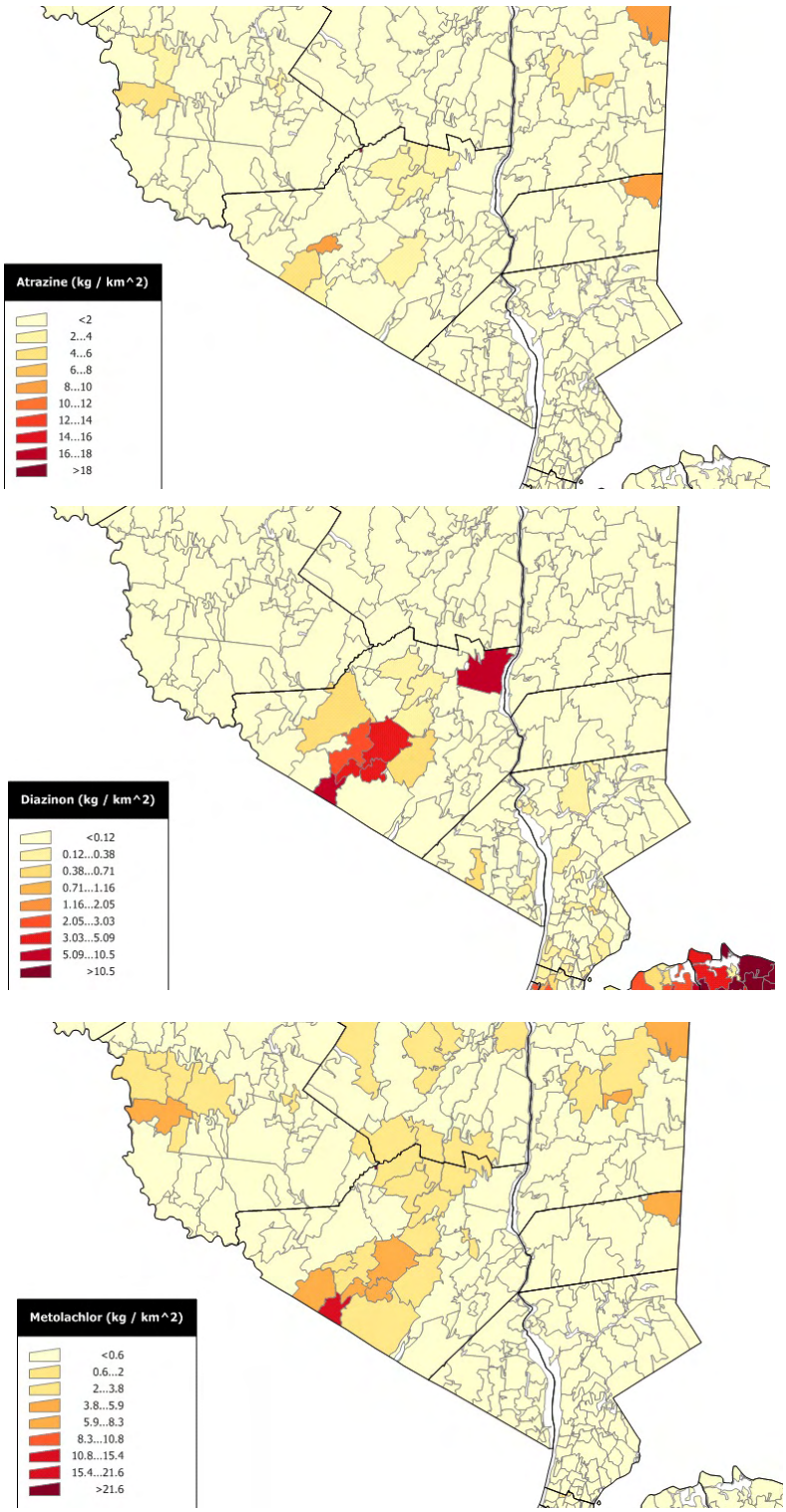

Figure 2.1.3. GIS representations of active ingredient use intensities (kg AI per sq. km) for atrazine, diazinon and metolachlor, based on publicly-available zip-code level data summaries for 2000-2005.

2.1.4. Landowner recruitment and confidentiality guidelines

Recruitment of landowners in selected study areas was carried out by the OCSWCD. 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.)

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 DEC as well as any academic or extension publications), only blurred georeferences – such as rounded map coordinates – would be reported.
- Reports indicating pesticide concentrations determined by Cornell and NYS DEC would be compiled and sent to individual landowners.
- In the event that pesticide concentrations exceeding drinking water standards were found, the landowner would be contacted and the well would be resampled twice to confirm the initial findings. If confirmed by resampling, the OCSWCD would be advised. The OCSWCD 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 NYS DEC upon reasonable request from NYS DEC.

Samples were acquired by OCSWCD personnel between June 22 and August 17, 2007.

2.2 Site Characterization and Sampling

2.2.1. Sampled Well Sites

Table 2.2.1 presents the sampled well information, including well use, depth, surrounding land use(s) and sampling date. Land uses were characterized during the site sampling visits and by subsequent detailed interactive viewing via Google Earth, which provides detailed coverage for Orange County that integrates topography with aerial photos.

Table 2.1.1. Sampling site and well characteristics. NA indicates well depth not available.

ID	Well use	Depth (ft)	Well position relative to land use and topography	Sample date
1	B	310	cornfield, hayfields; mixed wooded/hayfields N,W,S, suburban W	06/22/07
2	H	NA	pasture/hayfields with some turf; wooded toNW, W and SW	07/17/07
3	H	50-75	black dirt farms from NE to SW; wooded rises to S, topped by housing	07/17/07
4	H	340	turf/hayfield on flatland, large wooded hill to NW, W and SW	07/17/07
5	H	NA	surrounded by black dirt farms, wooded hill 0.5 mi to S	07/17/07
6	B	400	river nearby, black dirt farms to NE-SW. mixed wooded, hayfield to N-W	07/17/07
7	B	350	surrounded by black dirt farms, large wooded hill to S	07/17/07
8	H	180	large area of hayfield/pasture, surrounded by wooded (wooded upslope)	08/03/07
9	B	77	in middle of black dirt area	07/17/07
10	H	180	on knoll surrounded by hayfields; black dirt toE,S; upslope woods to W, N	08/03/07
11	H	NA	on small suburban knoll surrounded by wooded/scrub rolling terrain, cropland to S	08/17/07
12	B	140	dairy farm; black dirt S, rolling terrain with dairy farm N, scrub/mixed elsewhere	06/22/07
13	H	150	rolling terrain: house in saddle between crop fields; large wooded area to N	06/22/07
14	B	NA	livestock farm; knoll on mostly level terrain.	06/22/07
15	H	130	on knoll; rolling terrain, mixed wooded, forage/rowcrop, major utility ROW N	06/22/07
16	B	168	dairy farm on low rise; black dirt to S&SW, abandoned black dirt to NW-NE	07/17/07
17	H	NA	on side of drumlin; middle part farm stand/greenhouse and fields, rest wooded	08/03/07
18	B	220	on small drumlin; hay/pasture, some abandoned to scrub, light industry to NW	08/03/07
19	B	100	on hillside dominated by pasture/turf, rest wooded	08/03/07
20	B	NA	dairy rotation field N and W ; mountain to Emostly wooded, vineyards S	06/22/07
21	H	NA	dominated by wooded mountain; patches of large-lot suburban; ROW to S	06/22/07
22	B	600	on ridge in rolling terrain; hay/pasture with mixed wooded/scrub	06/22/07
23	B	110	farm on flat land; adjacent to large turfgrass area, urban to NE	06/22/07
24	B	8	farm on gently rolling terrain; large lot development S, wooded rise to NE-E	06/22/07
25	B	NA	hilltop horse farm; pasture/hay NW to E, rest wooded	08/03/07
26	H	NA	large lot development on saddle knoll; patchy farmland, wooded knolltops	08/03/07
27	H	NA	housing development on knoll surrounded by cropland; black dirt to S-W	07/17/07
28	H	530	small large-lot development on knoll; area dominated by woods	08/03/07
29	H	100	housing development on knoll surrounded by cropland; black dirt to S-W	07/17/07
30	B	NA	dairy farm on side of ridge; upslope hay/crops fields, woods	08/03/07
31	H	NA	housing development on knoll surrounded by cropland; black dirt to S-W	07/17/07
32	H	<100	black dirt farms from NE to SW; wooded rises to S, topped by housing	08/17/07
33	H	50	black dirt farms N to SW; suburban to urban elsewhere	08/17/07
34	H	NA	housing development on knoll surrounded by cropland; black dirt to S-W	08/17/07
35	H	NA	small hilltop development on wooded hill, E side of ridge extensive turf/hay	08/17/07

