Surveying Upstate NY Well Water for Pesticide Contamination: Cayuga and Orange Counties

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Abstract

Private wells in Cayuga and Orange counties in New York were sampled to determine the occurrence of pesticide contamination of groundwater in areas where significant pesticide use coincides with shallow or otherwise vulnerable groundwater. Well selection was based on local groundwater knowledge, risk modeling, aerial photo assessments and pesticide application database mapping. Single timepoint samples from 40 wells in each county were subjected to 93-compound chromatographic scans. All samples were nondetects (reporting limits ≤1 μg/L), thus no wells from either county exceeded any of 15 state groundwater standards or guidance values. More sensitive ELISA immunoassays found two wells with quantifiable atrazine in each county (0.1-0.3 μg/L), one well with quantifiable diazinon (0.1 μg/L) in Orange County, and one well with quantifiable alachlor (0.2 μg/L) in Cayuga County. Trace detections (<0.1 μg/L) in Cayuga County included atrazine (5 wells), metolachlor (6 wells) and alachlor (1 well), including 3 wells with multiple detections. All 12 Cayuga County wells with ELISA detections had either corn/grain or corn/forage rotations as primary surrounding land uses (although 20 other wells with the same land uses had no detections) and all quantified detections and most trace detections occurred in wells up to 9 m deep. Orange County trace (<0.1 μg/L) ELISA detections (atrazine 3 wells, diazinon 1 well, and metolachlor 5 wells) and quantified detections were only generally associated with agricultural land uses. Finding acceptable groundwater quality in vulnerable areas suggests that water quality in less vulnerable areas will also be good.

1. INTRODUCTION

Pesticide transport from agricultural and other sources to groundwater is a well-documented problem, occurring not only through coarse-textured soils (the rapid aldicarb contamination of Long Island aquifers (Zaki et al. 1982, Pacenka et al. 1987) being a prime example), but also through preferential flow paths in structured soils (Peranginangin et al. 2009). In view of typical application rates and water recharge rates, allowable contaminant levels can be exceeded if even a small percentage of surface-applied pesticides find their way to groundwater (Steenhuis and Parlange 1991, Boesten 2008, Shipitalo et al. 2000). Although substantial advances have been made in vadose zone sampling (Weihermüller et al. 2007) and predictive transport modeling (Kohne et al. 2009), sources of uncertainty remain (Domange and Gregoire 2006) and targeted groundwater monitoring is essential to determine whether pesticide registration policies and application practices are sufficiently protecting groundwater resources.

Walker and Porter (1990) noted that most studies to date in upstate New York (NY) dealt with spills or other accidental discharges, and they surveyed 29 sites within primary and principal upstate NY aquifers, targeting areas where significant use coincided with vulnerable soils. Samples from wells and shallow piezometers on or near pesticide use sites were tested for 8 pesticides based on mobility, persistence and analytical capabilities. The only site tested in Cayuga County had questionable detection (circa 1 μg/L) of alachlor, with no other analytes detected at 1 to 10 μg/L). No sites were tested in Orange County.

In 1999, Eckhardt et al. (2001) surveyed 32 community water supply wells in western and central NY deemed relatively vulnerable by virtue of depth (23-100 ft plus 2 springs) and aquifer type (sand/gravel, plus one karst) Of the 60 pesticides tested, the most frequent detections were atrazine, metolachlor and their metabolites, with correlations noted to surrounding land uses. All detections were at least one order of magnitude lower than relevant limits or advisory levels. The study of Phillips et al. (1998) examined surface water concentrations at 64 sites in New York under predominantly low flow (base flow) conditions and detected 25 of 47 compounds being tested. Detections occurred in agricultural, urban and mixed land-use areas, and correlated with land uses. The most ubiquitous detections were herbicides including atrazine (detected at 97% of sites), metolachlor (89% of sites), deethylatrazine (88% of sites), simazine (72% of sites) and alachlor (50% of sites), in most cases at low levels between method detection limits (ranging from 1 to 20 ng/L) and 1 μg/L. The most frequently detected insecticides were carbaryl, diazinon, and chlorpyifos, found at 20, 14 and 11 percent of sites, respectively, at levels up to circa 0.4 μg/L.

The present study was undertaken at the behest of the NY Department of Environmental Conservation (DEC) to survey 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). Of particular interest 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.

2. APPROACH and METHODS

County Overviews

Orange County represents an area with both significant agriculture and development of housing in rural areas. Land in farms declined from 300,000 acres in 1940 to just under 100,00 acres in 1998, with levels stabilizing near 108,000 in 2003 (NYASS 2005), which represented 21% of the county's area. The county ranked 19th in NY for total agricultural sales, primarily composed of nursery/greenhouse, dairy products and vegetables. Nursery/greenhouse and vegetable receipts ranked third and sixth in the state, respectively.

