

Surveying Upstate NY Well Water for Pesticide Contamination

Year 1 Final Report

to the

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EXECUTIVE SUMMARY

NYS DEC contracted with Cornell University to begin 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 at present are “worst case” areas of 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 first year of work documented here was a pilot-scale program in Cortland County shallow aquifer system, chosen in view of the range of land uses, a well-established groundwater program in place in the watershed, and proximity to Cornell University. The Cortland County Soil & Water Conservation District (CCSWCD) actively cooperated in this undertaking. Additional components presented here are: a GIS-based model to determine which areas in a landscape are at the greatest relative risk of pesticide contamination based on land use and geomorphic features; a similar statewide assessment reported on a county-by-county basis; and an assessment of the utility of the New York Pesticide Sales and Use Reporting (PSUR) database for targeting areas of potential vulnerability to pesticide contamination.

Cortland County sampling results Initial well selection was based on the expertise of CCSWCD personnel, based on their judgements of soil and aquifer conditions and patterns of likely or known pesticide use. Likely areas scouted visually, looking for land use and topographic patterns that would suggest well water vulnerability. The rate of affirmative response was low, primarily attributable to difficulty in getting any type of response from landowners. Additional potential sites were scouted by Cornell personnel during sample collection trips. Recruitment and sample collection to achieve the target of 40 wells took place between June and December 2003. Most wells sampled served either single houses (19) or barns (11). Four wells supplied small businesses or light industries, and five wells were existing monitoring wells. One large municipal well was also sampled.

All wells sampled had agricultural influence, with active croplands either immediately adjacent/nearby (30 wells) or somewhat more distant (10 wells). The most common adjacent or nearby land use was corn farming (27 wells). For 13 wells the nearby land use included forage crops and/or pasture, in many cases in addition to corn. Three wells were near horticultural and/or managed turfgrass areas. Of the 10 wells where the agricultural influence was more distant, 6 had fallow (grassland/scrub) or wooded areas immediately upgradient, while 4 were in industrial areas.

Enzyme-Linked ImmunoSorbent Assays (ELISA) assay results showed that levels of atrazine (and cross-reactive triazines) were below the 0.1 µg/L limit of quantitation, a level 1/30th of the 3.0 µg/L drinking water standard. This gives a high level of certainty that atrazine and related compounds are not present at levels of concern in the wells sampled. With many of the wells sampled in close proximity to corn culture, the fact that atrazine concentrations were so low is reassuring. The unexpectedly elevated detection limits experienced by the NYS DEC laboratory – due to interference from dissolved organics typically present with shallow groundwater and to the wide range of analytes that prevented optimization for particular classes – constrained the overall results to confirming that major contamination of other pesticides was not found in the sampled wells.

Nitrate concentrations ranged up to 12.2 mg/L, with a mean of 3.7 ± 3.4 mg/L. Of the 40 wells sampled, three had levels in excess of the 10 mg/L drinking water standard, and nine had levels between 5 and 10 mg/L. All 12 wells with nitrate-N levels in excess of 5 mg/L had corn fields in

near proximity, but close proximity to corn fields was not a guarantee of elevated nitrate-N levels.

Groundwater hazard assessment model A process-based preferential flow transport model was implemented in a geographic information system (GIS) to locate areas in the landscape with elevated potential exposure to contamination by agrochemicals, especially pesticides. Protecting groundwater resources necessitates a reliable groundwater quality monitoring strategy. It is valuable to be able to focus monitoring on areas with the highest risk of contamination because monitoring groundwater is an expensive activity, especially at the landscape scale. The objective of this component was to develop a tool that quantifiably estimates distributed groundwater contamination risk in order to develop reliable, cost-effective groundwater observation networks. The tool is based on a mechanistic model of chemical movement via preferential flow and uses land cover data, information about chemical properties, and modeled recharge to estimate the concentration of chemical reaching the groundwater at each point in the landscape. The distributed assessment tool was tested by comparing the predicted relative hazard with observed concentrations from 40 sampling wells in Cortland County, New York for atrazine and nitrate, the latter assumed to be an indicator of agricultural pollution. The tool predictions agreed well with observed nitrate concentrations and pesticide detections. An internet-based version of this tool is currently being developed for ready application to New York State.

Utility of pesticide database The PSUR database was examined for Cortland County for the years 1997 to 2001. About 81% of the nearly 40,000 applicator records and 77% of the nearly 5,000 sales records were determined to be valid in terms of valid address location and EPA identification number. Between 17 and 19% of the total records present were “restricted use” pesticides of primary concern in targeting potential groundwater sampling. Of these restricted use data records, 88% were successfully geocoded, indicating that transference to and utilization in GIS-based approaches is feasible.

No significant correlations were found between PSUR application data and the pattern of trace (<0.1 µg/L) atrazine detections that occurred in 20 of 40 wells sampled. In contrast, a strong positive correlation was found between trace atrazine detections and a qualitative land use/topography risk assessment based on observed characteristics near the well and in the well’s estimated contributing area. The utility of the PSUR database for atrazine in Cortland County was limited by that fact that private (farmer-applied) atrazine use is not reported on a geo-referenceable basis, leaving the PSUR database with an incomplete picture of spatial atrazine applications. This limitation does not necessarily extend to other counties (where farmer vs. commercial applicator patterns may differ) and/or to other pesticides that may be less likely to be farmer-applied.

State-wide assessment The statewide assessment integrated publicly-available datasets to identify those areas where population dependence on groundwater from hydrologically-vulnerable systems coincided with significant pesticide use. Cortland County emerged from the statewide screening process as one of the two most counties with the greatest potential exposure, based on the screening criteria used. Schenectady was the only county with a comparable score and was selected for year 2 sampling. Refinements of the model will include incorporation of more than one year of PSUR data, focus on fewer pesticides than the entire list of restricted use products, and updated land use and water dependence data.

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.

NYS DEC, the NY State Soil & Water Conservation Committee, and other stakeholders 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 “worst case” areas of 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.

The first year of work documented here was a pilot-scale program, focused on a single shallow aquifer system in the Cortland Valley. The area was chosen in view of the range of land uses, a well-established groundwater program in place in the watershed, and proximity to Cornell University. The Cortland County Soil & Water Conservation District (CCSWCD) actively cooperated in this undertaking. Also included in the first year effort was a draft design of an upstate-wide groundwater selection protocol for pesticide residue sampling, based on the experience of the first year program.

Cornell University used a landowner confidentiality approach where public reporting of data uses a general but not specifically georeferenced basis. Landowners receive confidential reports for their wells, but are not identified in any public reporting. This measure was taken as an incentive to attract landowner cooperation.

2. PROJECT COMPONENTS

Four distinct project components are reported here. First is the approach and the results of the well sampling carried out in Cortland County. Second is the development of a simple risk assessment model developed during this first year for use in guiding within-county site selection in subsequent studies. The third component reported is an evaluation of the usefulness of the confidential “street-level” data in the statewide Pesticide Sale and Use Reporting (PSUR) database in the process of sampling site selection. The fourth and final component is the development of a GIS-based statewide assessment of relative groundwater risk carried out on a county-by-county basis.

2.1. Cortland County Well Sampling

The first year of work documented here was a pilot-scale program, focused on the shallow aquifer system in the Cortland Valley. Cortland County was chosen in view of the shallow aquifer, a range

of land uses, a well-established groundwater program in place in the watershed, and proximity to Cornell University. As will be seen in the Statewide Risk Assessment, this intuitive choice was fortuitous, with Cortland County being subsequently ranked first among NY counties as to relative potential groundwater risk. The Cortland County Soil & Water Conservation District (CCSWCD) actively cooperated in this undertaking.

2.1.1. Site selection

Funding constraints dictated that a maximum of 40 well water samples be analyzed in the DEC pesticide laboratory. Because DEC's interest was targeted sampling of the most vulnerable sites, protocols for identification of the best potential sites was important. Three approaches were initially proposed to select candidate areas in which to recruit landowner participation for well sampling: local knowledge, groundwater modeling, and use of pesticide application data in the Pesticide Sales and Use Reporting (PSUR) database. Due to time constraints, sampling for the year 1 project was entirely based in the first local knowledge approach, with the other two approaches developed for use in subsequent years.

The first approach and most productive site selection approach in Year 1 was that termed local knowledge. We took advantage of the expertise of CCSWCD personnel to identify likely sampling areas, based on their judgements of soil and aquifer conditions and patterns of likely or known pesticide use. The existence of a well-established groundwater program within the CCSWCD enhanced this level of local expertise. Also useful in the immediate Cortland area were existing USGS groundwater maps that were previously developed in response to industrial contaminant plumes in the aquifer (Miller et al. 1995). Project members met with CCSWCD personnel and identified a number of potential areas. This approach was implemented iteratively, with likely areas scouted visually, looking for land use and topographic patterns that would suggest well water vulnerability. Additional potential sites were scouted by Cornell personnel during sample collection trips.

The second proposed method of site selection was the development of a GIS-based model to rank and identify areas with a relatively elevated risk of well water contamination by pesticides. This model was developed on the ESRI ArcGIS platform using readily-available spatially-distributed data, including land use as a surrogate for pesticide applications and depth to groundwater. The model spatially distributes the relative risk of pesticides reaching the groundwater and assumes that preferential flow paths pose the most acute risk. A mechanistic equation was developed describing how water and solutes flow through soil in preferential flow paths, which have a much higher velocity than traditionally assumed, making it more likely for chemicals to move through the soil and into the underlying water. Spatially distributed elevation, soil, and land use data were used to calculate values for concentration in the groundwater. These values were then used in ArcGIS, resulting in a spatially distributed map of relative risk of pesticide contamination in four categories: negligible, low, medium, high. This was a *conditional* risk assessment model because it assumes pesticides were applied (at the label rate) in all applicable land uses and thus gives an upper bounding estimate, with the goal of determining relative risk rather than absolute concentrations. Atrazine was used due to leachability and widespread use on corn, a primary crop in Cortland County.

The time required to complete and verify the model resulted in this being used in a *post hoc* manner after sampling was completed. Model development and application are described in Section II of

this report. The model is presently being implemented to assist Year 2 site selection.

The third proposed approach attempted to use detailed data from the NYS pesticide sales and use reporting database (PSUR) in a GIS framework in order to identify areas of greatest pesticide use. While data summarized at the zip code level is generally available, access to detailed confidential data is tightly controlled by statute (Public Health Law §2411 (1) (d)). A meeting with NYS Department of Health (DOH) which controls access to data was held in Albany in November 2002 at the behest of NYSDEC. At that time it became evident that Cornell was the first entity to apply for access to the confidential data, and that the legally-mandated review process that heretofore existed only in statute had to be initiated. Formal application was made by Cornell to Dr. Nancy Kim of DOH on January 20, 2003. The application was appended with supplementary materials several times in consultation with Dr. Kim and as specified by the Health Research Science Board (HRSB) of the DOH, which has final authority to authorize release of the data. A letter dated July 22, 2003 indicated that the HRSB had approved our request for access to the data. Confidentiality agreements were executed in August 2003, and a letter from Dr. Lawrence Sturman of the HRSB (September 25, 2003) authorized NY DEC to release the data. The Pesticide Sales and Use Reporting Database Group at Cornell University received notification in early December, and final delivery of the database occurred on December 23, 2003. As noted, the process was prolonged in part by the fact that required approval mechanisms heretofore existed only in statute. Sampling in Cortland County had concluded by the time that the data was released, so the confidential database was examined in a *post hoc* manner, evaluating 1) the utility of the database and 2) whether the pattern of application correlated with observed patterns in analytical results. This evaluation is discussed in Section III of this report.

2.1.2. Landowner recruitment and confidentiality guidelines

Recruitment of landowners in selected study areas was carried out in conjunction with CCSWCD. 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 CCSWCD would be advised. The CCSWCD would notify relevant county agencies (most likely the Cortland 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 local DOH or Agricultural Environmental Management) 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.

The process of securing permission from landowners took longer than anticipated. Initially, nearly 40 possible locations for sampling were identified in this region. Candidate sites were given to the Cortland County Soil and Water Conservation District for making initial landowner contacts. The rate of affirmative response was low, primarily attributable to difficulty in getting any sort of response from landowners, in addition to approximately one-third of respondents declining participation. The first 80 sites identified for potential sampling resulted in 27 samples collected between June and September 2003. A series of monitoring wells (and homes on regular monitoring) downgradient from extensive agricultural areas were included in the October 2003 sampling, with several more home and farm wells used to complete the sampling target of 40 wells on December 12, 2003.

Table 2.1.1 presents the sampled well information, including well use, depth, surrounding land use(s) and sampling date, with a generalized summary in Table 2.1.2. Most wells sampled served either single houses (19) or barns (11). Four wells supplied small businesses or light industries, and five wells were existing monitoring wells. One large municipal well was also sampled.

All wells sampled had agricultural influence, with active croplands either immediately adjacent/nearby (30 wells) or somewhat more distant (up to 2 miles upgradient; 10 wells). The most common adjacent or nearby land use was corn farming (27 wells), in some cases surrounding sampled wells on all sides and/or coming within a 30 or fewer feet of the wellhead. (Note that due to multiple adjacent/nearby land uses in some cases, a well may be listed in more than one subcategory on the right side of Table 2.1.2). For 13 wells the nearby land use included forage crops and/or pasture, in many cases in addition to corn. Three wells were near horticultural and/or managed turfgrass areas. Of the 10 wells where the agricultural influence was more distant, 6 had fallow (grassland/scrub) or wooded areas immediately upgradient, while 4 were in industrial areas.