Table 2.1.1, continued.

36	H	NA	dairy farm on rolling hillside with fields and woodlots; large pond to SW	08/17/07
37	B	180	small farm on knoll dominated by subdivision and woodlots, some fields	08/17/07
38	H	155	on rise below dairy farm, wooded downslope, large black dirt area to E	08/17/07
39	H	NA	farm with crop, grazing land; upslope is small subdivision	08/17/07
40	B	160	farm with fields and woodlots upslope to S, major highway crosses N of farm	08/17/07

Well depths and facilities served are summarized in Table 2.2.2. Most wells sampled (23) served single houses with 17 serving barns. Of the 24 wells for which the depths were known by landowners, 1 well was shallow (<30 ft.), 6 were between 30 and 100 ft. deep, and 17 wells exceeded 100 ft.

Table 2.2.2. Summary of sampled well uses (left) and reported depths (right).

Facility served by wells	Wells
house	23
barn	17
other	0
Total	40

Well depth class	Wells
less than 30 ft.	1
30 to 100 ft.	6
greater than 100 ft.	17
depth unknown	16

Table 2.2.3 summarizes the prioritized land uses in surrounding and upslope areas, which 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. Land uses were then ranked as primary (i.e. most extensive and occupying 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 were visually classified and coded in Table 2.2.3 as follows:

- W Woods, trees
- S Turf/lawns, including suburban development and managed turfgrass (golf courses etc.)
- U Urban areas with higher density housing or other urban land uses
- B Black dirt (also referred to as muck soil) vegetable farms
- C Dairy farm fields which include corn, typically found in rotation with forages
- H Other farm fields (including apparently forage-only dairy farms and horse farms) dominated by hayfields, small grains and pasture.
- R scrub (brush and small trees) and regrowth of abandoned farmland
- M Mixed uses too tightly integrated to delineate into categories
- O Other

Table 2.2.3. Prioritized land uses in surrounding and upslope areas.

Well	Well use	Land use(s) ranked by extent		
		Primary	Secondary	Tertiary
1	barn	C	W	S
2	house	H	W	S
3	house	B	W	S
4	house	W	S	
5	house	B		W
6	barn	B	W	H
7	barn	B	W	
8	house	H	W	
9	barn	B		
10	house	H	W	B
11	house	S	W	C
12	barn	C	S	B
13	house	C	W	
14	barn	C	W	
15	house	M	O	
16	barn	C	B	
17	house	O	W	H
18	barn	H	R	M
19	barn	H	W	
20	barn	C	W	O
21	house	W		S
22	barn	H	W	
23	barn	C	S	U
24	barn	C	S	W
25	barn	H	W	
26	house	S	C	W
27	house	S	C	B
28	house	W	S	
29	house	S	C	B
30	barn	H	C	W
31	house	S	C	B
32	house	B	W	S
33	house	B	U	
34	house	S	C	B
35	house	W	H	S
36	house	C	W	
37	barn	S	W	C
38	house	C	W	B
39	house	C	W	S
40	barn	C	W	O
	Legend and category totals by priority class			
	S	7	4	7
	U	0	1	1
	W	4	21	4
	R	0	1	0
	B	7	1	7
	H	8	1	2
	C	12	6	2
	M	1	1	1
	O	1	1	2

The wide range of land uses in Orange County are reflected in the land use categorization in Table 2.2.3. Agriculture dominated primary land uses with dairy corn/forage rotation around 12 wells, hay/pasture around 8 wells, and black dirt farms near 7. These agricultural land uses also represented secondary land uses at 8 sites and tertiary land uses at 11 sites (most notably 7 black dirt farm sites).

Managed turfgrass, either as lawns in suburban areas, large areas in localized clusters of non-suburban housing, or other turf areas, was primary for 7 wells, secondary for 4 wells and tertiary for 7 wells, in many cases representing fairly recent subdivisions interspersed in otherwise rural areas. More dense urban areas – typically small municipalities upslope from sampled areas – were secondary and tertiary land uses at one site each. Wooded areas were judged to be primary for 4 wells (typically dominating large upslope areas above wells that were surrounded by a different but less extensive land use), secondary for 21 sites, and tertiary for 4 sites. Areas of scrub/regrowth were surprisingly little represented, being a secondary use for only one site. Mixed land uses (representing an array of land uses too tightly integrated to meaningfully separate) were delineated at 3 sites (one in each priority class). The rationale for the classification of "other" (4 sites) is defined in each case by the description in Table 2.1.1: and represented single occurrences of the proximity of a major highway right-of-way, a utility right-of-way, a greenhouse operation and a vineyard.

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) narrow-mouth amber glass bottles were used for sample collection. Four 1 L bottles were collected for samples for submission to DEC, and four 125 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 were rinsed three times with the sampled water prior to filling. Bottles were filled approximately 40% full to allow subsequent freezing and were placed in an ice chest. Bottles were frozen (laying them horizontally in a freezer to prevent breakage) within 8 hours of collection.

To prevent in-transit breakage issues encountered in earlier years, frozen sample bottles were picked up from Orange County and hand-delivered to the NYS DEC laboratory.

2.3 Analysis and Results

Pesticide analysis conducted by DEC 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 imidacloprid.