Cayuga County has significant agricultural activity (including intensity of pesticide use) and widespread reliance on groundwater. Of the county's 433,600 acres, 54% was in farmland in 2003 (NYASS 2005). As of 2002, the county ranked third in NY state for total agricultural sales, with dairy products representing 62% of the total, field crops 12%, cattle and calves 8%, vegetables 6%, and other 12% (NYASS 2005). In terms of agricultural receipts, the county ranked third in the state for dairy, second for field crops and fifth for cattle and calves.

Site Selection

Program constraints dictated that a maximum of 40 well water samples be submitted for analysis by the DEC laboratory. The site selection process to identify vulnerable sites involved four components used interactively: 1) assessing local expert knowledge, 2) relative risk screening modeling based on soil type and depth to groundwater, 3) pesticide application mapping, and 4) examining landscapes and land uses using aerial imagery. Based on landowner response rates in prior projects, needed to generate 80 to100 candidate sites in order to yield the desired number of affirmative responses. Local expert knowledge assessments (primarily arising from personnel in the cooperating Cayuga County and Orange County Soil & Water Conservation Districts) were used to identify areas of likely vulnerability, based on informants' prior experience with farming patterns and other likely pesticide use, soil and aquifer characteristics, and reports of nitrate contamination or other groundwater problems.

Our development of a relative risk screening model based on the Generalized Preferential Flow Model (Steenhuis et al. 2001, 1994; Kim et al. 2005) was detailed elsewhere (Sinkevich et al. 2005). The model was implemented in a GIS using spatially-distributed estimates based on mean percolation velocity and depth to groundwater. The predicted relative concentration of a mobile model compound (atrazine) at the estimated groundwater depth was calculated for each soil type for a 3-year duration, assuming uniform application at label rates. Predicted scenario concentrations were then normalized to the greatest predicted concentration, and results were grouped into and mapped as relative risk classes. These maps thus identified areas of greater estimated transport vulnerability based on soil type and depth to groundwater.

Pesticide use mapping was based on the Pesticide Sales and Use Reporting (PSUR) database established as part of NY's pesticide reporting requirements (http://www.dec.ny.gov/chemical/27506.html) . We used publicly-available zip code level PSUR data summaries (available at http://pmep.cee.cornell.edu/psur/) for determining which regions within Cayuga and Orange Counties had the greatest intensities of "restricted use" pesticide applications. PSUR-reported data (which lists cumulative mass or volume of each commercial product) was converted to the cumulative applied mass of active ingredients (AIs) using product formulations and specific gravities. Applications of pesticides reported by commercial applicators were totaled for each active ingredient by zip code. In contrast, direct usage reports are not made for pesticides applied by farmers to their own fields, but sales of pesticides to said farmers are reported; our use of the sales data assumed that these pesticides were applied in the same year and within the same zip code area as the point of sale. The total (commercial use plus sales) was joined to a Zip Code Tabulation Area (ZCTA) boundary map, and totals were normalized by the area of each ZCTA to yield the total pesticide use per unit area (kg/km^2). To account for the varying potential for pesticides to persist and travel to groundwater, we incorporated the Groundwater Ubiquity Score (GUS) approach (Gustafson, 1989) using persistence and mobility parameters from the USDA Pesticide Properties Database (Wauchope et al. 1992; Augustijn-Beckers et al. 1994). GUS values above 2 indicate a moderate potential to persist and move to ground water, while values above 3 indicate a high potential. The amounts and GUS factors for the active ingredients with the greatest reported (for 2000-2005) sales and use in Cayuga and Orange counties are shown in Table 1.

This result was plotted using a GIS to show patterns of GUS-weighted application rates which varied significantly in the counties (Figure 1). Although there are multiple sources of potential error in this approach, including base data reporting errors, spatial ZCTA/zip code mismatch (Grubesic and Matisziw 2006), and transport of purchased pesticides between zip code areas, its application in our case was qualitative, focusing site selection attention on intensive use areas.

The fourth approach used in site selection in Cayuga County (and for *post hoc* assessments for Orange County) was the visual aerial assessment of land use and topography using integrated aerial landscape imaging available through the free Google Earth (version 4.2) software platform. This approach allows detailed "virtual flyovers" for visualizing not only agricultural and other land uses but also topography (Figure 2). The software's incorporation of a topographic elevation model in combination with the ability to change the angle of view creates virtual topography, increasing the available visual information about the juxtaposition between land use(s), landscape position and potential well sites, particularly useful for shallow wells that may be strongly influenced by local features. The ability to rotate, zoom and change the angle of view of areas of interest makes this a powerful interactive tool for locating and assessing potential sites.