2.1.3. Sampling and analytical protocols

Field sampling and on-site data

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, to 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.

Table 2.1.1. Sampling site and well characteristics. NA indicates well depth not available.				
ID	Well type	Depth (ft)	Well position relative to land use and topography	Sample date
1	home	60	downhill from long, steep corn fields	6/4/2003
2	home	NA	surrounded on all sides by extensive level corn fields	6/4/2003
3	business	~60	at base of hill with extensive corn and forage crop fields	6/4/2003
4	home	>40	at base of hill with corn fields; corn on all sides of house	6/4/2003
5	barn	shallow	surrounded by level pasture/forage; corn on one side	6/11/2003
6	barn	~40-50	on steep slope below pasture, corn fields to one side & below	6/11/2003
7	home	32-37	surrounded by level corn or corn/forage rotation fields	6/11/2003
8	municipal	~90	rolling topography; large corn fields upgradient in aquifer	6/19/2003
9	business	NA	downhill from corn/forage; managed turfgrass on sides & below	6/19/2003
10	home	188	downhill from extensive mixed croplands	7/1/2003
11	home	100	downhill from extensive row crop and corn fields	7/1/2003
12	barn	40	adjacent to extensive flat corn fields	7/1/2003
13	barn	40-50	adjacent to extensive flat corn fields	7/1/2003
14	home	NA	surrounded on all sides by extensive level corn fields	7/1/2003
15	home	~60	downhill from long, steep corn fields	7/24/2003
16	barn	~50	surrounded on 3 sides by extensive level corn fields	7/24/2003
17	barn	~50	surrounded on 3 sides by extensive level corn fields	7/24/2003
18	barn	~50	surrounded on 3 sides by extensive level corn fields	7/24/2003
19	home	58	downhill from large field: corn in past, currently forage	7/24/2003
20	home	NA	adjacent to large cornfield, downslope from pasture	8/7/2003
21	home	120	surrounded on 3 sides by extensive rolling corn fields	8/7/2003
22	barn	21	adjacent to extensive flat corn and alfalfa fields	8/7/2003
23	home	100-200	downhill from hillside with horticultural crops	8/7/2003
24	home	NA	downhill from corn fields on one side	8/12/2003
25	business	shallow	adjacent to extensive flat cornfield on one side	8/12/2003
26	farm	200	downhill from forage/pasture; downgradient mixed row crops	9/25/2003
27	home	NA	adjacent to large flat cornfield, downslope from pasture	9/25/2003
28	monitoring	46.5	downgradient from agricultural area (>1 mi) and industrial use	10/21/2003
29	monitoring	35	downgradient from agricultural area (>1 mi) and industrial use	10/21/2003
30	monitoring	59	downgradient from agricultural area (>1 mi) and industrial use	10/21/2003
31	monitoring	32	downgradient from agricultural area (<1 mi); below wooded hillside	10/21/2003
32	home	30	downgradient from agricultural area (<1 mi); below wooded hillside	10/21/2003
33	home	57	downgradient from agricultural area (<1 mi); below wooded hillside	10/21/2003
34	home	NA	downgradient from agricultural area (<1 mi); below wooded hillside	10/21/2003
35	monitoring	54	downgradient from agricultural area (<1 mi); below wooded hillside	10/21/2003
36	industrial	NA	downgradient from agricultural area (>1 mi) and industrial use	10/21/2003
37	home	shallow	downhill from horticultural operation	11/6/2003
38	home	NA	on steep slope below pasture, corn fields to one side & below	12/12/2003
39	barn	30	downhill from corn/forage rotation strip cropped land	12/12/2003
40	barn	NA	downhill from corn/forage rotation strip cropped land	12/12/2003

Facility served by wells	Wells	Significant surrounding and upgradient land use(s)	Wells
		Adjacent/nearby agriculture:	30
house	19	corn	27*
barn (dairy)	11	pasture / forage crops	13*
business/industrial	4	horticultural / managed turfgrass	3*
municipal water system	1	Other (agriculture somewhere upgradient)	10
monitoring only	5	fallow / woods	6
Total	40	industrial	4
		* due to multiple adjacent/nearby crops, a number of wells were represented in more than one subcategory	

Certified precleaned (Environmental Sampling Supply Inc.; PC class) narrow mouth amber glass bottles were used for sample collection. Two 1 L bottles were collected for samples for submission to DEC, and two 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). 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 within 8 hours of collection by laying them horizontally in a freezer to prevent breakage.

The primary water samples were shipped to NYS DEC in two installments: the first 20 in mid-August 2003, and the final 20 in December 2003. Frozen sample bottles were wrapped with padded packing and were shipped via overnight courier in a sealed high-insulation cooler. In the first installment, 3 bottles were cracked in transit, with the frozen contents salvaged where possible; of backup replacements shipped, 2 of 3 were similarly cracked and salvaged, with the third arriving intact. A number of bottles apparently cracked during refreezing at DEC, with the contents salvaged prior to thawing. Of the second installment, one sample arrived cracked and was replaced with a backup sample. Pesticide screening analysis conducted by DEC is detailed below. Analyses conducted at Cornell University included nitrate-N concentrations as well as ELISA screening for atrazine as the most likely to be detected pesticide, given the predominance of corn growing in the sampled areas.

DEC pesticide scans

This section is comprised of text forwarded by Peter Furdyna and Malissa Offerbeck of the NYS DEC analytical laboratory:

The water samples which were submitted to the NYSDEC Pesticides Laboratory under the group number 01A-041A were screened for pesticides, phenoxy acid herbicides and carbamates. All sample results were non-detect at the laboratory's method detection limit (MDL). The reporting levels for the non-detected compounds are the MDLs (Table 2.1.3).

The MDLs for the pesticides and carbamates were approximated at four times (4×) the background noise in the chromatograms nearest the corresponding peak of interest. For the phenoxy acid herbicides, MDLs are at the lowest calibration concentration on the calibration curve.

Due to the breakage of some sample containers as a result of freezing and expansion, it was not possible to analyze the entire sample set.

The pesticide compounds were extracted using the solid phase extraction (SPE) technique and analyzed by gas chromatography/mass spectrometry (GC/MS). The carbamates and phenoxy acid herbicides were directly injected onto an HPLC system and detected using a fluorescence and photo diode array UV detector, respectively.

Quality control for all three groups consisted of analyzing reagent blanks, method blanks (DI water), matrix spikes, matrix spike duplicates, and control spikes (DI water). A selection of eight pesticide compounds was made for the spiked samples. These compounds were chosen so as to cover the range of poor to good analytical performers. This insured that the pesticides which were difficult to analyze with acceptable levels of precision and accuracy were represented.

Due to the wide variety of pesticides screened, some compounds could not be adequately resolved chromatographically resulting in some high recoveries due to their coelution from the analytical column.

Control spike recoveries for the pesticides ranged from 25 to 200%. Matrix spike and matrix spike duplicate recoveries ranged from 67 to 216% with corresponding relative percent differences (%RSD) ranging from 0.0 to 60.9%. All blank sample results were non-detect at the MDL.

Control spike recoveries for the phenoxy acid herbicides ranged from 29 to 210%. Matrix spike and matrix spike duplicate recoveries ranged from 20 to 287% with corresponding relative percent differences ranging from 0.0 to 96.7%. All blank sample results were non-detect at the MDL.

Control spike recoveries for the carbamates ranged from 99 to 645%, the latter recovery reflecting that of carbaryl and coeluting compounds from the analytical column. Matrix spike and matrix spike duplicate recoveries ranged from 91 to 548%, again the latter high recovery being that of other compounds coeluting with carbaryl. The corresponding relative percent differences for the MS/MSD recoveries ranged from 0.0% to 41.6%. All blank sample results were non-detect at the MDL.

Table 2.1.3. NYS DEC laboratory results: pesticides tested and minimum detection limits (ppb).

Chlorophenoxy Acid Herbicides		General Pesticides, ctd.		General Pesticides, ctd.	
Clopyralid	48	Chlorneb	1.90	Metribuzin	3.62
5OH Diacamba	48	Chlorpropham	3.84	Mevinphos	2.16
Dicamba	48	Chlorpyrifos	0.75	mirex	1.29
2 4 D	48	Clomazone	0.59	Monocrotophos	2.86
Triclopyr	48	Crotoxyphos	1.07	Myclobutanil	1.76
Dichlorprop	48	Cyanazine	2.28	Nitrofen	3.72
Silvex	48	Cycloate	3.56	Norflurazon	0.61
Picloram	48	Cyfluthrin	2.24	O P DDD/O P DDT	1.74
MCPA	48	Cypermethrin	4.10	Oxadiazon	1.76
MCPP	48	Diazinon	0.63	Oxychlorane	4.02
2 4 5 T	48	Dichlobenil	1.21	Oxyfluorfen	4.00
2 4 DB	48	Dichloran	0.59	P P DDD/P P DDT	1.74
Carbamates		Dicofol	4.42	p p DDE	2.38
Aldicarb Sulfone	50	Dicrotophos	2.64	Parathion	1.22
Methomyl	30	Dieldrin	1.42	Parathion-M	7.50
3OH Carbofuran	40	Dimethoate	4.14	PCNB	1.24
Aldicarb	60	Dioxathion	1.32	Pebulate	1.69
Dioxacarb	80	Diphenamid	3.00	Pendamethalin	0.68
Carbofuran	80	Endosulfan	0.30	Phorate	4.96
Propoxure	70	Endo-Sulfate	0.87	Phosalone	1.72
Methiocarb	200	Endrin	1.07	Phosmet	4.96
Promecarb	200	EPN	2.00	Phosphamidon	2.20
Carbaryl	200	EPTC	2.54	Pirimiphos E	4.20
General Pesticides		Ethalfuralin	5.24	Pirimiphos M	3.44
Acephate	4.82	Ethion	2.74	Prometon	4.18
A-Endosulfan	0.95	Ethofumesate	5.50	Prometryn	0.65
Alachlor	2.32	Ethoprophos	1.76	Propachlor	2.58
Allethrin	0.52	Etridiazol	2.98	Propargite	1.73
Alpha HCH	2.56	Fenamiphos	2.92	Propazine	3.32
Ametryn	4.38	Fenarimol	1.65	Propetamphos	7.22
Aspon	0.62	Fenitrothion	1.92	Propiconazole	2.76
Atrazine	4.76	Fenpropathrin	0.61	Schradan	2.92
Azinphos M	5.06	Fensulfothion	0.57	Simazine	3.02
Azinphos-E	2.62	Fenthion	3.44	Sulfotep	3.54
B-Endosulfan	0.99	Fenvalerate	3.76	T. Permethrin	1.19
Benfluralin	3.74	Fluchloralin	5.10	TCMTB	1.80
Beta HCH	2.20	Folpet	4.70	Tecnazene	3.46
Bifenox	3.44	Fonofos	13.00	Terbacil	1.82
Bifenthrin	0.95	Heptachlor Epoxide	1.73	Terbufos	3.64
Bromocil	5.54	Hexazinone	1.06	Terbutryn	0.59
Butylate	1.17	Imazalil	0.63	Tetrachlorvinphos	1.90
C. Chlordane	1.73	Isofenphos	5.54	Tetradifon	1.13
C.Permethrin	1.29	Lindane	1.21	Tetrasul	2.20
Captan	1.05	Linuron	3.32	Thiobencard	6.38
Carbophenothion	2.56	Malathion	8.70	Triadimefon	5.14
Chlordane	0.67	Metalxyl	2.84	Triadimenol	4.94
Chlorfenvinphos z,e	3.34	Methiathion	0.40	Trifluralin	4.44
Chlorflurecol-M	1.40	Methoxychlor	1.26	Vernolate	1.47
Chloridazon	0.58	Metolachlor	4.32	Vinclozolin	3.04

Atrazine and nitrate assays

Water samples were screened at Cornell University for atrazine (as the most likely to be detected pesticide, given inferred widespread use and relative mobility). Screening was carried out with RaPID Assay test kits (Strategic Diagnostics, Inc., Newark, DE; <http://www.sdix.com>, part no. A00071). The method employs Enzyme-Linked ImmunoSorbent Assays (ELISA) to detect atrazine and related compounds. The contribution of individual compounds present cannot be distinguished by the screening test, and results are reported on an “as atrazine” basis; Table 2.1.4 summarizes the detection limits and the cross-reactivity of atrazine and related compounds. Samples were analyzed using a RPA-1 Photometer (Part No. A00003), which makes replicate absorbance readings of each sample tested. In contrast to standard colorimetric tests where increasing absorbance linearly correlates to increasing analyte concentration, atrazine and related compounds compete with reagents that favor color development in the ELISA assay. The RPA-1 photometer thus transforms absorbance data, expressing the absorbance reading (at 450 nm) as a fraction of the absorbance produced by the “negative control” (zero standard), or B/B₀. The calibration data is then linearized using natural logarithms and the logit function:

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

where B = sample absorbance

B₀ = absorbance of zero standard (negative control)

$\text{logit } (B/B_0) = \ln [(B/B_0)/(1-B/B_0)]$

C = standard or sample concentration, µg/L (ppb)

Table 2.1.4. Detection limits and cross-reactivity of atrazine ELISA test. MDL is the minimum detected level of atrazine and related compounds (ranked by MDL). LOQ is the lower limit of meaningful quantitation. IC ₅₀ is the analyte concentration that inhibits 50% of the color reaction produced by a negative control (blank) sample. Analytes with a lower IC ₅₀ (ametryn, prometryn) are proportionally more reactive than atrazine and may thus be detected at lower levels.			
— ppb (µg/L) —			
Compound	MDL	LOQ	IC ₅₀
atrazine	0.046	0.100	0.72
propazine	0.033	0.100	0.74
ametryn	0.053	0.050	0.39
prometryn	0.054	0.090	0.64
prometon	0.056	0.310	2.22
desethyl atrazine	0.062	0.45	3.21
terbutryn	0.09	0.76	5.5
terbutylazine	0.31	2.15	15.5
simazine	0.34	0.68	4.9
desisopropyl atrazine	0.8	30.1	217
cyanazine	1	>10,000	>10,000
6-hydroxy atrazine	1.1	20.6	148

Test kit calibration points include 5.0, 1.0 and 0.1 ppb (µg/L). Initial runs (in July 2003 for the first 14 samples, with the rest run after collection was completed) were calibrated using the linearization

routine integral to the RPA-1 photometer, yielding r correlation values of 0.98 or better. A confirming rerun of the samples was performed in February 2005, and in addition to the automated calibration, a two-point linearization was calculated manually using Eq. 2.1.1 between the lower two standards (0.1 and 1.0 ppb). This was done to maximize linearity in the lower range, since all absorbance readings were below the 0.1 ppb LOQ.