2.3.1. Analytical Protocols

DEC pesticide scans
This section consists of text forwarded by Peter Furdyna of the NYS DEC Pesticides Laboratory:

The water samples which were submitted to the NYSDEC Pesticides Laboratory under the group numbers OC01 – OC40 were screened for pesticides, phenoxy acid herbicides and carbamates. All sample results were non-detect at the laboratory's method detection limit (MDL). The minimum reporting levels were 1 ppb (µg/L) for all compounds except for the following chemicals and their respective reporting limits (listed in parentheses): Aldicarb + Methomyl (0.35 ppb), Diazinon (0.7ppb), Dicamba (0.44 ppb), and MCPA (0.44ppb). With the exception of these five chemicals, the mimimum reporting levels are the lowest levels used in the calibration standards. For the five chemicals with lower reporting levels, raw data was examined for the sample analyses and compared to low (1ppb) standard response for that chemical. In each and every case, it could confidently be determined that no response was present at a level corresponding to these lower reporting levels.

All samples submitted to the laboratory were successfully analyzed.

All of the pesticide and herbicide compounds except trifluralin, benfluralin, dithiopyr, and chlorpyrifos were analyzed by direct injection followed by HPLC/MSMS. The remaining four chemicals were extracted using a liquid-liquid (QUECHERS) 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 between 5 and 10 ppb.

The chlorophenoxy acid herbicides were spiked at 10 ppb, in 3 sets of MS, MSDs. Spike recoveries ranged from 98% to 130%, with relative percent differences ranging from 0.0% to 18.5%.

For HPLC/MSMS direct injection pesticide samples, with the exception of the compound pyridate, recoveries ranged from 10% to 259%, with RPD’s ranging from 0.0% to 76.40%. In two of the spike samples, pyridate did not recover. This appeared to be matrix specific for those samples as pyridate recovered well (80%, and 83%, and 68%, and 64%)Chemicals were spiked between 5 and 10 ppb, in 9 sets of duplicates, noting that not all duplicate sets were spiked with all chemicals, but all of the chemicals were spiked in at least 4 sets of duplicates.

For GC/MS extraction and analysis samples, chemicals were spiked at 5 ppb in 4 sets of duplicate samples. Recoveries ranged from 26.4% to 64.4%, with RPD’s ranging from 0.4% to 48.7%.

Table 2.2.4. Method detection limits (MDL) of pesticide/herbicide analyses run by the NYS DEC laboratory. All MDL concentrations are reported as ì g/L (ppb).

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

ELISA and nitrate assays

Water samples were screened at Cornell University for atrazine, diazinon and metolachlor (as the most likely to be detected pesticides, given significant reported use and relative mobility). The method employs Enzyme-Linked ImmunoSorbent Assays (ELISA) to detect the analyte and related compounds. In contrast to conventional colorimetric tests where increasing absorbance linearly correlates to increasing analyte concentration, the analyte compounds compete with reagents that favor color development in the ELISA assay.

Atrazine (Strategic Diagnostics Kit No. A00071) and metolachlor (Strategic Diagnostics Kit No. 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 diazinon kit (Strategic Diagnostics Envirogard Kit No. 7270000) was a 96-well plate test had a quantitation range of 0.03-0.5 ì g/L, with a trace detection level of 0.022 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. Potential cross-reactive compounds are reported in the results section.

Magnetic particle assays were analyzed with a Milton-Roy Spectronic 501 using 1 cm path length cuvettes. The diazinon test was analyzed using a Biotek ì Quant 96-well plate spectrophotometer. 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, for magnetic particle kits, logit functions. For the atrazine and metolachlor test kits, the form of the regression equation is:

$$\ln(C) = \text{intercept} + \text{slope}\ (\text{logit}\ (B/B_0)) \qquad \text{Eq. 2.1.1}$$

For the diazinon test kit, the regression form is

$$\ln(C) = \text{intercept} + \text{slope}\ (100B/B_0) \qquad \text{Eq. 2.1.2}$$

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

The analysis was run on frozen samples in August 2008 for diazinon. Initial analyses for other analytes in the fall of 2008 were discarded due to analysis kit deficiencies (different manufacturer), and the final analyses were successfully completed in December 2008.

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

2.3.2 Analysis Results

DEC analysis

Pesticide analysis at the NYS DEC laboratory was completed and final reports transmitted in June 2007. As noted in the prior section, the NYS DEC pesticide screening found that *all analytes were*

below the detection limits specified in Table 2.2.4. DEC analytical results are summarized in Table 2.2.5.

Table 2.2.5. Results of analyses run by the NYS DEC laboratory. All concentrations are reported as ì g/L (ppb). ND indicates non-detects, indicating concentration less than the associated 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 < 2
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 < 2
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 < 2	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 2.2.6. Comparison of NYS ambient groundwater (GA) MCL standards with DEC pesticide scan method detection limits:

Analyte	NYS MCL (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	10	1	Yes
Oxamyl	50	1	Yes
Trifluralin	35	1	Yes

*guidance levels rather than actual standards

In Table 2.2.6 we compare the maximum allowable MCL (NYS DEC 1998; with the addition of a more recent metolachlor standard) with the DEC pesticide 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 DEC scan detection limits that were equal to or lower than the MCL, which means that the tests that yielded nondetects ruled out MCL exceedence.

Cornell analysis

The three ELISA scans conducted at Cornell University for atrazine, diazinon and metolachlor indicated only three quantifiable detections (Table 2.2.7), all at levels well below the detection limits of the corresponding DEC scans. Note that one of the atrazine detections occurred in a sample pair where the corresponding replicate was lost.

In addition, there were nine potential trace detections, with analyte responses greater than the method detection limit (MDL) but less than the minimum limit of quantitation (LOQ). There was no overlap among detections or trace detections for any given well, with analytes occurring independently of other analytes.

Table 2.2.7. 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 needs to generate response equivalent to primary analyte at LOQ or 50% B/B_0 response level.

Well No.	ATRAZINE	DIAZINON	METOLACHLOR
LOQ:	0.1	0.03	0.1
MDL:	0.05	0.022	0.05
1	nd	nd	nd
2	nd	nd	nd
3	nd	nd	nd
4	nd	nd	nd
5	nd	nd	nd
6	nd	nd	nd
7	nd	nd	nd
8	nd	nd	nd
9	nd	nd	nd
10	nd	nd	nd
11	nd	nd	trace <0.1
12	nd	nd	nd
13	trace <0.1	nd	nd
14	nd	nd	nd
15	nd	nd	nd
16	nd	nd	trace <0.1
17	nd	nd	trace <0.1
18	nd	nd	trace <0.1
19	nd	nd	nd
20	nd	nd	trace <0.1
21	nd	nd	nd
22	nd	nd	nd
23	nd	nd	nd
24	nd	nd	nd
25	trace <0.1	nd	nd
26	nd	nd	nd
27	nd	nd	nd
28	nd	nd	nd
29	nd	nd	nd
30	0.14	nd	nd
31	*0.27	nd	nd
32	trace <0.1	nd	nd
33	nd	nd	nd
34	nd	nd	nd
35	nd	0.07	nd
36	nd	nd	nd
37	nd	nd	nd
38	nd	nd	nd
39	nd	nd	nd
40	nd	trace <0.03	nd

*single replicate only

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
Diazinon (SD Envirogard 7270000)	
	at 50% B/B_0
Diazinon	0.1
Diazoxon	0.9
Pirimiphos-ethyl	0.7
Pirimiphos-methyl	5
Metolachlor (SD A00080)	
	at LOQ
Metolachlor	0.1
Acetochlor	0.77
Metalaxyl	0.66
Butachlor	6.12
Propoachlor	294
Alachlor	9.9

Cornell results for well nitrate-N are shown in Table 2.2.8. Nitrate concentrations were all below the 10 mg N/L drinking water standard, with the observed maximum concentration of 5.6 mg/L and a mean of 0.7 ± 1.1 mg N/L (using a detection limit values of 0.1 for the thirteen nondetects, a negligible error). Only six values were in excess of 1 mg/L, and only one of these coincided with a well that had detects or trace detects for ELISA pesticide analyses.