Table 1. Most-applied pesticide active ingredients in Cayuga and Orange counties (ranked by mean annual use in 2000-2005) and Groundwater Ubiquity Score (GUS).

Cayuga County			Orange County		
Active ingredient	**Sales+Use (kg/yr)**	**GUS**	**Active ingredient**	**Sales+Use (kg/yr)**	**GUS**
Metolachlor	23,800	3.32	Mancozeb	26,100	1.29
Atrazine	23,300	3.56	Chlorothalonil	9,400	1.27
Glyphosate (all forms)	13,900	very low	Chlorpyrifos	8,000	0.32
Pendimethalin	13,100	0.59	Pendimethalin	6,300	0.59
Alachlor	4,700	2.08	Maneb	6,200	1.29
Mancozeb	2,600	1.29	Glyphosate (all forms)	4,900	very low
Terbufos	1,700	0.91	Dimethanamid	4,100	na
Chlorothalonil	1,500	1.27	Propachlor	3,500	na
Pentachloronitrobenzene	1,500	na	Captan	3,400	0.68
Carbofuran	1,200	4.52	Metolachlor	3,100	3.32
Tefluthrin	1,000	na	Atrazine	2,700	3.56

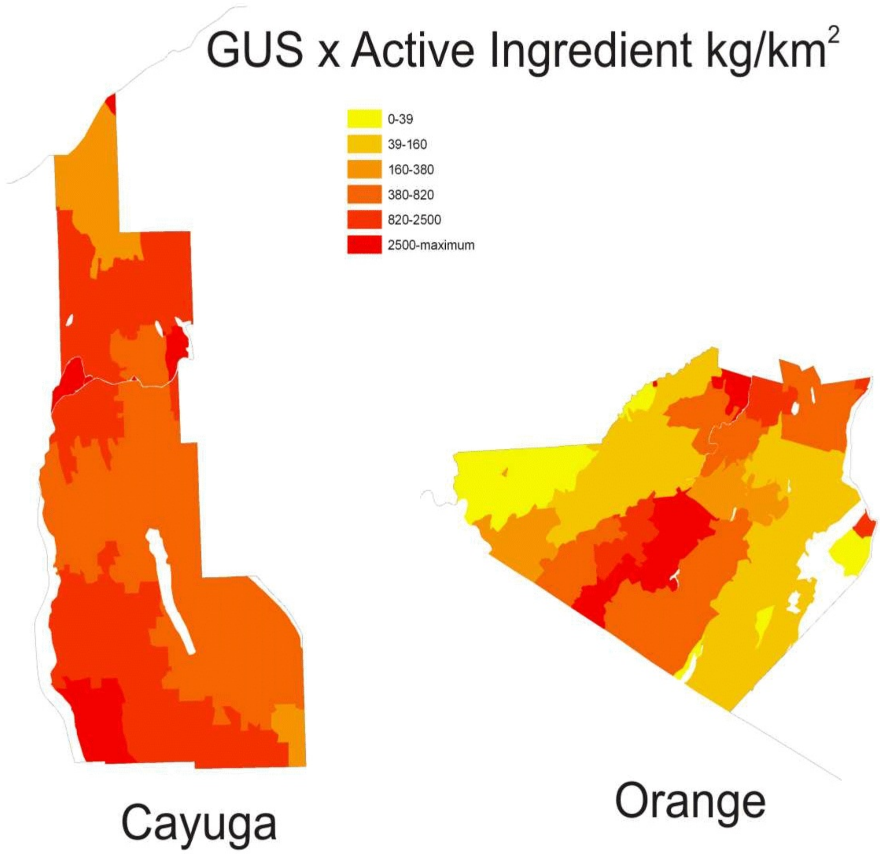

Figure 1. Total active ingredient application intensity weighted for Groundwater Ubiquity Score by zip code based on PSUR-reported sales and use (2000-2005), expressed as GUS×kg/km^2. Inset indicates locations of Cayuga and Orange Counties in New York State.

Figure 2. Example of GoogleEarth aerial imagery using location chosen at random from within Cayuga County and not representing a sampled site. Standard aerial photo image *(L)* conveys significant land use information, but altered angle of view *(R)* allows better visualization of topography in relation to farm fields, nonfarm areas, and potential well sites. Image © 2009 Tele Atlas, used in accordance with permitted terms of use.