Nitrate was analyzed at the Cornell Nutrient Analysis Laboratory by ion chromatography, (Dionex DX-100 with AS4A-SC anion column) and was expressed as ppm (mg/L) of nitrate-N.

2.1.4 Analysis Results

Analytical results are summarized in Table 2.1.5. Pesticide analysis at the NYS DEC laboratory was substantially delayed, due in part to instrument failures and facility upgrades, with general pesticide scans completed by May 2004, acid herbicides by July 2004, and carbamates by November 2004, and final reports transmitted in February 2005. As noted in the prior section, the NYS DEC pesticide screening found that all analytes were below the detection limits specified in Table 2.1.3. For acid herbicides and particularly carbamates, instrumental detection limits were quite high: as noted in the prior section: “some compounds could not be adequately resolved chromatographically resulting in some high recoveries due to their coelution from the analytical column.” Another confounding factor was the presence of soluble organics in many well samples (typical of shallow groundwater) that caused difficulties with extractions and analysis. As a result, the nondetects in the DEC scans can be used to confirm that major contamination was not found in the sampled wells only for the analytes listed as “general pesticides” in Table 2.1.3; the same conclusions are not tenable with the acid herbicides and carbamates due to the elevated detection limits.

All ELISA scans conducted at Cornell University indicated no quantifiable levels of atrazine and related compounds (listed in Table 2.1.4). The data is reported in two ways in Table 2.1.5: “nd” indicates no detection of atrazine at all (sample absorbance below that of the zero standard), while “<0.1” indicates a potential trace of atrazine, but calculated concentrations were below the 0.1 $\mu\text{g/L}$ lower limit of quantitation (LOQ), and thus must be reported as a non-detect, as per the analytical protocol. As can be seen by comparing the two sets of ELISA runs (the second using optimized calculations for low levels as previously noted), 26 of 40 samples had identical results between the two runs. Of those that differed, 11 first tested as *nd* were reported as <0.1 in the second run, while the converse was true for 3 samples. The fact that all samples were below the 0.1 $\mu\text{g/L}$ limit of quantitation – and that this level is substantially below the 3 $\mu\text{g/L}$ drinking water standard – gives a high level of certainty that atrazine and related compounds are not present at levels of concern in the wells sampled.

Nitrate concentrations ranged widely, with the peak observed concentration of 12.2 mg/L. Of the 40 wells sampled, three had levels in excess of the 10 mg/L drinking water standard, and nine had levels between 5 and 10 mg/L. The mean nitrate-N concentration among all wells was 3.7 ± 3.4 mg/L (using values of zero for non-detects, a negligible error). Among wells where at least one of the ELISA runs found possible traces of atrazine (as indicated by “<0.1” in Table 2.1.5), mean nitrate levels were 5.5 ± 3.4 mg/L. In contrast, wells where atrazine was not detected (“nd”) for both runs had mean nitrate levels of 2.0 ± 2.4 mg/L. All 12 wells with nitrate-N levels in excess of 5 mg/L had corn fields in near proximity. However, close proximity to corn fields was not a guarantee of elevated nitrate-N levels. Well owners with levels exceeding 10 mg/L are currently being contacted for resampling as per the protocols stated above.

Table 2.1.5. Summary of well sample analytical results. NYS DEC pesticide screening, Cornell University atrazine ELISA scans (initial and reruns) and nitrate-N. *NA* = sample not available; *nd* = analyte(s) not detected; *<0.1* = apparent trace levels of atrazine below the 0.1 µg/L limit of quantitation (LOQ) but above the ~0.046 µg/L level of detection. Nitrate-N levels below 0.2 mg/L reported as *nd*.

ID	Well type and primary area land use		DEC Pesticide Scans (µg/L)	Atrazine (µg/L)		Nitrate-N (mg/L)
				initial	rerun	
1	home	steep corn fields	NA	<0.1	<0.1	12.2
2	home	corn fields	nd	<0.1	nd	4.7
3	business	corn/forage fields	nd	nd	nd	1.8
4	home	corn fields	nd	<0.1	<0.1	11.5
5	barn	pasture/forage/corn fields	nd	nd	nd	nd
6	barn	pasture, corn fields	nd	nd	nd	8.5
7	home	corn, corn/forage	nd	nd	<0.1	7.1
8	municipal	distant corn fields	nd	nd	nd	4.2
9	business	corn/forage; turfgrass	nd	nd	nd	6.8
10	home	mixed croplands	nd	nd	nd	3.9
11	home	row crop& corn fields	nd	nd	nd	4.4
12	barn	corn fields	nd	<0.1	<0.1	3.5
13	barn	corn fields	NA	nd	<0.1	4.5
14	home	corn fields	nd	<0.1	<0.1	8.3
15	home	steep corn fields	nd	nd	nd	0.6
16	barn	corn fields	nd	<0.1	<0.1	6.0
17	barn	corn fields	nd	<0.1	<0.1	6.3
18	barn	corn fields	nd	<0.1	<0.1	6.7
19	home	steep forage field	nd	nd	nd	nd
20	home	cornfield, pasture	NA	nd	<0.1	nd
21	home	corn fields	nd	<0.1	<0.1	5.0
22	barn	corn/forage fields	nd	nd	nd	nd
23	home	horticultural fields	nd	nd	nd	0.4
24	home	corn fields	nd	nd	<0.1	1.0
25	business	cornfield	nd	<0.1	nd	11.3
26	farm	forage/pasture, row crops	nd	nd	<0.1	2.0
27	home	cornfield, pasture	nd	<0.1	nd	4.9
28	monitoring	industrial; farms >1 mi	nd	nd	<0.1	2.0
29	monitoring	industrial; farms >1 mi	nd	nd	<0.1	0.8
30	monitoring	industrial; farms >1 mi	nd	nd	<0.1	1.7
31	monitoring	wooded hill; farms <1 mi	nd	nd	nd	nd
32	home	wooded hill; farms <1 mi	nd	nd	nd	2.0
33	home	wooded hill; farms <1 mi	nd	nd	<0.1	1.8
34	home	wooded hill; farms <1 mi	nd	nd	nd	1.8
35	monitoring	wooded hill; farms <1 mi	nd	nd	nd	0.2
36	industrial	industrial; farms >1 mi	nd	nd	nd	2.2
37	home	horticultural operation	NA	nd	<0.1	0.2
38	home	pasture, corn fields	nd	<0.1	<0.1	4.2
39	barn	corn/ forage stripcrop	nd	nd	<0.1	6.9
40	barn	corn/ forage stripcrop	nd	nd	nd	nd

2.2. Groundwater Exposure Assessment Modeling

This section was originally prepared as an article published in *Ground Water Monitoring & Remediation* 25 (4): 82-91, entitled A GIS-BASED GROUNDWATER CONTAMINATION RISK ASSESSMENT TOOL FOR PESTICIDES. The authors were Michael G. Sinkevich, M.Todd Walter, Arthur J. Lembo Jr. *, Brian K. Richards, Natalia Peranginangin, Sunnie O. Aburime**, and Tammo S. Steenhuis (*Department of Crop & Soil Science, Cornell University, Ithaca, NY, **Dept. of Civil & Environmental Engineering, Clark Atlanta University, Atlanta, GA 50314).

2.2.1. Introduction

Groundwater is an important natural resource that should provide drinking water for future generations. However, in recent decades groundwater pesticide contamination from agriculture has become a problem that requires monitoring. Because such monitoring is expensive – especially for groundwater over large areas of agriculturally dominated landscapes – reliable and flexible tools are needed to identify potential hazard areas in the landscape so that monitoring strategies can focus on the highest risk areas. By focusing monitoring activities on the highest risk areas, fewer observation wells are needed and the potential cost and detection effectiveness of the monitoring is improved. The goal of this project was to develop a distributed landscape-scale, physically based groundwater risk assessment tool that can be implemented with readily available, open access data.

While landscape scale water quality risk assessment has been revolutionized by the advent of geographical information systems (GIS), most, if not all, the risk assessment tools regularly used by water quality professionals employ logical factor- or index-based rubrics for assessing risk that are only loosely linked to physical processes and fail to predict actual chemical concentrations. This is especially true for groundwater (e.g., Grayman, 1977; Hamlett et al., 1992; Nizeyimana et al., 1996; Peterson et al., 1996). Traditional mechanistic predictions of groundwater risk are generally only applied at a single point in the landscape and assume pesticide leaching through soils is accurately characterized by the convective-dispersive equation, which neglects preferential flow phenomena. The reliable, mechanistic or physically-based models developed to predict the groundwater contamination from land-applied chemicals that meaningfully consider preferential flow (e.g., Wagenet and Hutson, 1986, Ramos and Carbonell, 1991; Steenhuis et al., 1987; Steenhuis and Parlange, 1991; Nguyen et al., 1998; Kim et al., 2003) have not been incorporated into GIS to assess contamination risks at a landscape scale, probably because they require either a copious amount of input data or data that are not readily available.

Perhaps the most important transport process to be included in groundwater risk assessment is preferential flow, the rapid, non-uniform transport of solutes via these flow paths which can result in contaminants reaching the groundwater before they degrade or can be adsorbed by the soil (e.g., Stagnitti et al., 1994, Camobreco et al., 1996). Indeed, the surprise discovery of pesticide contamination of the Long Island aquifers in the early 1980s clarified that groundwater contamination by toxic chemicals cannot be reliably characterized by the convective-dispersive equation, which assumes relatively uniform water flow throughout the soil matrix (Parlange et al., 1988). The Long Island findings stimulated interest in preferential flow; since then the occurrence and effect of preferred flow paths on water quality have been widely researched (e.g., Steenhuis et al., 1990; Steenhuis et al., 1994; Pivetz and Steenhuis, 1995; Geohring et al., 1999; Lodgdon, 2002; Gazis and Feng, 2004). Several preferential flow mechanisms have been identified: 1) macropore flow, which is common in well-structured soils (e.g., Quisenberry and Phillips, 1976; Beven and

Germann, 1982); 2) fingered flow, which generally occurs in unstructured soils and water repellent soils due to unstable wetting fronts (e.g., Hill and Parlange, 1972; Bauters et al., 1998); and 3) funnel flow, which occurs at some textural interfaces in the soil profile (Kung, 1990; Walter et al., 2000, Heilig et al. 2003). It is widely accepted that preferential flow is not an exception but the rule when dealing with solute flow through field soils (Dekker and Ritsema, 1994, Vanclouster et al., 2000) and therefore it is extremely important that it be included when trying to accurately model the distribution of potential well water contamination.

The objective of this project was to employ a mechanistic model of preferential flow within a GIS to generate maps of distributed groundwater contamination risk. We modified the Generalized Preferential Flow Model (GPFM) proposed by Kim et al. (2004) that is based on work by Darnault et al. (2004) and field-tested by Peranginangin (2003); modifications included including chemical degradation factors appropriate for the deeper soil profile and incorporating the model into a GIS. As an example, we applied the distributed model to Cortland County, New York and compared model-generated risk predictions to field observations for atrazine and nitrate. We cannot report specific sample locations and concentrations due to a confidentiality agreement signed at the beginning of this study, and therefore data will be presented in a generalized fashion through graphical methods.

2.2.2. Model Description

The Generalized Preferential Flow Transport Model

The GPFM describes solute transport between the land surface and the groundwater. Figure 2.2.1 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., 2003; Steenhuis et al., 2001). In the distribution zone, water and solutes are funneled into preferential flow paths, which transports the solutes through the transmission zone. The thickness of this distribution zone depends on land use or geomorphology, e.g., plow depth in cultivated land.