Table 2.2.8. Nitrate-N analysis (mg/L). Mean and standard deviation calculated using detection limit of 0.003 mg/L for all non-detects.

Well	Nitrate-N	Well	Nitrate-N
1	<0.1	21	<0.1
2	0.33	22	<0.1
3	2.20	23	<0.1
4	1.05	24	3.66
5	0.59	25	0.34
6	<0.1	26	1.59
7	<0.1	27	<0.1
8	<0.1	28	<0.1
9	<0.1	29	2.24
10	<0.1	30	1.08
11	<0.1	31	<0.1
12	5.60	32	2.30
13	<0.1	33	0.66
14	<0.1	34	0.84
15	<0.1	35	0.28
16	<0.1	36	1.60
17	0.71	37	<0.1
18	<0.1	38	<0.1
19	<0.1	39	<0.1
20	0.71	40	<0.1
Mean	0.7	Std. deviation	1.1

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 other 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 our GIS system 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 Appendix E.

However, as indicated previously, the initial county selection protocol aggregated data at the county level in the final step. This 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 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. (Note that Orange County was selected earlier based on 2000-2001 PSUR 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 2.4.1 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/kilometer squared, by 2.205 lbs/kilogram, and by 0.4049 hectares per acre, yielding a conversion factor of 0.0089 lbs/acre per kg /km^2.

Figure 2.4.2 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, while Orange County has comparatively lower use of pesticides within NY. Figure 2.4.3 focuses on Orange County and vicinity. The most intense use of pesticides is in the black dirt area south-southwest from Goshen to the New Jersey border.

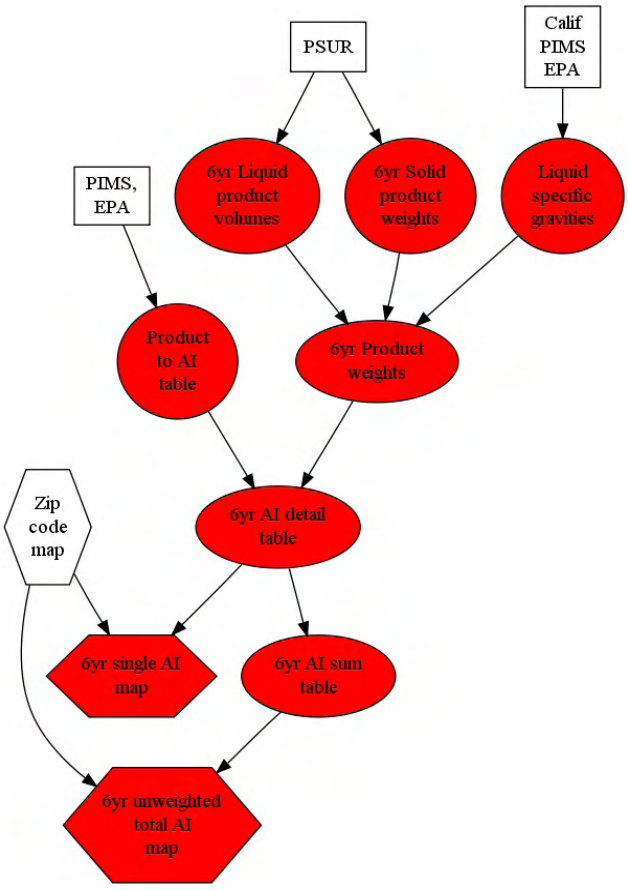

Figure 2.4.1. Schematic of procedure used to synthesize cumulative active ingredient data

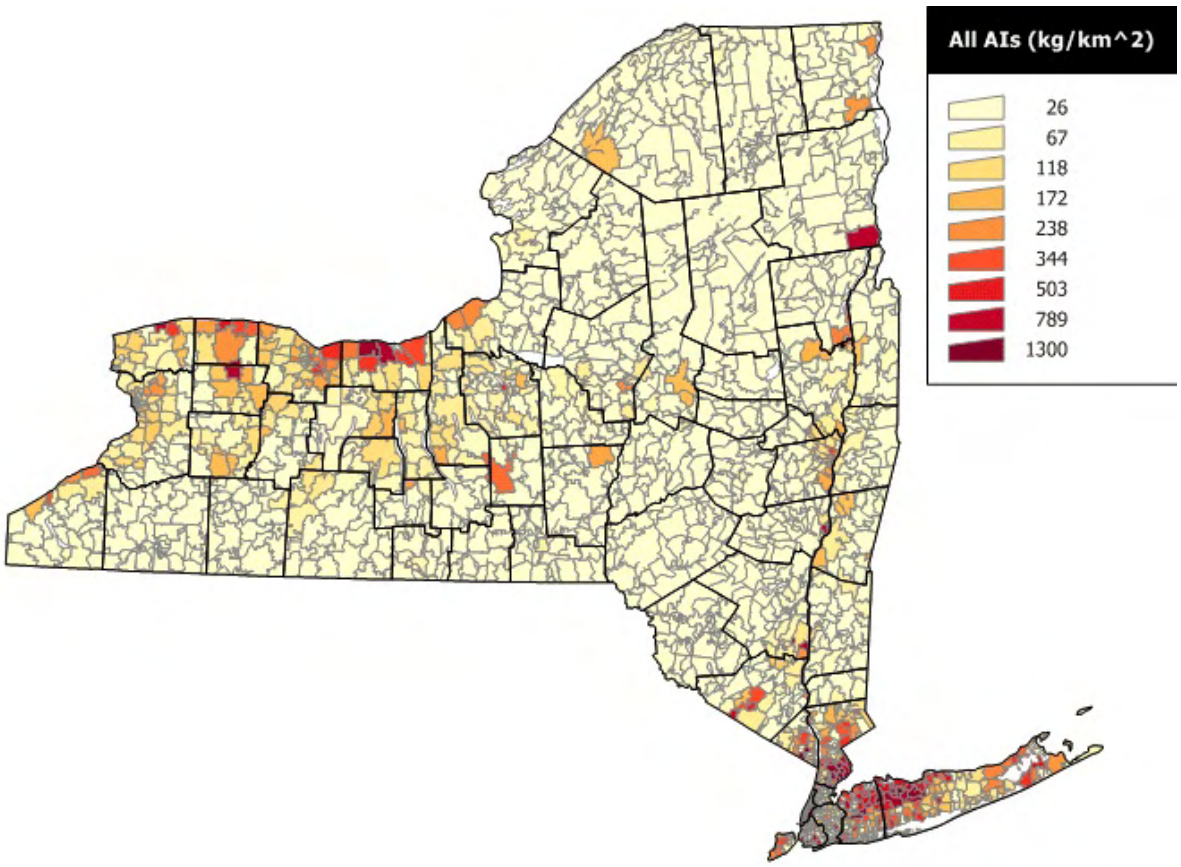

Figure 2.4.2. Summary of the use intensity of all active ingredients (kg/km^2) in New York State, 2000 to 2005.