Landowner confidentiality guidelines

Landowner cooperation was regarded as essential for gaining access to sites deemed to have elevated risk of contamination. A confidentiality/disclosure protocol was developed in concert with state agencies and the Cortland County Soil & Water Conservation District (Amanda Barber, District Manager) during earlier work (Sinkevich et al. 2005). Landowners received confidential reports for their wells, but neither they nor their well(s) are identified in any public reporting, which involves generalized but not specifically georeferenced results. Concerns regarding potential detections are addressed by retests and connecting the landowner to the local cooperating district.

Sampling and Analytical Protocols

Samples from Orange County sites were acquired from June to August 2007. Samples in Cayuga County were collected between May 2008 and January 2009, with five Cayuga County sites subsequently resampled in June 2009 based on results of initial sampling. Landowners were asked to identify taps closest to the well and preceding, if possible, any water treatment equipment such as softeners or carbon filters, and taps were allowed to run for several minutes to purge the plumbing lines. Samples were collected using precleaned polyethylene containers, chilled upon collection and frozen until analysis. Frozen samples were shipped via overnight courier to the NYS DEC laboratory.

Pesticide analysis conducted by the NYS DEC Pesticides Laboratory consisted of 93 pesticides, phenoxy acid herbicides and carbamates. All compounds except trifluralin, benfluralin, dithiopyr, chlorpyrifos were analyzed by direct injection followed by HPLC/MS-MS. The remaining four compounds were extracted using the liquid-liquid (QUECHERS) extraction technique and analyzed by Gas Chromatography/Mass Spectrometery in the Selected Ion Mode (GC/SIM-MS). Reporting levels (which were the lowest calibrant concentration on each calibration curve) were 1µg/L for all compounds except dicamba, diazinon, MCPA, and the sum of aldicarb and methomyl, which had detection limits of 0.44 ppb, 0.7 ppb, 0.44 ppb, and 0.35 ppb respectively.

Water samples were analyzed at Cornell University using enzyme-linked immunosorbent assays (ELISA) kits for atrazine, metolachlor, alachlor (Cayuga County only), and diazinon (Orange County only). Kit selection was based on likelihood of detection (based on reported use and GUS score) as well as availability. ELISA magnetic particle kits (Strategic Diagnostics Inc; SDIX) for atrazine (kit # A00071), alachlor (A00072) and metolachlor (A00080) had quantitation ranges of 0.1 to 5 µg/L and trace (nonquantifiable) detection limits of 0.05 µg/L. The diazinon 96-well plate kit (SDIX Envirogard Kit No. 7270000) had a quantitation range of 0.03-0.5 µg/L and a trace detection level of 0.022 µg/L. Assays were analyzed on duplicate samples via spectrophotometer, and analyte responses greater than the method detection limit (MDL) but less than the minimum limit of quantitation were reported as nonquantifiable trace detections. Nitrate content was analyzed at Cornell via ion chromatography (Dionex ICS-2000) and reported as NO_3-N. Additional details including matrix spike recoveries and potential ELISA cross-reactivities are summarized in annual project reports available at the following URL: http://soilandwater.bee.cornell.edu/research/pesticides/index.html.

3. RESULTS

Site and Well Characterization

Table 2 presents the sampled well information, including well use, type, and depth. For Cayuga County, most wells sampled (34) served single households, with 4 serving barns and 2 listed as utility (garage/shop etc.). Of the 37 wells for which the depths were known by landowners, 11 were shallow (up to 9 m) with two additional spring-fed, 14 were between 9 and 30 m deep, and 10 wells exceeded 30 m. Of the dug wells, two were artesian, as was one driven well, with two of these artesian wells were classified as flowing. Orange County wells sampled were split between single houses (23), with 17 serving barns or other agricultural uses. Of the 24 wells for which depths were known, one was <9m, six were 9 – 30 m deep, and 17 were deeper than 30 m. Land uses were visually characterized during sampling visits as well via aerial viewing during site selection and/or subsequent rechecks. The prioritized land uses (Table 3) for surrounding and upslope areas were judged to be more likely (though by no means certain, depending on the complexity of the underlying strata) to serve as potential contributing areas to each well, particularly for shallow wells. Land uses were qualitatively ranked as primary (i.e. most extensive; dominating general and upslope areas), and, if other uses were 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.