The model uses the assumption that percolating water and solutes mix uniformly in the distribution zone and the zone behaves as a linear reservoir, resulting in an exponential loss of solutes (Steenhuis et al. 1994; Shalit and Steenhuis, 1996). At $t = 0$, $C_d = C_o$ (e.g., Kim et al., 2004):

$$C_d = C_o \exp[-(\lambda + \beta)t] \quad (2.2.1)$$

where C_d is the solute concentration in the distribution layer, λ and β represent the rates of loss due to leaching and biochemical degradation, respectively [T^{-1}], and t is time [T]. C_o is the initial dissolved chemical concentration [ML^{-3}] and can be written as:

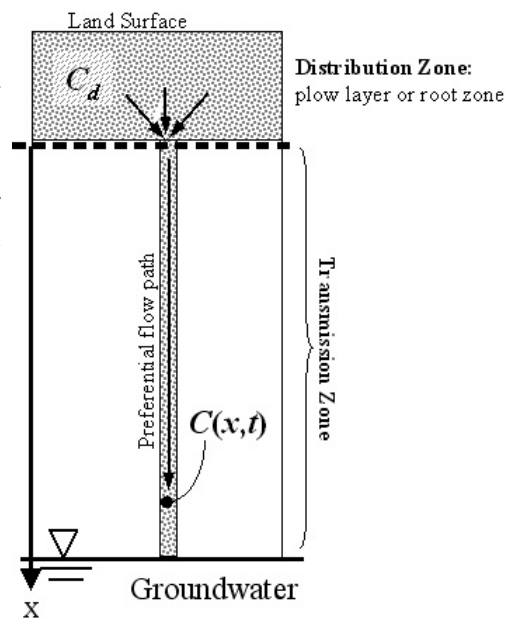


Figure 2.2.1. Schematic diagram of the preferential solute transport process in the vadose zone.

$$C_o = \frac{M}{W} \quad (2.2.2)$$

and M = the mass of pollutant applied per unit area of land [ML^{-2}] and W is the apparent water content of the distribution zone and incorporates chemical adsorption and is calculated (Shalit and Steenhuis, 1996) as:

$$W = d(\theta_s + \rho_b k) \quad (2.2.3)$$

where d [L] is the depth of the distribution zone, θ_s [L^3L^{-3}] is the saturated moisture content, ρ_b [ML^{-3}] is the soil dry bulk density, and k [L^3M^{-1}] is the sorption partition coefficient.

Solute degradation in the distribution zone (β) due to chemical and microbial breakdown is characterized by the chemical half-life, $t_{1/2}$ [T]:

$$\beta = \ln\left(\frac{2}{t_{1/2}}\right) \quad (2.2.4)$$

Half-life values are widely available in the literature for common pollutants; e.g. DelVecchio and Haith (1993). The leaching of solute from the distribution zone is be characterized by the ratio of the average percolation rate, R [LT^{-1}], to apparent soil water content, W [L], i.e.:

$$\lambda = \frac{R}{W} \quad (2.2.5)$$

Water and pesticides are released to the transmission zone via preferential and matrix flows. Because preferential flow paths are the most relevant with respect to water quality and we assume that all water moves through the preferential flow paths at an average characteristic velocity, v (Kim et al., 2004), through the transmission zone. This transport via the preferential flow paths of the transmission zone can be described with the convective-dispersive equation with a sink term for pesticide degradation (e.g., Peranginangin, 2003):

$$D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} - \beta^* C \quad (2.2.6)$$

where C [ML^{-3}] is the chemical concentration in the preferential flow paths at depth x and time t , D [L^2T^{-1}] is the dispersion coefficient, v [LT^{-1}] is the velocity of the solute, x [L] is the vertical axis with the origin at bottom of the distribution layer (positive downwards), and β^* [T^{-1}] is the first order chemical degradation rate in the transmission zone. D/v is assumed to be constant with values in the range of 1-4 (Walter, 1974). Pesticide degradation in the transmission zone is lower than in the more microbially and biogeochemically active distribution zone (Federle et al, 1986; Brockman et al., 1992; Kruger et al., 1997; Vanderheyden, et al., 1997, Shaw and Burns, 1998, Accinelli, et al., 2001; Mbuya et al., 2001). Integrating Eq. 2.2.6 using Laplace transforms with the initial condition $C = 0$ for $x > 0$ and $t = 0$ and a solute concentration at upper boundary condition at $x = 0$ for $t > 0$ is given by Eq. 2.2.1, the concentration in the distribution zone can be written as for $4D(\lambda + \beta - \beta^*)/v^2 < 1$,

(Toride et al., 1995; Darnault et al., 2004):

$$C = \frac{1}{2} C_0 \exp(-(\lambda + \beta)t) \left[\exp\left(\frac{vx}{2D}(1-a)\right) \operatorname{erfc}\left(\frac{x-vta}{2\sqrt{Dt}}\right) + \exp\left(\frac{vx}{2D}(1+a)\right) \operatorname{erfc}\left(\frac{x+vta}{2\sqrt{Dt}}\right) \right] \quad (2.2.7)$$

where:

$$a = \sqrt{1 - \frac{4D(\lambda + \beta - \beta^*)}{v^2}}$$

At $x=L$, the depth of the groundwater, Eq. 2.2.7 gives a value for pollutant concentration in the groundwater at time t after the application of the chemical. When x or t is sufficiently large, such that $(x + vta)/(4Dt)^{1/2} > 3$, then the last term of Eq. 2.2.7 is negligible, i.e.,

$$\exp\left(\frac{vx}{2D}(1+a)\right) \operatorname{erfc}\left(\frac{x+vta}{2\sqrt{Dt}}\right) \approx 0$$

The GPFM (Eq.2.2.7) has been successfully tested with both lab and field experiments: e.g., Figure 2.2.2 shows the agreement between model predictions and field observations of chloride and atrazine collected below the root zone (Peranginangin, 2003) and Figure 2.2.3 shows results comparing model predictions and time-series field measures of tritium (H^3) radiation in picocuries (Aburime et al., 2002) collected at 60 cm and 120 cm over a ~1-year period. Tritium differs from most agro-chemicals: in that it has a long half-life (12.5 years) and a sorption partition coefficient, k , of zero.

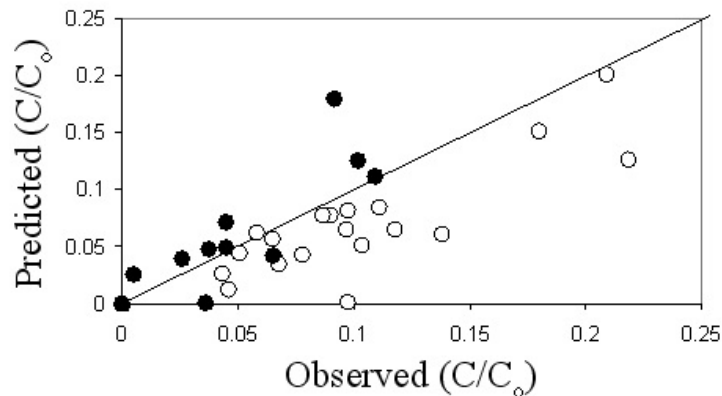


Figure 2.2.2. Predicted relative concentrations compared to observed relative concentrations taken from field data (Peranginangin, 2003), with $R^2 = 0.6$. Chloride is represented with the open circles and atrazine is the dark circles.

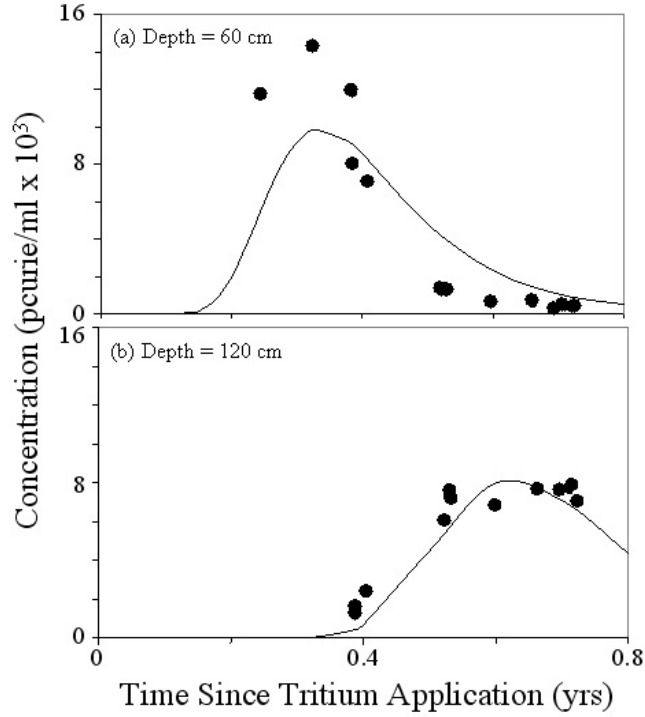


Figure 2.2.3. Comparison of the Generalized Preferential Flow predictions (lines) to field data (symbols) for tritium at depths of (a) 60 cm and (b) 120 cm (Aburime et al., 2002).

Landscape Scale Risk Assessment Model

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. The percolation or transport velocity depends on the propensity for preferential flow; we used a conservative estimate for the fraction of area participating in preferential solute transport, A_f , proposed by Selker et al. (1995):

$$A_f = \frac{I_{max}}{K_s} \quad (2.2.8)$$

where I_{max} is the maximum annual daily precipitation [LT^{-1}] and K_s is the saturated hydraulic conductivity of the soil [LT^{-1}], usually the surface layer. The velocity of the solute can be expressed as:

$$v = \frac{R}{(\theta_s + k\rho_b)(A_f)} \quad (2.2.9)$$

where R is the groundwater recharge, same as in Eq. 2.2.5 [LT^{-1}], θ_s is the saturated moisture content

[L³L⁻³], k is the sorption partition coefficient [L³M⁻¹], and ρ_b is the bulk density [ML⁻³]. The inclusion of the sorption in Eq. 2.2.9 retards the velocity of chemicals prone to soil adsorption relative to the water velocity. This is similar to the equation that would be used in traditional matrix flow situations except for the fractional area term in the denominator, which makes the preferential flow velocity typically more than one order of magnitude greater than that of matrix flow. The saturated moisture content θ_s in Eq. 2.2.9 can be obtained through open access soil data or, when unavailable, can be estimated from other commonly available soil data as follows (Fetter, 2001):

$$\theta_s = 1 - \left(\frac{\rho_b}{(\rho_m (1 - Om)) + (\rho_o (Om))} \right) \quad (2.2.10)$$

where Om is the percent organic matter content in the soil, ρ_m is the mineral particle density (≈ 2.65 g/cm³), and ρ_o is the organic soil particle density (≈ 1.00 g/cm³) (Boelter, 1969; Boelter and Blake, 1964). Adsorption/desorption partition coefficients for many pollutants are published (e.g., Bailey et al., 1974; Baker et al., 1978; Davidson et al., 1975; Haan, 1971; Helling, 1971; Smith et al., 1978); for pesticides, k can be estimated using the percent organic carbon, Oc , and the pesticide organic carbon adsorption coefficient, K_{oc} (DeVecchio and Haith, 1993):

$$k = K_{oc} \left(\frac{Oc}{100} \right) \quad (2.2.11)$$

Little organic matter exists in the subsoil, and k tends toward zero in the transmission zone. Although groundwater recharge, R in Eqs. (2.5) and (2.9), may be spatially variable, for small areas with reasonably homogenous climate it is commonly calculated as an average distributed flux using a Thornthwaite-Mather (1957) water balance (e.g., Steenhuis and Van der Molen, 1986; Varni and Usunoff, 1999). This procedure uses soil available water capacity data, precipitation data, and estimated potential evapotranspiration (PET) to estimate recharge (see Steenhuis and van der Molen (1986) for a complete description.)

The health risk of groundwater contamination due to pesticides can be estimated using the hazard ratio (Steenhuis and Naylor, 1987):

$$H = \frac{C^*}{h} \quad (2.2.12a)$$

$$C^* = \frac{\int_0^t CRd\bar{t}}{\int_0^t Rd\bar{t}} \quad (2.2.12b)$$

where C is the pesticide concentration at depth L as estimated by the distributed GPFM (Eq. 2.2.7) [ML⁻³], C^* is the average concentration of pollutant in the groundwater [ML⁻³] over time t , R is the

percolation rate or, alternatively, the groundwater recharge [LT^{-1}], and h is the maximum safe drinking water concentration as determined by the U.S. Environmental Protection Agency (EPA) [ML^{-3}]. Values of H near or greater than 1 indicate potential concern for drinking water safety.

2.2.3. Model Application

Site Description

We applied our risk assessment model to Cortland County in central New York State because much of the area relies on groundwater from the region's glacial aquifers and because its range of different soils types and land uses provided substantial spatial distribution for this case study. Additionally, a GIS-based assessment done within our research group (Section IV) found that Cortland County had the greatest relative risk of pesticide contamination of groundwater, based on land use, population groundwater use, and aquifer characteristics. The shallow depth to the water table and the high permeability of these aquifers make them highly vulnerable to contamination. The aquifer system in Cortland County consists of an unconfined sand and gravel aquifer 10 to 25 m thick and a lower confined sand and gravel aquifer that is 1 to 50 m thick. The two-aquifer systems are separated by a lacustrine and till stratum that is anywhere from 1 to 50 m thick. The two aquifers are hydraulically connected in some areas near valley walls where the confining layer is thin or absent (Miller et al., 1998). Land uses in Cortland County (Figure 2.2.4) are primarily agriculture (28%), forest (62%), and urban (8%). Agriculture is fairly evenly distributed throughout the rural parts of the county. Cortland County has diverse topography that ranges from flat valley bottoms to steep valley walls and hillsides; elevations range from approximately 1100 to 2000 feet above mean sea level.