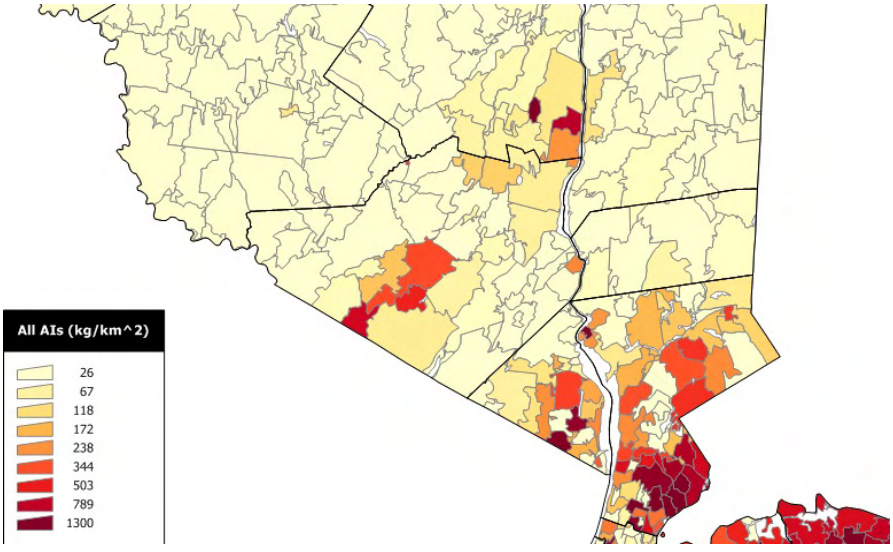

Figure 2.4.3. Summary of the use intensity of all active ingredients (kg/km^2) in Orange County and surrounding areas, 2000 to 2005.

2.4.2. Implications for future testing

This selection approach further highlights the band of relatively heavily-applied areas spanning the intensive agricultural areas of central and western NY counties south of Lake Ontario earlier identified (i.e. Appendix Figure E.7). Based on this, we initiated work Genesee County for Year 5 activities. Vulnerable aquifers (not shown on Figure 2.4.2) in that region include substantial karst formations with close connections with surface flow.

Further developments currently underway include weighting applications for the potential mobility and/or persistence of individual pesticides as reflected in the Groundwater Ubiquity Score discussed in Section 2.1.3. Maps generated using this approach was used to help guide the well site selection process in the Year 4 work in Cayuga County, and will be discussed in the forthcoming Year 4 report.

3. DISCUSSION and ONGOING WORK

The wide range of land uses in Orange County was well reflected in the sample set. Land use categorization (as summarized Table 2.2.3) was based on site visit reports as well as detailed aerial imagery. Agriculture dominated primary land uses (dairy corn/forage rotation near 12 wells, hay/pasture near eight wells, and black dirt farms near seven wells), as well as being the secondary land use near eight sites and tertiary at 11 sites. Managed turfgrass (primarily suburban lawns or localized clusters of non-suburban housing) was the primary proximal land use for seven wells, secondary for four wells and tertiary for seven wells. In many cases these appeared to be fairly recent subdivisions interspersed in otherwise rural areas. Wooded areas were judged to be primary for 4 wells (typically dominating large upslope areas above wells that were surrounded by a different but less extensive land use), secondary for 21 sites, and tertiary for four sites.

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 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 in Table 2.2.6. These nondetects thus established that the 40 well samples from Orange 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, diazinon and metolachlor). Three samples had quantifiable detection of atrazine (two samples) or diazinon (one sample), all at levels lower than the detection limit of the DEC laboratory tests. In addition there were three nonquantifiable “trace detections” (falling between the quantitation limit and the trace detection limit) of atrazine, one of diazinon and five of metolachlor. Nitrate values (tested at Cornell) were low, with mean levels below 0.7 mg/L and a maximum single well value of 5.5 mg/L. There appeared to be no interaction among well detections or trace detections (no multiple detections in any single well) nor with nitrate: of six wells with nitrate-N over 1 mg/L only one well had a trace or quantifiable detection with the ELISA analyses.

The statewide assessment protocol was further adapted during Year 3 activities to improve future targeting by avoiding the county-level aggregation of final data. This has facilitated identifying

regions of markedly greater vulnerability that occur within counties (or that run across multiple counties) that would be otherwise masked by aggregation with other lower vulnerability areas.

At the time of writing, sampling in Cayuga County (Year 4) is completed, as is the on-site analysis of those samples at Cornell University. Sampling is underway in Genesee County (Year 5), and a candidate county for Year 6 work has been identified. Improvements to the county-level selection process have been made and additional changes are underway. Current in-county site selection procedures are yielding greater rates of positive landowner response and better-characterized sites.

4. ACKNOWLEDGMENTS

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6. APPENDICES

A) Landowner Information Handout

B) Sampling Protocol

C) Well Sampling Log

D) Landowner Reporting Form

E) Initial Statewide Vulnerability Assessment

A) Landowner information handout

ORANGE COUNTY
SOIL & WATER
CONSERVATION DISTRICT

Cornell University
College of Agriculture and Life Sciences
Department of Biological and Environmental Engineering

Research Project:
Surveying Orange 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 Orange County, in cooperation with the Orange County Soil & Water Conservation District (SWCD) and the New York 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, 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. Orange 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 SWCD and/or 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.), and will record a description of the setting of the well (local topography and nearby land uses).

Sampling procedure:

1) Personnel will use certified glass 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 40% 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 one to three 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 NY DEC for a complete pesticide scan. Because of program limitations, we can submit only 40 samples to DEC for full analysis. Samples that test free of pesticide residues at Cornell would be less likely to be submitted to DEC.

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 advise the landowner to safeguard the health of people consuming water from the well(s) by taking appropriate remedial and/or preventative measures, including encouraging landowner to contact relevant agencies that could assist.

3) In cases where levels are somewhat elevated but not in excess of drinking water standards, landowners will be encouraged by the SWCD 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 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 NY DEC upon reasonable request from DEC.

If you have any questions contact Kevin Sumner of the Orange County SWCD (815-343-1873; kevin.sumner@ocsoil.org) or Brian Richards of the Department of Biological & Environmental Engineering (607-255-2463; bkr2@cornell.edu)

B) Sampling Protocol

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

☐ Label new, certified precleaned (ESS Inc. PC class) narrow mouth amber glass 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 1000 mL bottles will be for DEC submission; and four small 125 mL 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 40% full to allow freezing if needed, and cap tightly.

☐ Place bottles in ice chest.

☐ Return samples to laboratory for immediate preservation: freeze DEC samples and Cornell replicate C immediately; refrigerate Cornell replicate D if analysis will be in the next day; otherwise freeze.