Widespread agriculture in Cayuga County (particularly in areas not served by public water supplies) is reflected in agriculture as the primary land use category for 39 wells (Table 3), primarily corn/soybean/small grains or corn/forage rotations. The most prevalent secondary land use (17 wells) was woods as scattered woodlots or wooded hillslopes on steeper drumlins. In a number of cases there were no secondary (14 sites) and/or tertiary (22 sites) land use assigned, indicating the predominance of the primary land use. Scattered or more distant woods were the most common tertiary assignment (14 cases), and other uses were little represented.

In Orange County agriculture also dominated primary land uses, but with a broader distribution of types, with dairy corn/forage rotation around 12 wells, hay/pasture around 8 wells, and muckland (locally known as black dirt) farms near 7 wells. These agricultural land uses also represented secondary land uses at 8 sites and tertiary land uses at 11 sites (most notably 7 muck farm sites). Managed turfgrass, either as lawns in suburban or localized clusters of housing, or as other turf areas, was the primary land use for 7 wells, secondary for 4 wells and tertiary for 7 wells. In many cases these represented recent subdivisions interspersed in otherwise rural areas. Small municipalities upslope from sampled wells 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 other but less extensive land uses), secondary for 21 sites, and tertiary for 4 sites. "Other" land uses (4 sites) represented single occurrences of the proximity of a major highway right-of-way, a utility right-of-way, a greenhouse operation and a vineyard. Mixed land uses represented closely integrated multiple land uses at 3 sites.

Well water analysis

Pesticide scans by NYS DEC found that all analytes were below reporting limits for all samples from both counties, as summarized in Table 4. ELISA scans conducted for atrazine, diazinon and metolachlor for Cayuga County samples two quantifiable detections (0.21 to 0.26 µg/L) of atrazine, and one (0.18 µg/L) of alachlor, all at levels well below the 1.0 µg/L reporting limits of the corresponding DEC scans. In addition, there were twelve nonquantifiable trace detections (analyte responses between the 0.05 µg/L MDL and the 0.1 µg/L minimum limit of quantitation): five of atrazine, one alachlor and six metolachlor. Of the twelve wells that had ELISA detections, there were three cases of multiple analyte detection: alachlor and metolachlor in wells 8 and 12, and atrazine plus metolachlor in well 15. The five wells resampled in June 2009 based on previous detections or trace detections had fewer subsequent atrazine and metolachlor detections, with one quantifiable and one trace detection of atrazine (vs. two each for the original sampling) and no detections of metolachlor (alachlor not retested).

Nitrate concentrations in Cayuga County were below the 10 mg N/L drinking water standard, with an observed maximum concentration of 9.3 mgN/L. Seven sites had concentrations in excess of 5 mgN/L; of these sites, six had shallow well depths (0 to 9 m). Overall mean nitrate values were not computed given the uncertainty of 10 measurements due to interference caused by large sulfate concentrations (in some cases exceeding 500 mg SO_4/L), a known issue in the area due to dissolution of gypsum deposits. Examination of individual chromatograms of 10-fold dilutions indicated that sulfate was not masking any nitrate values exceeding 1 mg N/L, and thus high sulfate samples were reported as <1 mg/L nitrate-N. Nitrate testing of June 2009 resamples yielded slightly lower results.

ELISA scans of Orange County samples for atrazine, diazinon and metolachlor indicated only three quantifiable detections (Table 6), again all at levels well below the reporting limits of the corresponding DEC scans. There were nine trace detections, and there was no overlap among detections or trace detections for any given well. Mean nitrate concentrations were 0.7 ± 1.1 mg N/L (assuming a detection limit value of 0.1 for the thirteen nondetects), with the observed maximum of 5.6 mg/L. Only six values exceeded 1 mg/L, and only one of these occurred in a well with a trace ELISA detection.

Table 2. Number of sampled wells by well use, classes of reported well depth, and well construction type.

Use	Cayuga	Orange	**Depth**	Cayuga	Orange	**Type**	Cayuga	Orange
			Spring (0 m)	2	0	Drilled	23	28
House	34	23	Up to 9 m	11	1	Driven	3	7
Barn	4	17	9-30 m	14	6	Dug	9	3
Utility	2	0	>30 m	10	17	Spring	2	2
			Unknown	3	16	Unknown	3	0

Table 3. Numbers of wells classified by primary (1°), secondary (2°) and tertiary (3°) surrounding land uses.