Cold winters, with an average temperature of $1^{\circ}C$, and dry summers, with an average temperature of $17^{\circ}C$, climatically characterize Cortland County, as well as much of upstate NY. Lake Ontario, which is 70 km north, moderates air temperatures and supplies moisture to the cold air masses during the winter. The average annual precipitation is 100 cm and the average annual temperature is $9^{\circ}C$.

Groundwater Quality Data Collection

During the spring and summer of 2003, we collected groundwater samples at 40 locations throughout the county from private residences, farms, small businesses, monitoring wells, and public water supplies. This data collection was done during model development, i.e., prior to generating any risk predictions and thus sampling bias was avoided. Permission to sample was granted voluntarily. The Cortland County Soil and Water Conservation District (CCSWCD) and US Geological Survey (USGS) cooperated in selecting the sampling sites. Approximately 60 locations were initially identified, selected in part based on the CCSWCD's intuitions about where there might be an elevated risk of pesticide contamination due to factors such as proximity to likely pesticide application, areas down slope of pesticide application, presence of a high water table, permeable soils that allow leaching, and cooperative land owners. The groundwater samples were tested for atrazine and nitrate, the latter was included because elevated NO_3-N concentrations in groundwater have been used as an indicator of the presence of pesticides (e.g., Panno et al., 2002; Panno and Kelly, 2004).



Figure 2.2.4. Land use (LU-LC) broken up into the three major land cover types in Cortland County, New York: forested, urban, and crop land.

Nitrate was analyzed at the Cornell Nutrient Analysis Laboratory by ion chromatography, (Dionex DX-100 with AS4A-SC anion column, MDL = 0.001 mg/L). Atrazine was analyzed at the Cornell Soil and Water Laboratory using Strategic Diagnostics Inc.'s RaPID Assay Atrazine Test Kit, which uses an enzyme-linked immunosorbent assay (ELISA) for the determination of atrazine (MDL = 0.05 µg/L; lower limit of quantitation = 0.1 µg/L).

Model Parameterization

Land Use Land use influences the spatial distribution of pesticide or other potential contaminant use. We used Land Use and Land Cover (LULC) data files (www.webgis.com), which describe the vegetation, water, natural surface, and cultural features on the land surface. These were obtained from the USGS's National Mapping Program and from the EPA. Land use is always changing, especially in upstate NY where farms are constantly going out of business and residential areas are rapidly expanding, thus the most current data were used, i.e. 1995 (Figure 2.2.4). Because it constitutes such a large amount of the area, agricultural land use is the primary concern with respect to pesticide contamination. We assumed for risk assessment purposes that all agricultural lands are in use and that these cropped fields receive the pesticide for which risk predictions are to be determined.

Pesticide Parameters This study focused on atrazine and assumed pesticide application rates recommendations posted by the USDA. For this study we followed one complete pesticide pulse, which is one year's worth of pesticide application because atrazine is generally applied only once in the early spring. Table 2.2.1 summarizes the atrazine parameters used in this study.

Table 2.2.1. Pesticide Parameters for Atrazine		
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 x 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).

Soils Currently, all of New York State's soil information is compiled in the soil survey database, STATSGO (www.essc.psu.edu), which contains digitized maps of soil parameters needed to implement the GPFM in GIS, namely, bulk density, organic matter content, and saturated moisture content. It also provides estimated average high water table information, used to parameterize ground water depth for our model. These data were compared to USGS field measurements of water table depth over a small portion of Cortland County and the relative distributions of STATSGO water table depth compared well with the field measurements (Sinkevich 2004).

Groundwater Recharge The Thornthwaite-Mather (1955, 1957) method, as described by Steenhuis and Van der Molen (1986), was used to estimate annual groundwater recharge, R . This procedure for calculating recharge was chosen because of its modest data requirements and ease of calculation. The Thornthwaite-Mather method requires the soil available water capacity, daily precipitation, and daily potential evapotranspiration (PET). PET was estimated using the Priestly-Taylor (1972) equation. We used average daily precipitation and temperature from over 30 years with data obtained from the weather station in Cortland, NY. Using these weather data, average annual groundwater recharge, R , was calculated as 40.4 cm/year.

The Preferential Flow Parameter The fraction of soil participating in preferential solute transport, A_f , is not well known. We used $A_f = 0.3$ based on field studies using dyed macropores (images available at <http://www.bee.cornell.edu/swlab/SoilWaterWeb/Research/pfweb/index.htm>). We checked this value against Eq. 2.2.8 using I_{max} equal to average intensity of the 1-year 24-hour rainfall in Cortland ($I_{max} = 2$ cm/hr -- U.S. Dept. of Commerce, 1961) and an average K_s from the local soil survey. Values of K_s ranged over several orders of magnitude, but reasonable “average” values yielded $A_f = 0.2$ to 0.4, which agreed with our own field studies.

Hazard Index Mapping – The hazard index map was created using the spatial datasets for land use (LULC) and soils (STATSGO), as well as the non-spatial aspects solved for in Eqs. 2.2.2 to 2.2.12. Using ESRI’s ArcGIS, the LULC data were joined with the STATSGO data. An attribute table containing the necessary land use and soils data was imported to a spreadsheet program to solve Eqs. 2.2.7 and 2.2.12 and the results were imported back into a GIS to display a map of H . For a step-by-step procedure using ArcGIS, see Sinkevich (2004). Although Eq. 2.2.12 is shown for a general case, here we used long-term average R and replaced the integrals with monthly summations. For simplicity, we assumed no temporal variation in R .

2.2.4. Results and Discussion

Figure 2.2.5 shows the atrazine hazard index map for Cortland County, NY divided up into four major risk groups: negligible, low, moderate, and high. Negligible risk areas, $H = 0$, correlate almost exclusively to areas that do not receive pesticides, i.e., areas that are not cropland, and/or areas with deep water tables, generally > 8 m deep. The low risk areas indicate some potential pesticide leaching, $0 < H \leq 0.05$, but at concentrations well below the EPA standard. The moderate areas were predicted to have concentrations up to $1.5 \mu\text{g L}^{-1}$, i.e., $0.05 < H \leq 0.5$, which indicates substantial potential pesticide leaching that is nevertheless still below the EPA standard for groundwater contamination by atrazine. The high-risk areas are all locations with a potential atrazine leaching risk index of $H > 0.5$. Note that the high risk areas constitute only a small portion (5%) of the watershed; focusing groundwater monitoring on these areas would be substantially more cost-effective than implementing an evenly distributed, county-wide program. Most of the areas are actually at negligible to low risk, $> 70\%$, which corresponds to the fact that 70% of the county is forest or urban areas that do not typically receive atrazine, and for which a low intensity monitoring strategy would probably suffice.

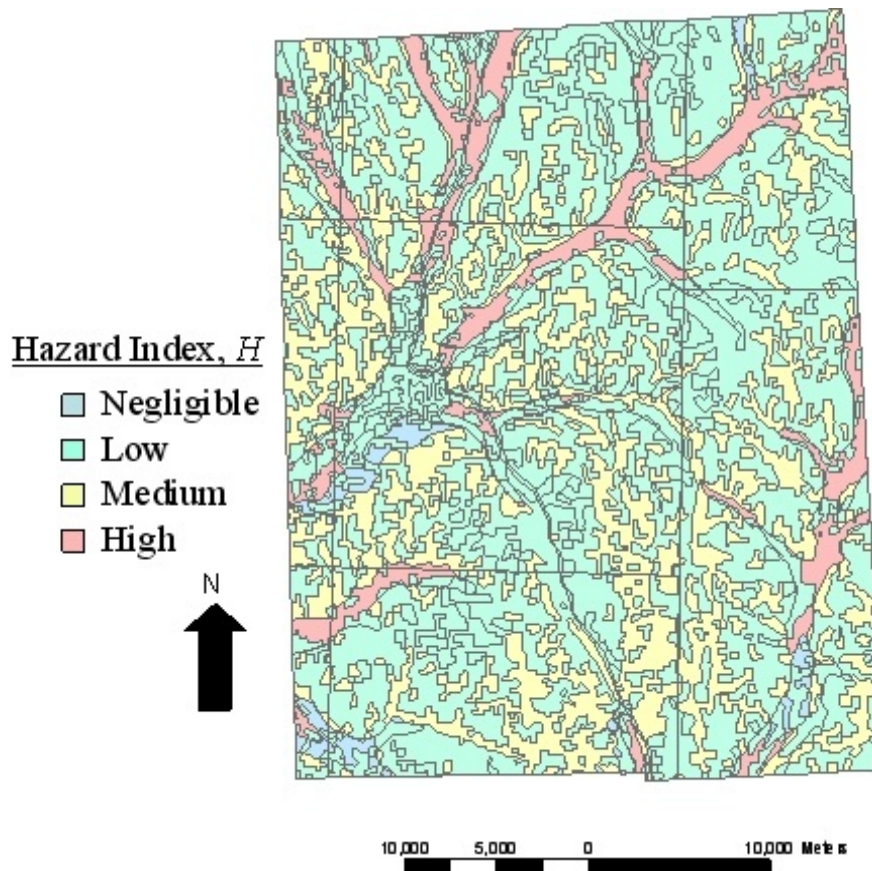


Figure 2.2.5. Relative risk assessment map for potential groundwater contamination by atrazine in Cortland County, New York. Light blue, dark blue, yellow, and red correspond to negligible, low, moderate, and high relative risk, respectively.

Figures 2.6a and 2.6b show the comparison between our atrazine hazard indices and field measurements of atrazine and nitrate, respectively. Because the scope of sampling was limited, our sample set unfortunately only included one well from a high-risk area, although this sample contained atrazine and the highest observed concentration of nitrate. Out of the 40 samples, 14 had trace levels of atrazine (i.e., $> 0.05 \mu\text{g/l}$) that were, however, below the limit of quantitation ($< 0.1 \mu\text{g/l}$). Assuming that the propensity of atrazine detection is a good indicator of pesticide contamination risk, we found a good correlation between atrazine detection frequency and our risk predictions (Figure 2.2.6a). We used nitrate as a general agro-chemical tracer for which we could detect a larger range of concentrations than we found for atrazine and, as shown in Figure 2.2.6b, the concentration of nitrate correlated well with the atrazine risk indices, i.e., higher risk areas correlated to higher nitrate concentrations. Although nitrate is a better indicator of overall groundwater recharge from agricultural areas than preferential flow *per se*, these tests corroborate the reliability of our risk assessment tool's ability to predict groundwater-contaminant vulnerability.

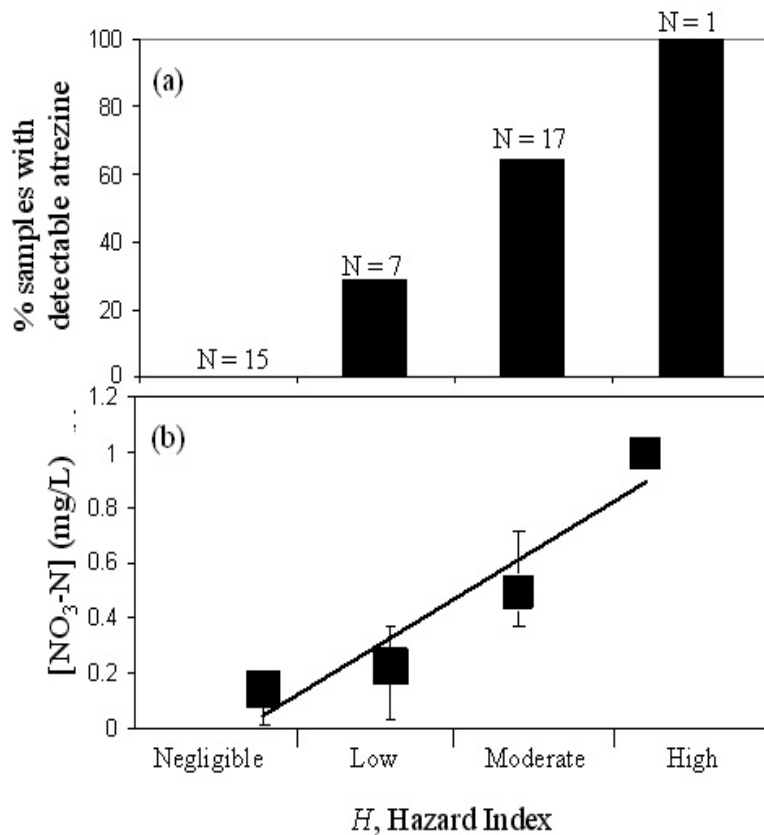


Figure 2.2.6. Comparisons between predicted atrazine hazard indices (H) and observed groundwater quality with respect to (a) atrazine and (b) nitrate. Graph (a) shows the percent of samples "N" collected within each hazard class that had detectable trace concentrations of atrazine, while (b) shows the average nitrate concentration in groundwater for each hazard class; error bars represent the 90% confidence interval of the observed values and the line is a linear regression ($R^2 = 0.90$) emphasizing the relationship.