C) Well Sampling Log

Surveying Upstate NY Well Water for Pesticide Contamination

Department of Biological & Environmental Engineering, Cornell University
NY Water Resources Institute
Orange County Soil & Water Conservation District

SAMPLE Code: _____
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***

_____

_____

_____

_____

_____

D) Example Well Owner Report

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

You are receiving this mailing because you participated in the voluntary testing of drinking water wells in selected areas of Orange County carried out by Cornell University's Department of Biological & Environmental Engineering, in cooperation with the Orange County Soil & Water Conservation District. **These results are confidential and are provided without cost to landowners.** Your sample code number: _____

Results for the analysis of the well water samples included *pesticides/herbicides* and *nitrate*.

1) Pesticides/herbicides Samples (identified only by a sample code) were analyzed by a NYS DEC laboratory for 93 different pesticides/herbicides.

Chemical 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 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.

2) Nitrate-nitrogen We also tested for nitrate levels, which are sometimes of concern in New York wells. The drinking water limit for nitrate-nitrogen (NO_3-N) is 10 milligrams per liter (also stated as 10 parts per million or ppm), based on levels that protect the health of infants who are sensitive to nitrate.

Analysis of the sample from your well indicated a nitrate-N level of _____ milligrams per liter. We have checked the appropriate response below:

❑ this level is far lower than the drinking water limit.
❑ this level is below the drinking water limit but occasional testing in the future might be advised

Please contact either of us with any questions.

Brian Richards
Cornell University
607-255-2463
email: bkr2@cornell.edu

Kevin Sumner
Orange Co. Soil &Water Conservation District
Phone: (845) 343-1873
kevin.sumner@ocsoil.org

The assesment protocol developed during year 1 was presented in the year 1 report and is summarized here for the reader's convenience.

E.1. Protocol Considerations

A risk-based selection process overlays vulnerable aquifers, population dependence on groundwater and several indices of pesticide use. This procedure was first carried out by graduate research assistant Benjamin Liu (BEE) with guidance and input from Steven Pacenka (NYS WRI), with assistance from the Cornell University Pesticide Management Education Program (PMEP).

The process for determining potential exposure of groundwater consumers to pesticide residues involved assessment of two major components: 1) population dependence on groundwater, and 2) pesticide application intensity. These two components were overlaid and masked to vulnerable aquifer areas using ArcGIS, to determine the NYS counties with the most population potentially exposed to pesticide residues via groundwater used as drinking water.

Key Aquifers and Dependence Upon Them for Drinking Water
New York State has identified principal aquifers based on existing or potential major use for water supply. Many rivers and larger streams have unconsolidated alluvial and glacial outwash deposits yielding sufficient water to supply municipalities and industries. Sandstone and carbonate rock aquifers typically yield less water but sometimes support smaller public systems when unconsolidated aquifers are absent.

New York pays special attention to unconsolidated aquifers due to the large dependence on them and their greater vulnerability than deeper confined aquifers (NYS DOH, 1999). They may not be the most vulnerable type. A USGS review of sampling in the Middle Atlantic region found carbonate aquifers to have the highest rate of pesticide residue detections of any aquifer type, attributing this to both land use above them and the effect of solution cavities on transit time between land surface and aquifer (Ator and Ferrari, 1997). Some New York communities have used carbonate sources. Deeper non-carbonate aquifers such as sandstone should receive a lower selection priority than carbonate and unconsolidated types.

The NYS Health Department tracks population served and source types for public supply systems. Beyond public systems, it is a conservative assumption that persons not served by a public supply system use private wells. (An exception is that households along larger lakes tap those lakes.) Notable areas of high spatial density of ground water use include Rockland, Orange, Dutchess, Putnam, and Westchester Counties in southeastern NY, and Broome, Cortland, Chemung, Cortland, Monroe, Saratoga and Onondaga counties farther upstate. Monroe and Onondaga Counties stand out even more when considering that large numbers of their residents use Lake Ontario and Finger Lakes sources.

Pesticide Use
Other factors equal, a greater amount of a given active ingredient applied per unit area of total land above an aquifer will lead to higher residue concentrations in the aquifer. Thus it would be helpful to estimate pesticide use rates over the aquifers to help set priorities. (Usage near wells becomes important when selecting individual wells to sample within an area.) As in the Cortland County geographic assessment, there are two sources of data to utilize, the State Pesticide Sales and Usage Reporting (PSUR) database and land use data.

One part of the PSUR database covers pesticides applied by commercial applicators; farm owners who apply pesticides themselves are required to keep records but not to report routinely. Thus the "use" PSUR data provide a lower bound of usage in agricultural areas. A second type of records in PSUR are "sales" records. These do include sales to farm owners who do not report use but the only tracking available is the probable zip code of use. While imperfect, the combination of sales and use records in the PSUR database is the best available indicator of pesticides used in an area.

A consideration is that the PSUR database began in 1997. Ground water reflects pesticide use and transport over a years-to-decades time scale. (In eastern Suffolk County the aquifers contain significant residues of pesticides last used before 1980.)

Annual PSUR reports have mapped solid and liquid pesticide application and sales by county, separately for solid and liquid types. Because different forms of the same pesticide have different active ingredient (AI) concentrations, for use in exposure assessment the PSUR data were re-expressed as AI applied per unit area. PMEP's Product Ingredient Management System (PIMS) provides weight percentages of each AI in each registered or discontinued product.

For liquid pesticides, it is necessary to convert the liquid volume to a weight before applying the AI weight concentrations. PMEP provided preliminary data about specific gravities (or densities) for the majority of the liquid formulations of interest.

To get a closer spatial match between pesticide application and ground water use, year 2001 5-digit zip-code level data were used instead of county data. Besides this variant from the maps published by PMEP and DEC, the following additional refinements were done:

- conversion of product liquid volumes to weights
- conversion of product weights to active ingredient weights
- coverage of only "restricted use" pesticides.

All of the caveats about data quality and completeness mentioned in the 2001 annual report (NYS DEC, 2003) apply to these interpretations, as well as additional caveats from working with finer spatial detail and non-authoritative liquid densities.

E.2. GIS Procedures

Presented here are the stepwise GIS procedures used and resulting GIS maps. Note that the objective is to rapidly identify large potentially higher exposure areas, such as single counties or small clusters of counties, for sampling. Some of the input data are weak in values or spatial locations, but averaging and grouping to the county level compensate for most of the limitations.

Population dependence on groundwater

Public systems

USEPA's Safe Drinking Water Information System (SDWIS) provides water supply source (ground water, surface water, purchased ground water, etc), population served, and mailing zip code, for each regulated water supply system. Besides the obvious community systems, restaurants, institutions, fairgrounds, and other group water users are covered. Populations served by ground water (excluding ground water under the influence of surface water) were summed for each zip code. This table was then joined to the *ZCTA (Zip Code Tabulation Area) Boundary* map. Population dependent on groundwater was normalized by the area of each ZCTA to yield the *Population Dependent on Public Groundwater* per km^2, as shown in Figure E.1 (top).