Category	**CAYUGA**			**ORANGE**		
	1°	**2°**	**3°**	**1°**	**2°**	**3°**
Corn/forage/grain rotation typical of dairy/cash crop farms	32	5	1	12	6	2
Hay/pasture (continuous, no apparent rotation to field crops)	2	0	0	8	1	2
Wooded	0	17	14	4	21	4
Turf/lawns, managed turfgrass	0	1	0	7	4	7
Muck soil (black dirt, organic soil) vegetable row crops	1	1	1	7	1	7
Other crops or likely pesticide applied-areas (rights-of-way)	4	0	1	1	1	2
Urban areas with higher density housing or other urban land uses	0	0	0	0	1	1
Mixed use too tightly integrated to delineate into categories	1	1	0	1	1	1
Scrub/regrowth, typically abandoned farmland	0	1	1	0	1	0
No secondary/ tertiary land use sufficiently extensive/close to site	-	14	22	-	3	14

Table 4. Results of analyses run by the NYS DEC laboratory for both Orange and Cayuga Counties. *ND* indicates non-detects, indicating results were less than the specified method reporting limit. Numbers in brackets represent current NY groundwater standards or guidance values (µg/L)

Analyte	**Conc. (µg/L)**	**Analyte**	**Conc. (µg/L)**
2,4-D **[50]**	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 **[0.35]**	ND < 0.35	Malathion **[7]**	ND < 1
Aldicarb Sulfone **[2]**	ND < 1	MCPA **[0.44]**	ND < 0.44
Aldicarb Sulfoxide **[4]**	ND < 1	MCPP	ND < 1
Amidosulfuron	ND < 1	Metalaxyl	ND < 1
Atrazine **[7.5 / 3*]**	ND < 1	Metamitron	ND < 1
Azinphos Methyl **[4.4]**	ND < 1	Methamidophos	ND < 1
Azoxystrobin	ND < 1	Methiocarb	ND < 1
Bendiocarb	ND < 1	Metolachlor **[9]**	ND < 1
Benfluralin	ND < 1	Metsulfuron-Methyl	ND < 1
Butocarboxim	ND < 1	Monocrotophos	ND < 1
Butoxycarboxim	ND < 1	Nicosulfuron (Accent)	ND < 1
Carbaryl **[29]**	ND < 1	Omethoate	ND < 1
Carbendazim	ND < 1	Oxamyl **[50]**	ND < 1
Carbofuran **[15]**	ND < 1	Oxydemeton-Methyl	ND < 1
Chlorosulfuron	ND < 1	Pendimethalin	ND < 1
Chlorpyrifos	ND < 1	Primicarb	ND < 1
Cinosulfuron	ND < 1	Promecarb	ND < 1
Clethodim	ND < 1	Propamocarb	ND < 1
Clopyralid	ND < 1	Propoxur	ND < 1
Cyprodinil	ND < 1	Prosulfuron	ND < 1
Daminozid	ND < 1	Pymetrozine	ND < 1
DCPP	ND < 1	Pyridate	ND < 1
Demeton-S-Methyl Sulfone	ND < 1	Pyrimethanil	ND < 1
Diazinon **[0.7]**	ND < 0.7	Quinmorac	ND < 1
Dicamba **[0.44]**	ND < 0.44	Quizalofop Ethyl	ND < 1
Dimethoate	ND < 1	Rimsulfuron	ND < 1
Dithiopyr	ND < 1	Spiroxamine	ND < 1
Diuron	ND < 1	Tebuconazole (Folicur)	ND < 1
Ethiofencarb	ND < 1	Tebufenozide	ND < 1
Ethiofencarb-sulfone	ND < 1	Thiacloprid	ND < 1
Ethiofencarb-sulfoxide	ND < 1	Thifensulfuron-Methyl	ND < 1
Fenhexamid	ND < 1	Thiodicarb	ND < 1
Fenoxycarb	ND < 1	Thiofanox-sulfone	ND < 1
Fenpropimorph	ND < 1	Thiofanox-sulfoxide	ND < 1
Flazasulfuron	ND < 1	Triadimefon	ND < 1
Fluazifop-p-butyl	ND < 1	Triasulfuron	ND < 1
Flufenoxuron	ND < 1	Trichlorfon	ND < 1
Furathiocarb	ND < 1	Triclopyr	ND < 1
Halofenozide	ND < 1	Trifluralin **[35]**	ND < 1
Haloxyfop Ethoxyethyl	ND < 1	Triflusulfuron-Methyl	ND < 1
Haloxyfop Methyl	ND < 1	Vamidothion	ND < 1

* atrazine guidance value of 3 for surface waters used for human consumption

Table 5. Cayuga County well characteristics and analytical results for wells with ELISA detections. ELISA values of "tr<0.1" indicates trace detection; "nd" indicates not detected. Values in parentheses represent subsequent resampling results.