To illustrate the importance of considering preferential flow in ground water risk assessment, Figure 2.2.7 shows the risk predictions with preferential flow removed, i.e., $A_f = 1$ (Eq. 2.2.8). Interestingly, in the absence of preferential flow, there is very little predicted risk of groundwater contamination by atrazine. Traditional leaching models typically ignore preferential flow and assume uniform, convective-dispersive transport like that used to generate Figure 2.2.7. Figure 2.2.8 replicates the analyses shown in Figure 2.2.6, but without preferential flow transport; note the propensity for detectable levels of atrazine in negligible risk and low risk areas (Figure 2.2.8b) as well as high nitrate concentrations for negligible risk and low risk areas.

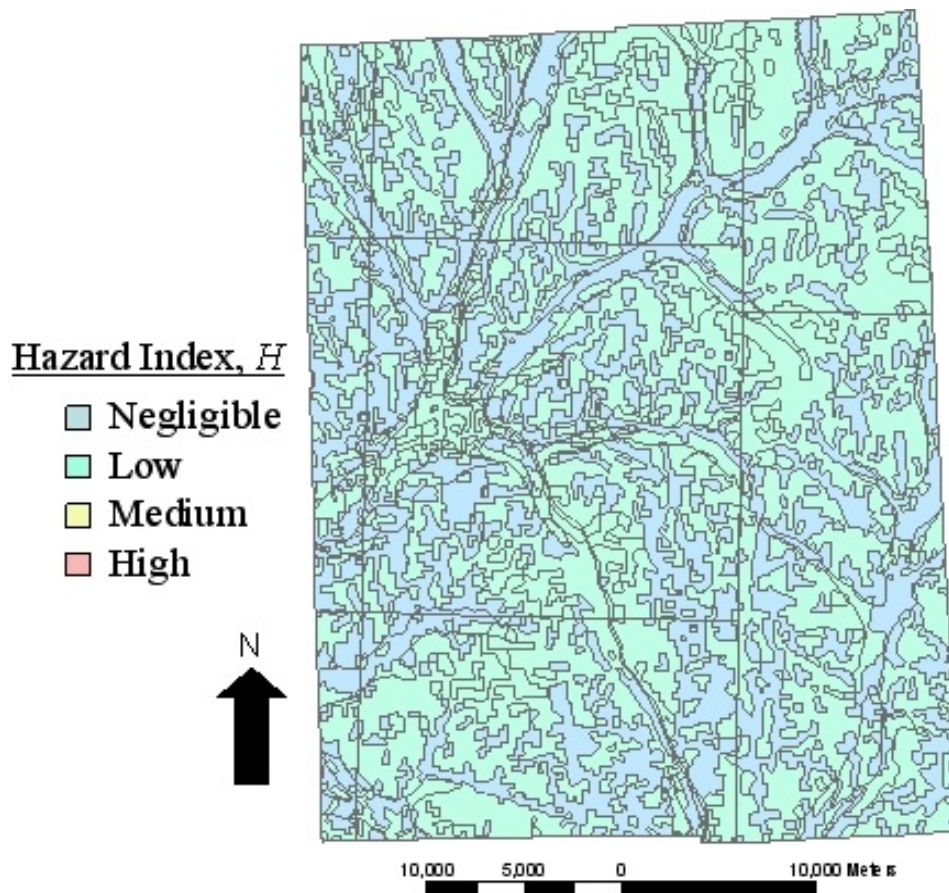


Figure 2.2.7. Relative risk assessment map for potential groundwater contamination by atrazine neglecting preferential flow ($A_f = 1$).

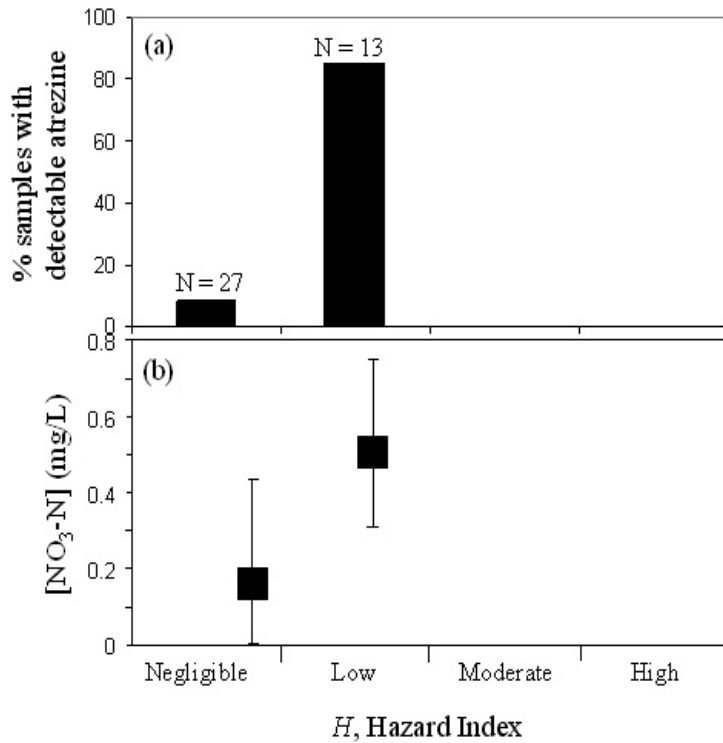


Figure 2.2.8. Comparisons between predicted atrazine hazard indices (H) ignoring preferential flow and observed groundwater quality with respect to (a) atrazine and (b) nitrate. Graph (a) shows the percent of samples "N" collected within each hazard class that had detectable concentrations of atrazine, and (b) shows the average nitrate concentration in groundwater for each hazard class; error bars represent the 90% confidence interval of the observed values

To evaluate the role of chemical degradation on contaminant risk, we used our tool to create a hazard index map for Cortland County, NY with respect to 2,4-D (Figure 2.2.9), which has a decay rate 4 to 8 times faster than atrazine (Hamaker, 1972). For 2,4-D the maximum contaminant levels in drinking water are $70 \mu\text{g L}^{-1}$ (EPA), the sorption partition coefficient is spatially distributed but remains around $20 \text{ cm}^3/\text{g}$, the application rate is $2.24 \times 10^{-5} \text{ g/cm}^2$, and $t_{1/2}$ is 10 days. The hazard map is scaled proportionally the same as for the atrazine analysis, e.g., high-risk corresponds to $H > 0.5$. Notice that the risk of 2,4-D contamination is considerably less than for atrazine (Figs. 2.9 and 2.5, respectively). Most of the areas are negligible to low risk, 70% and 25% of the county, respectively. Because of the fast degradation rate of 2,4-D, there are actually no areas of high risk for water contamination in Cortland County, and the moderate risk areas only represent about 5% of the county. This is in agreement with many survey studies that find atrazine concentrations in drinking water wells but find little to no 2,4-D concentrations (Tindall and Vencill, 1995; Franklin et al., 1994).

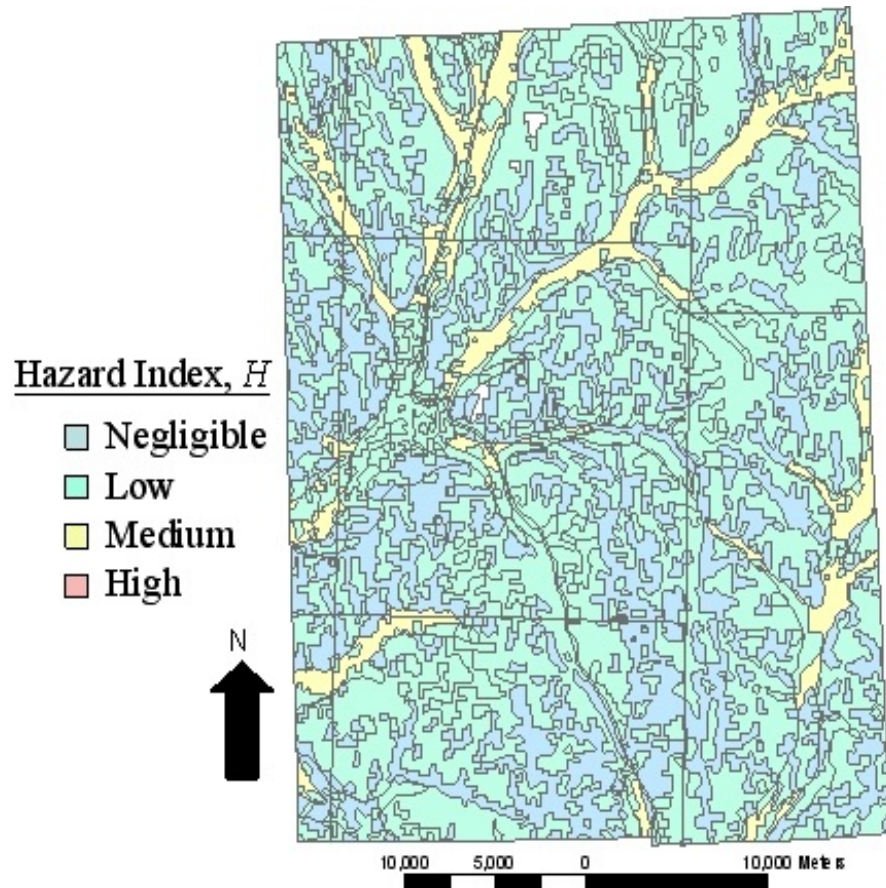


Figure 2.2.9. Relative risk assessment map for potential groundwater contamination by 2,4-D in Cortland County, New York.

2.2.5. Summary and Conclusions

We developed and tested a risk assessment tool to assist in developing reliable and cost-effective well sampling strategies. Our tool is based on a spatially distributed version of the Generalized Preferential Flow Model (GPFM) that accounts for the preferential flow of pesticides downward through the soil, acknowledging that degradation rates may be lower at depth than in the root zone, i.e., the distribution and transmission zones, respectively. Our risk assessment tool translates the GPFM predicted concentrations into hazard indices that show the degree of potential groundwater contamination by pesticides across a landscape. We applied our model to Cortland County, NY and found good agreement between risk predictions and field measurements of atrazine and nitrate. Our GIS-based risk assessment tool can be parameterized entirely with open-access data and published information on agro-chemical characteristics. The next goal of this project is to implement our tool on the Internet so that water quality professionals have easy access to it.

2.3. Utilization of the PSUR Database

This section is derived from the MPS project report completed by Sophia Garcia in May 2005.

This section details our activities in processing and evaluating the utility of the Pesticide Sales and Usage Reporting (PSUR) database as a means for targeting sampling of vulnerable wells in Cortland County. As described previously, nearly a year elapsed between formal application for the database for Cortland County and data delivery. As noted, the process was prolonged in part by the fact that required approval mechanisms heretofore existed only in statute. Sampling in Cortland County had concluded by the time that the data was released, so the confidential database was examined in a *post hoc* manner, evaluating 1) the utility of the database and 2) whether the reported patterns of application correlated with observed patterns in analytical results. The methodology and results of each of these investigations are presented separately.

2.3.1. Utility of the PSUR database

Database descriptions

The Pesticide Sales and Usage Reporting (PSUR) database was developed in response to the NY State Pesticide Reporting Law of 1996 which requires all pesticide commercial applicators to report the use and sales of pesticides to the New York State Department of Environmental Conservation (NYS DEC). The database includes only those pesticides applied by commercial applicators as well as point-of-sale records. Conditional access to the PSUR database was secured as noted below. PSUR data was received in large Excel files for the years 1997 to 2001 and saved on a secure hard drive on a password- and firewall-protected designated computer. Only approved individuals involved in this research study that are signatories to a confidentiality agreement are permitted to access this information. The data is accessible by password known only by the allowed individuals. The database records include the following fields: pesticide DEC ID, name of applicator, building number and street, city, zip, and county of application; pesticide EPA ID, quantity applied in (lbs or gals), and date applied (start to end).

The NYS Pesticide Product, Ingredient, and Manufacturer System (PIMS) database, managed by the NYS DEC Pesticide Management Program as supplied to the Pesticide Management Education Program (PMEP) at Cornell University, is designed to facilitate searches for pesticide product information. The PIMS database lists information on all registered pesticides in New York State. Information includes EPA ID; usage (i.e. industrial, agricultural); type (i.e. herbicide, insecticide); formulation (i.e. liquid, granular); active ingredient name; active ingredient ID and % w/w of active ingredient typically used in pesticides. Most useful to this study was the active ingredient information, which was used to make a quantitative account of the pesticide active ingredients mass applied and sold in Cortland County. We obtained a list of restricted/registered pesticides with all appropriate information listed in the PIMS database from the PMEP of Cornell University. Before we used this list, the PMEP list was compared and updated with one found online available for public use in order to assure we had the most recent information. For this study only restricted pesticides were examined.

2.3.2. Methodology

PSUR data quality assessment

Much of the information in the database required a detailed examination for data quality. Due to anticipated data errors (alluded to in caveats in the 2001 PSUR annual report), the complete PSUR data was closely reviewed for each year. Two critical preliminary fields were examined for accuracy: *location of application* and *existing/valid EPA ID*. Initially, *existing/valid DEC ID* was examined as a criterion but was later found to be noncritical to database utility.

It was first necessary to validate the locations of pesticide applications. Errors in location were due to records being either unrecognizable or simply outside of Cortland County (such as one notable record listing “Avenue of the Americas” in New York City). In order to properly identify the application locations were in Cortland County, a list of cities, towns and villages was compiled from the Cortland County website and compared with the list of cities recorded in the database. Both lists of cities were sorted in ascending alphabetical order and visually compared. Only addresses within Cortland County were considered, with all others eliminated.