Individual Households

The 1990 U.S. Census tabulated households by water source per municipality, including individual wells as a source. (The 2000 Census would have been used had it included this variable.) Household counts were multiplied by 4 persons/household to have the same units as the public supply data, and this estimated population served by individual wells was summed by municipality. This table was then joined to a *Municipality* map. Analogously to pesticide application data, population dependent on groundwater was divided by the area of each municipality to yield the *Population Dependent on Private Groundwater* per km^2, as shown in Figure E.1 (bottom).

Combining public and household systems

The populations dependent on groundwater were summed when the *ZCTA Boundary* and *Municipality* maps were combined. ArcMap was used to overlay the two maps which are based on different polygons. Essentially, to get a zip code value for household well users, ArcMap determined which municipal polygons fall into the zip code polygon and formed an area-weighted mean of the household values. Then the derived zip code map was added to the public system zip code map to yield the *Combined Population Dependent on Groundwater* map (Figure E.2).

Pesticides Applied

Sales and Commercial Use

For commercial applications of restricted use pesticides, kilograms of active ingredient(s) were summed by zip code. This table was joined to the *ZCTA Boundary* map. Pesticide use sums were normalized by the total area of each ZCTA to yield commercial pesticide use per km^2, as shown in Figure E.3 (top) *Commercial Pesticide Use*.

For pesticides not applied by commercial applicators, direct usage statistics were not available, so sales data of restricted use pesticides were used. It was assumed that the pesticides sold would be applied in the same year and within the same zip code area as the sale. Again, kilograms of active ingredient(s) were summed by zip code then joined to the *ZCTA Boundary* map. Pesticide use was normalized by the area of each ZCTA to get *Pesticide Sales* per km^2, displayed as Figure E.3 (bottom).

When working at a zip code level, there will be urban locations where a single business reports a large use of a single pesticide within a zip code area that does not occupy much land. There is one zip code in the Cortland area where reported use of one pesticide, probably all indoors at a single business, inflates the zip code's aggregate kilograms/square kilometer value far beyond a value that is reasonable when considering ground water. Future refinements of these maps will adjust for such outliers.

Land Use

A separate method of estimating pesticide usage was to use land cover information. From the National Land Cover Database map, the percentage of agricultural and residential land in each ZCTA was calculated and joined to the *ZCTA Boundary* map. This statistic was represented as *Likelihood of Pesticide Use* for each zip code, Figure E.4.

Combining commercial use, private sales, and land use

The commercial pesticide use per km^2 and pesticide sales per km^2 were summed for each zip code. This number was then divided by the area of land likely to involve pesticide use based on land use (Figure E.4) to yield the combined pesticide use per km^2 in the combined *Restricted Use Pesticide Applied* map (Figure E.5).

Finding Relative Potential Exposure Areas

Combining Combined Population Served and Combined Pesticide Use maps

For each ZCTA, population dependent on groundwater per km^2 was multiplied by combined pesticide use (lbs) per km^2 to find the value called "Relative Potential Exposure" per km^2. This combined result was an intermediate ZCTA map, not shown.

The two maps were multiplied since both persons using ground water and pesticide application are required for there to be an exposure; if either is absent there is no current concern. (There could be a future concern, if population density increases significantly. In this case the pesticide use map could be used without combining with population dependence.)

By itself, the map is misleading since it gives an illusion of spatial precision by using zip code polygons, the smallest polygons in any of the underlying data.

Selecting vulnerable aquifers

Carbonate-rock and unconsolidated surficial aquifers were singled out as especially vulnerable in this study. Carbonate-rock aquifers were taken from the USGS 2002 Aquifers of Alluvial and Glacial Origin map and combined with a Surficial Aquifers map to obtain the targeted aquifers in New York. The selected aquifers were buffered by 1 km to account for runoff (with pesticide loads) being able to travel laterally – this resulted in the vulnerable *Carbonate and Surficial Aquifers* map, Figure E.6.

Eliminating land not over vulnerable aquifers

The *Relative Potential Exposure by ZCTA* map was clipped by the vulnerable *Carbonate and Surficial Aquifers* map and then integrated (Union function) with the County Boundaries map, creating many small polygons. The area was calculated for each of the polygons, then a Relative Potential Exposure value derived by multiplying the area by Relative Potential Exposure per km^2.

As noted previously, the refinement developed this year involved evaluating the data at the zip-code level rather than forcing a final summarization at the county level, thus avoiding data blurring when averaging results across an entire county.

E.3. Exposure assessment results

Figure 2.4.1 shows the result of overlaying GIS maps of pesticide use (normalized by land use, thus reflecting a pesticide use intensity) and vulnerable aquifers.

Any zip code regions in the figure denoted with “outlier” reflect the case where a single active ingredient accounted for over 70% of the total pesticide weight reported for that zip code and where there are at least nine other active ingredients reported in that zip code. This reflects a situation where a single highly intensive use such as industrial wood preservative use tends to skew results for the entire zip code.

The results in Figure E.7 show that the band of reported use spanning across the intensive agricultural areas of central and western NY counties south of Lake Ontario is particularly significant, as are clusters of intensive use areas in the Southeast of the state. Based on these observations, we targeted both regions for the Year 3 and 4 efforts, resulting in work in Orange County in the Southeast and Cayuga County in the lake plain.

Figure E.1. Population dependence on public (top) and private (bottom) groundwater supplies.

Figure E.2. Combined population dependence on public and private groundwater supplies.

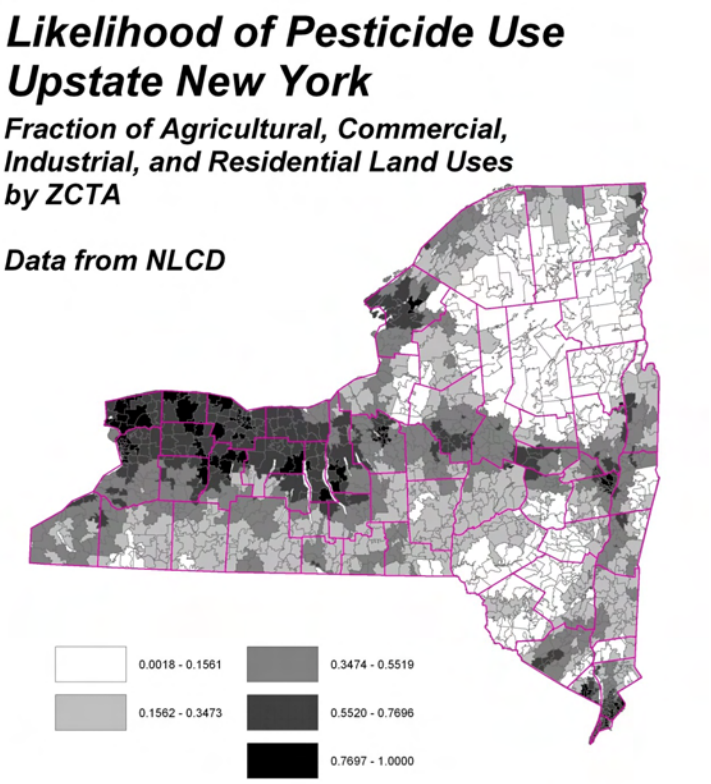

Figure E.4. Likelihood of pesticide use based on land use.