Well characteristics*			Land use**			NO_3-N	ELISA detections (µg/L)		
No.	Depth (m)	Type	1°	2°	3°	(mg/L)	Atrazine	Alachlor	Metolachlor
7	26	D	**C**	-	**W**	<0.1	nd	nd	tr <0.1
8	3.6	G	**C**	**W**	-	5.6	nd	0.18	tr <0.1
10	26	D	**C**	**C**	**W**	<1	nd	nd	tr <0.1
11	22	D	**C**	**C**	**W**	<1	nd	nd	tr <0.1
12	8	G	**C**	**W**	-	3.7 (3)	nd (nd)	tr <0.1	tr <0.1 (nd)
15	11	D	**C**	-	-	4.4	tr <0.1	nd	tr <0.1
24	4.6	D	**C**	**W**	-	5.3 (3)	0.21 (0.12)	nd	nd (nd)
25	9	G	**C**	**W**	-	9.3 (9)	0.26 (tr<0.1)	nd	nd (nd)
26	shallow	G-A	**C**	**W**	-	8.2	tr <0.1	nd	nd
30	0	S	**C**	**W**	-	5.5 (4)	tr <0.1 (nd)	nd	nd (nd)
33	0	S	**C**	-	**W**	4.7	tr <0.1	nd	nd
37	6	G	**C**	-	**W**	3.3 (2)	tr <0.1 (nd)	nd	nd (nd)

*Well type key: *D* - drilled, *G* - dug, *S* - spring; *-A* suffix indicates artesian well.
**Land use key: *C* - corn/cash crop or corn/forage rotation; *W* - wooded.

Table 6. Orange County well characteristics, land use, ELISA analysis and nitrate-N results for wells with ELISA detections. ELISA values of "tr<0.1" indicates trace detection; "nd" indicates not detected.

Well characteristics*			Land use**			NO_3-N	ELISA detections (µg/L)		
No.	Depth (m)	Type	1°	2°	3°	(mg/L)	Atrazine	Diazinon	Metolachlor
11	na	R	T	W	C	<0.1	nd	nd	tr <0.1
13	46	R	C	W		<0.1	tr <0.1	nd	nd
16	51	D	C	M		<0.1	nd	nd	tr <0.1
17	na	G	O	W	H	0.71	nd	nd	tr <0.1
18	67	D	H	R	M	<0.1	nd	nd	tr <0.1
20	na	S	C	W	O	0.7	nd	nd	tr <0.1
25	na	D	H	W		0.3	tr <0.1	nd	nd
30	na	G	H	C	W	1.1	0.14	nd	nd
31	na	D	T	C	M	<0.1	0.27	nd	nd
32	<30	R	M	W	T	2.3	tr <0.1	nd	nd
35	na	D	W	H	T	0.3	nd	0.07	nd
40	49	R	C	W	O	<0.1	nd	tr <0.03	nd

*Well type key: *D* - drilled, *R* - driven, *G* - dug, *S* - spring; "na" indicates well depth unknown.
**Land use key: *C* - corn/cash crop or corn/forage rotation, *H* - hay/pasture/small grain, *M* - muckland vegetables, *O* - other, *R* - scrub/regrowth, *T* - turf or suburban landscape, *W* - wooded.

4. **DISCUSSION**

Comparison with NY groundwater standards

As shown in Table 4, the reporting limits for the scans run in the DEC laboratory were adequate to determine that nosamples were in exceedence of the fifteen Class GA ambient groundwater standards or guidance values currently promulgated for NY (NYS DEC 1998; updated with a more recent metolachlor standard). The detections and trace detections via more sensitive ELISA procedures all occurred at levels below the limits of the DEC scans and were thus similarly lower than all standards and guidance values.

Land use and ELISA detections

In Cayuga County, all 12 wells with trace or quantifiable detections had corn/cash crop or corn/forage rotation as the primary land use. However, this land use was not predictive of detections: there were no detections or trace detections for 20 other wells with the same primary land use. The limited resampling of five wells in June 2009 resulted fewer quantifiable and trace detections for atrazine and metolachlor; DEC laboratory scan results for these resampled wells again indicated nondetects for all analytes.