Data for applications located in Cortland County were next reviewed for existing or valid EPA ID. The EPA registers all pesticides used in the U.S. with an ID number. This number is required to be on pesticide labels and is used to identify pesticides when reporting use and application. When EPA ID's are reported correctly, the PSUR database lists a valid number. In cases where there is an error, the PSUR database lists the number as irregular, or invalid. Irregular numbers are caused by a pesticide report where two values were submitted for a single field. The system is not able to handle multiple components for one field. The reporting database expects one EPA ID with one address, etc. for each entry, or else the data will be irregular. Invalid numbers are reported when there is a mismatch in EPA ID's from the pesticides reported as used or applied and from those registered in New York State for a particular reporting year. Only those pesticide applications with a valid EPA ID were considered, and all others were eliminated from the study data.

Finally, the data were initially reviewed for existing/valid DEC ID number. Although NYS DEC designates an ID number to all registered pesticides in New York State, this number is not required by law to be reported and therefore the number was often missing or invalid in the PSUR database. (For example, over 5000 records were without DEC ID's in the year 2000 reporting.) The DEC ID was thus not considered a critical field in determining the usability of the records.

Manipulation of PSUR data

This study required identification of active ingredients (AI) and their concentrations in only restricted pesticides reported in the PSUR database. The PSUR and PIMS databases were combined in order to differentiate between restricted and unrestricted pesticides and to identify the AI of the pesticides as listed in PIMS.

Registered/restricted pesticides As noted previously, the PIMS and PSUR databases list all pesticides registered in NY State, but our study used only records for *restricted* pesticides. When the databases were combined for matching, the amount of data relevant to our study was significantly reduced by 77% of the valid data (81% of the overall data) as seen in Table 2.3.2. Once matched, the PIMS database filtered the non-restricted use pesticides resulting in the necessary data specific to this study.

Matching databases using lookup functions Microsoft Excel provides a lookup function that will utilize a similar variable found in two separate workbooks to match up specific data between two files. Using the vlookup function, EPA ID's were used as the matching variable. The function performed a search for each EPA ID listed in the PSUR database and matched it with the list of EPA ID's listed in the PIMS database. The match returned the active ingredient name and active ingredient %w/w concentration for each pesticide applied. Once this information was combined, the mass of active ingredients applied was calculated.

Volumetric unit conversions The PSUR database provides only the volume of applied pesticides that are reported as applied and sold in liquid form. Conversion of volumes to mass is not done by the PSUR database because validation data is not yet available to report the data congruently in mass and volume. Therefore the database lists both measurements as reported by applicators. It was necessary for this study to convert all data to total mass of active ingredient, but as noted complete records of pesticide specific densities were not available. We therefore assumed a specific gravity of 1 g/cm³ (8.34 lbs/gal, equal to water) for all pesticides in liquid form. This was assumed to be a safe if somewhat conservative assumption, since most specific gravities would tend to be close to (if aqueous) or less than (if pesticide was in an organic matrix) this value. The conversion was done by using “if” conditional statements to identify the information reported as a volume. If the conditional statement recognized a mass, then no conversion was necessary. The conversion formula used was thus:

$$\text{AI Mass applied (lbs.)} = \text{Qty. applied (gal)} \times 8.34 \text{ lbs/gal} \times (\%w/w \text{ of active ingredient}/100) \quad \text{Eq. 2.3.1}$$

For the solid pesticides (applications reported as mass), the following calculation was performed:

$$\text{AI Mass applied (lbs.)} = \text{Qty. applied (lbs)} \times (\%w/w \text{ of active ingredient} / 100) \quad \text{Eq. 2.3.2}$$

Manipulation of the data yielded a table with the necessary fields, as summarized in Table 2.3.1.

DEC ID	Name	Street	City	In County?	Zip Code	EPA ID No.	Qty. Applied (lbs.)	Qty. Applied (gals.)	Date Applied (Start)	Date Applied (End)	Active Ingredient	Active Ingredient % w/w	Active Ingredient Applied (lbs.)
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Table 2.3.1. Database fields for pesticide application data

Geocoding procedures

GIS maps of the PSUR application data were generated by geocoding – a process that converts address locations to latitude and longitude coordinates – and were superimposed on physical and hydrological maps of Cortland County. The GIS system used for this study was Manifold GIS, which was selected for its integrated geocoding system. The geocoding tool uses a database based on the US government's official address database published in the TIGER/Line data set to find estimated positions for street addresses in the United States. It works best in urban and suburban areas where street addresses follow reasonably regular patterns. The pesticide data with all fields listed in Table 2.3.1 were imported into Manifold for geocoding purposes. Manifold then created two additional columns for latitude and longitude coordinates. The table was then copied and pasted as a drawing and the locations plotted on a map that also included imported geographical and

hydrological data of the region. Incomplete or unidentified locations were marked for subsequent review and editing before geocoding was again attempted.

Individual maps of hydrologic features, freshwater areas, county boundaries, and agricultural land-use areas for Cortland County were downloaded from the Cornell University Geospatial Information Repository (CUGIR) Census 2002 agricultural data and imported for use as a base map. CUGIR coordinates its activities with the National Spatial Data Clearinghouse and the New York State GIS Clearinghouse to provide geospatial data and metadata for New York State with special emphasis on those natural features relevant to agriculture, ecology, natural resources, and human-environment interactions.

Blurring of Information

Any data reported visually was blurred to prevent identification (either directly or by inference) of individual application sites in compliance with the New York State Pesticide Reporting Law. The data was blurred in any GIS maps prepared for disclosure by overlying a coarse uniform grid created on the maps so that each grid cell had an associated area. The information for any points within an individual cell was added to the lumped data for the cell. This procedure provided a means of summing and showing the general patterns of application data without disclosing application locations. An example blurred plot is shown in Figure 2.3.1.

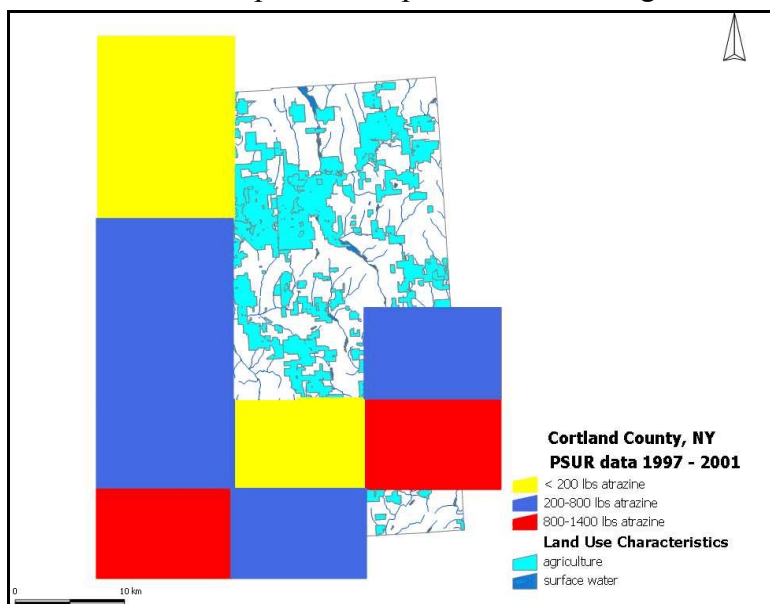


Figure 2.3.1. Blurred PSUR-reported cumulative atrazine applications, Cortland County 1997-2001.

2.3.3. Results

Database Summary

Table 2.3.2 is a numerical summary of the data assessment performed for quality assurance and specificity of this study. The table includes data for both application and sales databases. The table lists the years of the study followed by the number of records reported in the PSUR database for each year. The column for “Outside County” has records that were either unidentifiable or were not found within Cortland County. The valid records that had an address within Cortland County were then examined for irregular or invalid EPA ID's. Records with missing EPA ID's were counted and

listed in the column for “Missing EPA ID”. These records could not be used for matching purposes because they were missing the matching variable. The column for “No DEC ID” was included as an observation of the number of records that did not report a DEC ID. Records with “No DEC ID's” were still included for matching if they had both a valid address location and EPA ID.

The second half of the table is considered the useable data for this study, which was focused on restricted-use (i.e. requiring certified applicators) pesticide data. The column with “Valid records” is the total records minus invalid records, expressed as a number as well as the percent of total. The final filter applied was that of restricted use pesticides, which significantly reduced the number of usable records for this study. Only 23% of the valid records were restricted use pesticides and therefore valid for this study. The overall percentage of records useful for this study from the PSUR database was 18.7%.

For the Sales Data, a similar trend in incomplete information was observed, with 77% of records regarded as valid and a slightly lower percent of data (17%) covering restricted use pesticides.

Year	Total Records	Invalid Records		No DEC ID	Valid records		Valid restricted use records		
		Outside county	Missing EPA ID		number	% of all records	number	% of valid records	% of all records
Commercially applied pesticides database									
1997	6486	1627	1000	45	3859	59.5	939	24.3	14.5
1998	8595	1091	1111	29	6393	74.4	1440	22.5	16.8
1999	5211	737	247	1613	4227	81.1	1031	24.4	19.8
2000	8499	222	210	5150	8067	94.9	1198	14.9	14.1
2001	10199	839	300	6	9060	88.8	2676	29.5	26.2
Total	38990	4516	2868	6843	31606	81.1	7284	23.0	18.7
Pesticide Sales Database									
1997	201	2	3	105	196	45.3	22	24.2	10.9
1998	2138	1002	5	185	1131	44.3	244	25.8	11.4
1999	939	20	4	28	915	94.5	204	23.0	21.7
2000	975	28	0	20	947	95.1	218	23.5	22.4
2001	577	28	5	5	544	93.4	151	28.0	26.2
Total	4830	1080	17	343	3733	77.3	839	24.7	17.4

General and specific challenges of the PSUR database

The Pesticide Usage Reporting (PSUR) database group of Cornell University warned database users early on of the challenges they faced in collecting the pesticide application data from the commercial applicator community. “Users of the data are cautioned against the use of the data to draw specific conclusions regarding pesticide sales and use in New York State.” Sources of error included transferring hand-written records into the database, missing information, and ambiguity in addresses recorded only with a zip code. The Pesticide Reporting Law allows data to be turned in by the

commercial applicator and pesticide sales community on handwritten forms; in fact most data are submitted in this form. Keying in the data sometimes in writing is difficult to decipher and can create missing and misinterpreted information.

In cases where pesticides are applied in rural or large farmlands, identifying a specific address in these locations was challenging. Since these locations rarely have specific mailing addresses within them, zip codes are not designated to these areas and therefore it becomes difficult to closely identify their location. In the same way, zip codes that are assumed for these areas might be incorrectly recorded by commercial applicators.

After evaluation of critical fields required for validating the PSUR records it was determined the following fields required for this study were: an address within Cortland County and a valid EPA ID. Some challenges were presented in verifying both addresses and EPA ID's. For instance, there were significant errors in location, which reduced the usable data and later affected geocoding efforts. The number of records reporting applications outside of NY State comprised 12% of the PSUR records for the five year study. The number of records missing at least EPA ID's was 7 % of the overall PSUR records. This revision of the data reduced our sample size by roughly 19% from the original list of recorded pesticide applied, and by 81% of the overall data due to the observation of only restricted pesticides required for this study.

Ambiguity in location of application resulted in further challenges in geocoding the locations. Although much of the information from the database was missing one or several of the necessary address identification fields such as building number, street name, city, and zip code, an attempt to geocode the addresses was still executed. However due to limitations with the geocoding program, many addresses were recorded only by city or zip code, which would thus yield results erroneously indicating elevated concentrated pesticide application quantities concentrated in or around cities and towns.

As noted previously, simply securing permission to access the database was a lengthy and time-consuming process because the process had heretofore existed only on paper. It is anticipated that the process will become more streamlined and more rapid in future years.

Challenges of the NYS PIMS website database

This study focused on registered/restricted pesticides applied from 1997 to 2001 in Cortland County. In order to identify active ingredients in registered pesticides that are of restricted use, the EPA ID for each pesticide was used as the matching variable from the application data with the PIMS database. Therefore the accuracy of EPA ID's reported was crucial in identifying the restricted pesticides in the database. Although the PIMS restricted list database was mostly used for this study, in addition, the NYS PIMS website database was also used as a reference. Factors for which the NYS PIMS website database reduced the amount match-able data was 1) the current EPA ID reporting method 2) the nature of active ingredients listed in the NYS PIMS website. As mentioned earlier in this report, errors in EPA ID's are listed as irregular or invalid, and thus reduce the amount of valid data for matching with the PIMS database.

Although a marginal concern, the current EPA ID reporting method in the publicly accessible PIMS database found on the NYS PIMS website, which was used for identifying pesticides and active ingredients for this study in addition to the PIMS list which only contains restricted pesticides, presented a minor concern. By federal implementation, the NYS PIMS website database lists EPA ID's that contain up to three sets of numbers, a company number, product number, and a distributor number. In the NYS PIMS website, a minimum of two unique numbers - the company and product numbers are necessary to identify an active ingredient corresponding to a unique pesticide. Occasionally, the third and unique number - the distributor number, is recorded. For most pesticides the first two numbers of the EPA ID are sufficient for identification of pesticide characteristics such as active ingredient. It is often found that the first two sets of numbers will list several pesticides of the same brand having the same active ingredient and percent concentration. In these cases, determining the active ingredient is uncomplicated, and it is unnecessary to differentiate between pesticide names. Using either pesticide name will yield the same active ingredient concentration, making a third and unique number negligible. However, in several cases where the distributor number was not recorded, omitting this number produced an inaccurate identification of a particular pesticide with a specific third set of number identification and different active ingredient and percent concentration. This was likely a limitation of the search criteria used and not the database itself.