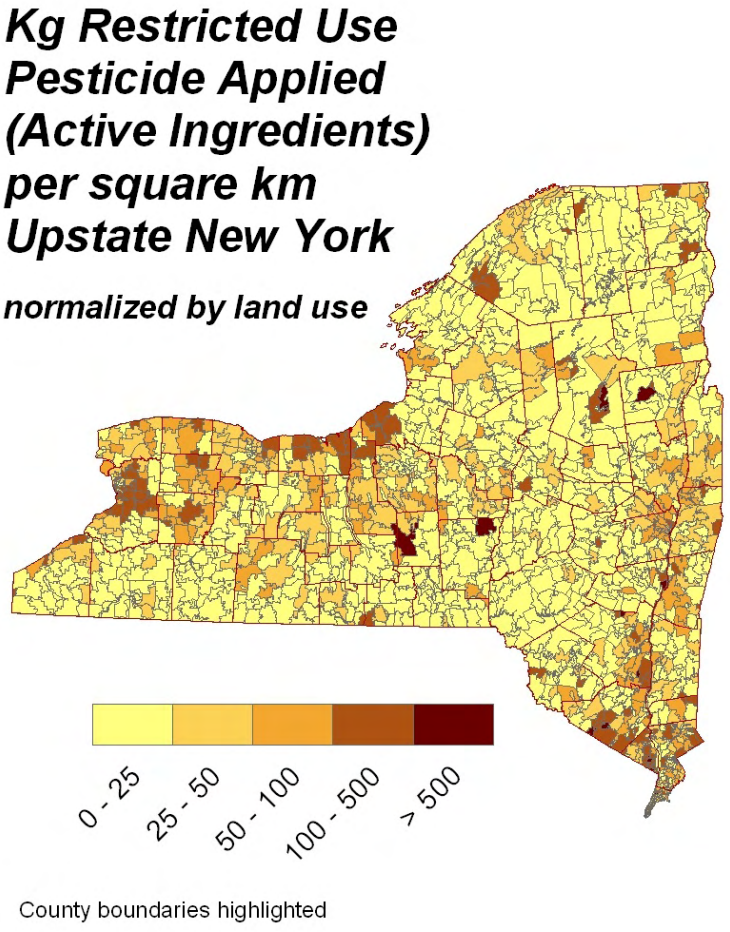

Figure E.5. Pesticide applications (restricted use active ingredients) normalized by land use.

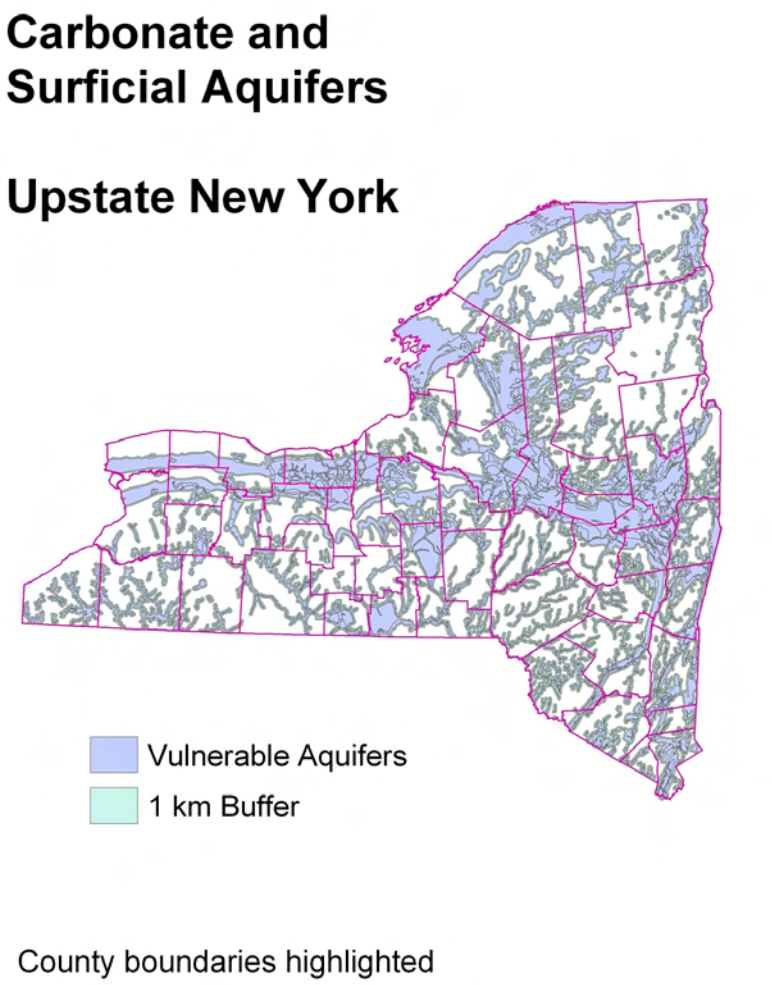

Figure E.6. Carbonate rock and surficial aquifers, including 1 km buffer zone.

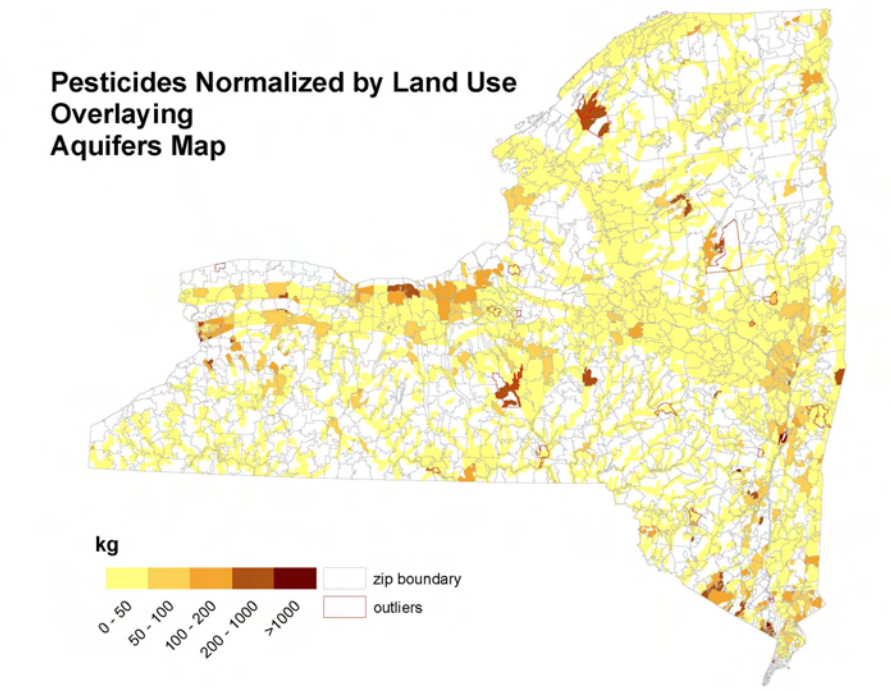

Figure E.7. Overlay of normalized pesticide use and vulnerable aquifers.