Given the siting priority that avoided areas with municipal water supply, agriculture in Orange County also dominated primary land uses near sampled wells, although it was more diverse than in Cayuga County. This greater complexity resulted in no clear association of any single primary land use category with trace or quantifiable detections in Orange County. In the heavily-applied muckland areas (evident as intensive application areas in the southwest of Orange County in Figure 1) there was only one trace detection where muck was the primary land use, one where it was secondary, and one quantifiable and one trace detection where it was the tertiary use. This is not surprising given that organic soils have, by definition, extremely pesticide complexation capacities. If all agricultural uses (cropped, muckland, hay/pasture) are lumped in an overall "agricultural" category, that larger category is the primary land use for 4 of 5 atrazine detections, 3 of 5 metolachlor detections, and 1 of 2 diazinon detections. However, given disparate pesticide use patterns and conditions among these various uses, this categorization is weak. No other land uses had any association with detections in Orange County. It is important to note that land use associations also imply localized (and recent) landscape contribution to groundwater present in wells, which may not be a tenable assumption given the greater well depths and greater geomorphic complexity of the Orange County landscape.

Well depths, nitrate levels and ELISA detections

Detections in Cayuga County were strongly associated with shallow well depths: all three quantifiable detections and 9 of 12 nine trace detections occurred in wells with depths up to 9 m (the remaining three wells with trace detections had depths of 22 to 26 m). In fact, of the 13 wells with known depths up to 9 m, eight had ELISA detections or trace detections. While all nitrate-N concentrations were below the 10 mg N/L standard, seven wells had concentrations in excess of 5 mgN/L; of these sites, six had shallow well depths (<9m), with the seventh having a depth of 27 m.

Of the 12 wells with ELISA detections in Orange County, only five had depths reported by landowners, and none were reported as shallow aside from one reported as "<30m" and the fact that two of the "unknown depth" wells were reported as having been dug and thus of limited depth. As such, no links between detections and well depths were attempted aside from observing that one of three quantified detections occurred in a dug well of unknown but presumably shallow depth. There appeared to be no interaction among quantifiable or trace detections (i.e. no multiple detections in any single well) nor with nitrate: of the 6 wells with nitrate-N >1 mg/L, only one well had a trace or quantifiable ELISA detection.

PSUR records and pesticide detections

It is of interest that the two counties with markedly different pesticide application portfolios (Table 1) had similar rates of detection for ELISA atrazine and metolachlor tests (the only tests run in common for both counties) as well as similar nondetections for the broad 93-compound scans. As can be seen in Table 1, field crop herbicides (atrazine and metolachlor, both with elevated GUS scores over 3) predominated in Cayuga County, while atrazine and metolachlor ranked only tenth and eleventh in Orange County and at circa one eighth the total mass applied as compared to Cayuga County. Somewhat counterbalancing this is the fact that pesticide applications inferred from PSUR data in Orange County tended to be more regionally concentrated (Figure 1) as opposed to somewhat more evenly distributed in Cayuga County, although the spatial resolution of the data at the ZCTA level is poor. In any case, comparisons of results from the two counties are complicated by several factors, the most significant being that the study was not targeted at providing a statistical snapshot of a given county but rather selecting and assessing groundwater quality at the most vulnerable sites, which may or may not reflect "average" county conditions. Surrounding land uses among sampled wells in Cayuga County tended to be more uniform, and wells tended to be shallower and presumably more reflective of nearby land uses. In contrast, greater diversity of land uses in Orange County coupled with greater well depths (Table 2) and complexity of the Orange County landscape make land use/well concentration correlations (and comparisons based thereon) tenuous at best. Given the low (in statistical terms) number of samples per county, the fact that detection patterns appeared similar may be coincidental or may suggest that we identified and samples areas of comparable vulnerability. In any case, but the more important conclusion is that no exceedences of current water quality standards or guidance levels were found for any active ingredient in either county.

Application and ongoing work

The approach used in this study represents a flexible model for assessment of potentially vulnerable areas. The combination of multiple approaches to candidate site selection integrates publicly-available data (PSUR data indicating compounds applied and as a means for estimating application intensity; simple soil survey inputs for relative risk modeling) and resources (local knowledge/assessments; online aerial photo tools). Robust landowner confidentiality protocols help secure participation from farmers and others in application areas who are the most likely to be affected by any groundwater contamination. Even if the valuable broad analyte scans such as those carried out by the NYS DEC laboratory are not available, ELISA immunoassay kits make reliable and sensitive analyses possible in even rudimentary laboratories for a modest investment (albeit restricted to kits available for a limited number of active ingredients).

Finding that groundwater quality meets current standards in areas judged vulnerable due to application intensity and groundwater characteristics provides strong evidence that water quality in less vulnerable areas is similarly being protected by existing label restrictions and application practices. Ongoing work in NY includes sampling in especially vulnerable karst-dominated areas with rapid surface-to-groundwater interaction, and continuing surveys with improved analytical arrays that include pesticide degradation products (which may have greater mobility than applied compounds) and with more sensitive detection limits.

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