Geocoding results

The geocoding software was effective for converting the pesticide data onto maps. However, geocoding the address locations caused a 12% reduction in valid data due to 1) further ascertained errors in address locations, 2) the geocoding software's preference for urban and suburban regions, and 3) limitations on address listings from the geocoding address source, Tiger/Line dataset.

Initially, PSUR data was examined for valid address location by city in order to determine whether the addresses were located in Cortland County. Building number and street name of address was not examined prior to geocoding. Once geocoded, some addresses were unidentified by the geocoding database due to error in locations such as unknown building numbers, or street names. Many of these addresses were linked with other similar addresses in other cities and counties but were still considered invalid.

Furthermore, the geocoding software is designed for more effective use in urban and suburban locations where street addresses follow a pattern of regularity in building numbers. Once the city and street name are identified, the building number is estimated along the street. Because many addresses were located in rural locations such as farmland where restricted pesticides may be applied, those addresses are more difficult to identify because of the scarcity of rural address resources. Consequently, some addresses in our study located in rural areas were identified at the nearest urban area addresses, by street, city or even zip code, slightly misallocating the data by displaying a significant portion of the data in or around cities, towns and villages. The 12% of the data was omitted due to serious errors in all address fields, however most were still identifiable by at least one address field.

In addition, not only are the rural addresses difficult to estimate, but also they may not be listed at all in the geocoding database. Agriculture census statistics show an annual variation in farmland in Cortland County such as 540 farms in 2001 and an increase to 565 farms in 2003 . The Tiger/Line

census database might be limiting in information and therefore cannot identify some rural addresses for geocoding.

In summary, the geocoding effort succeeded in plotting 88% of the valid PSUR data records in this study. Utilization of the geocoded data is discussed below.

2.3.4. Correlating PSUR application records with trace atrazine detections

As reported above, ELISA analyses conducted at Cornell yielded only trace detections of atrazine in 50% of samples tested (in the second low level-optimized run reported in section 1), with all those detections being below the 0.1 µg/L limit of quantitation. We attempted to correlate these trace detections with patterns of PSUR-reported applications as well as with an alternative qualitative assessment of land use-based risk.

Methodology: well contributing areas and mapping PSUR applications

Well contributing areas were approximated based on topography, regarded as a safe assumption given the fact that groundwater is shallow in the region and that most wells were located in terrain where hilltops/ridges, sampled wells and groundwater-fed streams were in relatively close proximity. Digital elevation maps were used, and, in the absence of overriding topographic trends, a minimum 100 m catchment width was assumed. The lateral catchment distances typically extended 100 m to 1 km, resulting in areas of 10,000 to 100,000 sq meters (2.5 to 25 acres). Catchments areas were compared with field notes that verified observed topography around the well areas. A groundwater elevation map depicting groundwater flow direction was used to identify groundwater flow to wells that were located in the area to the southwest of Cortland, an area intensively mapped by the USGS in response to industrial water contamination (Miller et al, 1995).

PSUR application locations were plotted on a GIS map so that juxtaposition between applications and sample wells could be determined. Since PSUR records only specify a single point of application and not the actual fields/areas applied, an application area was estimated by defining a radius of application. This radius was determined by the mass of atrazine applied and the typical product label-specified rate of application, which determined the area of land that would be treated. Estimated treated areas varied from 0.4 km to 1.4 km in radius.

Methodology: qualitative land use assessments as an alternative predictor

The ELISA screening results detected trace levels atrazine (all below the 0.1 µg/L LOQ) in 20 of the 40 samples. cursory examination of the well types and land usage around wells suggested trace atrazine detections correlated with agricultural use, predominantly those wells surrounded by cornfields. To provide an alternate predictor of trace atrazine detections, we generated a qualitative land-use based risk assessment based on our observations of land use – presuming that the presence of corn implied atrazine applications – and topography surrounding each well. This assessment was ranked 1 to 5, with 5 implying that surround land use and topography would contribute strongly to potential atrazine use and mobility, as summarized in Table 2.3.3.

Table 2.3.3. Qualitative land use-based risk (LU risk) assessment for atrazine contamination potential of groundwater based on well type and surrounding land use and topography: assessment criteria.		
Risk Level	Surrounding land use(s)	
	Near to well	Overall catchment region
1 (least)	Residential/commercial, non-agricultural	Suburban/urban or non-agricultural rural area
2	Residential/ commercial, non-agricultural	Some groundwater recharge from more distant agricultural areas
3	Level crop and forage land	Flat area, no major cornfields nearby in catchment
4	Sloping cornfields	Sloping croplands and some nearby cornfields; some wooded hillside drainage
5 (greatest)	Surrounded by sloping cornfields	Sloping area heavily farmed with corn; some wooded hillside drainage

Table 2.3.4 shows the breakdown of qualitative risk level assignments to various wells. Level 1, the lowest condition for areas with no agricultural influence in the well catchment, was not assigned to any sample wells due to occurrence of at least some agriculture in the contributing catchments of all wells sampled. Level 2 wells – consisting of 4 domestic, 5 monitoring, 1 municipal, and 1 industrial well – all were sited in a suburban area with known groundwater directional flow from distant agricultural fields. Level 3 wells included 3 domestic, 3 farm, and 2 commercial wells. Level 4 wells represented the plurality of sample wells, with : 6 domestic, 1 commercial, and 5 farm wells. Level 5 well consisted of 6 domestic and 3 farm wells.

Table 2.3.4 Breakdown of number of well sites by well type and land use-based risk factor.					
Risk Level	Domestic	Farm/barn	Commercial /Municipal	Monitoring	TOTAL
1 (least)	0	0	0	0	0
2	4	0	2	5	11
3	3	3	2	0	8
4	6	5	1	0	12
5 (greatest)	6	3	0	0	9

Methodology: testing correlations

In order to determine possible correlations between trace atrazine detections, PSUR-reported usage and the LU-based risk level, three hypotheses were tested using the Spearman’s rank correlation coefficient (r') for comparing two ranked data sets, (X, Y),:

- 1) decreasing distance to PSUR-reported atrazine applications correlates to increasing likelihood of trace atrazine detections (r'_1);
- 2) decreasing LU-based risk level correlates with increasing distance from PSUR-reported atrazine applications (r'_2); and
- 3) increasing LU-based risk level correlates with increasing likelihood of trace atrazine detections (r'_3).

The following formula was used:

$$r' \equiv 1 - 6 \sum \frac{d^2}{N(N^2 - 1)}$$

where r' is the rank correlation coefficient and d is the difference between X and Y , and N is the number of values in the data set; for this study, $N = 40$. The closer the correlation coefficient is to ± 1 , the greater the likely correlation. Conversely, coefficients approaching to 0 indicate insignificant or no correlation. The significance of the r' relationships between the datasets were examined by graphing (Barcelona Field Studies Centre SL, 2005) the Spearman's rank coefficients and degrees of freedom ($df = 40 - 2 = 38$). Exercising the null hypothesis analysis for each coefficient determined the likelihood of the correlation to have occurred by chance, which would require the hypothesis to be rejected.

Results: correlating PSUR-reported applications to trace atrazine detections

Table 2.3.5 lists the sample well characteristics, distances to PSUR reported atrazine applications (in km as well as ranked in increasing distance), the land-use based risk ranking and the ELISA trace detections from the second low level-optimized run (ranked 0 or 1). Distances from wells to nearest PSUR applications varied from 0.6 km to 5.6 km.

Only two wells (21 and 22) were located within an estimated radius of any PSUR-reported atrazine applications. Wells 21 and 22 were 0.61 km and 0.67 km on either side of a reported application, which had an estimated radius of 0.7 km. Well 21 was a 120 ft deep domestic well surrounded by cornfields located at a higher elevation from the application location. Well 22 was a 21 foot deep barn use well located in a flat area with distant cornfields and other crops at a lower elevation than the application location. Atrazine screening analysis found a trace detection in well 21 but no detection in well 22, a detection percentage identical to the overall dataset.

The distances to the PSUR-reported areas had no correlation to trace atrazine trace detections. The Spearman correlation coefficient for hypothesis one r'_1 was equal to -0.50, with a significance level between 1% and 0.1%. However, the hypothesis of positive correlation is rejected because the correlation was negative (-0.50). The most likely reason for this lack of correlation between PSUR-applications and the pattern of detections is that the PSUR database does not reflect all atrazine applications. Given the prevalence of cornfields in proximity to wells vs. few reported applications anywhere near wells, it is evident that many atrazine applications are made by farmers and are thus not reported to the PSUR database, as opposed to commercial applicators who must report all applications.

Results: correlations with land-use based risk assessments

Relatedly, our qualitative land use-based risk rankings – which include the presence of cornfields and thus presumptive atrazine use – also showed no correlation with PSUR-reported applications, as reflected in the correlation coefficient r'_2 of -0.31, with a significance level of less than 5%. The second hypothesis that the land-use based risk level would show some correlation with PSUR-reported applications was thus rejected. Again, this would reflect the impact of the apparent prevalence farmer atrazine applications

In contrast to prior correlation results, it was found that the pattern of atrazine detections strongly correlated with our land-use based risk ranking, based on observations of land-use and topography. The correlation for r'_3 was +0.96, with a 99.9% level of confidence that hypothesis 3 is valid.

Table 2.3.5. Sampling site and well characteristics, land use-based atrazine contamination (LU) risk potential rank (as per Table 2.3.2), atrazine ELISA detection rank (no detection =0, trace detection below 0.1 ug/L LOQ =1), and distance to nearest PSUR-reported atrazine application shown in km as well as ranked by increasing distance.

ID	Well type	Surrounding land use and topography	Distance to PSUR applic.		LU Risk Rank	Atrazine Detect. Rank
			km	Rank		
1	home	downhill from long, steep corn fields	4.1	18	5	1
2	home	surrounded on all sides by extensive level corn fields	3.0	12	3	0
3	business	at base of hill with extensive corn and forage crop fields	0.9	2	4	0
4	home	at base of hill with corn fields; corn on all sides of house	3.2	13	5	1
5	barn	surrounded by level pasture/forage; corn on one side	1.7	6	4	0
6	barn	on steep slope below pasture, corn fields to one side & below	0.9	2	4	0
7	home	surrounded by level corn or corn/forage rotation fields	3.0	12	5	1
8	municipal	rolling topography; large corn fields upgradient in aquifer	4.0	17	2	0
9	business	downhill from corn/forage; managed turfgrass on sides & below	2.2	9	3	0
10	home	downhill from extensive mixed croplands	2.4	10	4	0
11	home	downhill from extensive row crop and corn fields	2.4	10	4	0
12	barn	adjacent to extensive flat corn fields	2.5	11	4	1
13	barn	adjacent to extensive flat corn fields	2.2	9	4	1
14	home	surrounded on all sides by extensive level corn fields	3.0	12	3	1
15	home	downhill from long, steep corn fields	3.0	12	4	0
16	barn	surrounded on 3 sides by extensive level corn fields	4.0	17	5	1
17	barn	surrounded on 3 sides by extensive level corn fields	4.0	17	5	1
18	barn	surrounded on 3 sides by extensive level corn fields	4.0	17	5	1
19	home	downhill from large field: corn in past, currently forage	3.9	16	3	0
20	home	adjacent to large cornfield, downslope from pasture	5.6	20	5	1
21	home	surrounded on 3 sides by extensive rolling corn fields	0.6	1	5	1
22	barn	adjacent to extensive flat corn and alfalfa fields	0.6	1	3	0
23	home	downhill from hillside with horticultural crops	0.6	1	4	0
24	home	downhill from corn fields on one side	5.1	19	4	1
25	business	adjacent to extensive flat cornfield on one side	3.4	15	3	0
26	farm	downhill from forage/pasture; downgradient mixed row crops	3.0	12	4	1
27	home	adjacent to large flat cornfield, downslope from pasture	1.9	7	4	0
28	monitoring	downgradient from agricultural area (>1 mi) and industrial use	1.4	4	2	1
29	monitoring	downgradient from agric. area (>1 mi) and industrial use	2.5	11	2	1
30	monitoring	downgradient from agric. area (>1 mi) and industrial use	2.5	11	2	1

Table 2.3.5., continued.

ID	Well type	Surrounding land use and topography	Distance to PSUR applic.		LU Risk Rank	Atrazine Detect. Rank
			km	Rank		
31	monitoring	downgradient from agric. area (<1 mi); below wooded hillside	3.3	14	2	0
32	home	downgradient from agric. area (<1 mi); below wooded hillside	3.4	15	2	0
33	home	downgradient from agric. area (<1 mi); below wooded hillside	3.4	15	2	0
34	home	downgradient from agric. area (<1 mi); below wooded hillside	3.2	13	2	1
35	monitoring	downgradient from agric. area (<1 mi); below wooded hillside	3.2	13	2	0
36	industrial	downgradient from agric. area (>1 mi) and industrial use	3.4	15	2	0
37	home	downhill from horticultural operation	2.1	8	2	1
38	home	on steep slope below pasture, corn fields to one side & below	1.0	3	5	1
39	barn	downhill from corn/forage rotation strip cropped land	1.6	5	3	1
40	barn	downhill from corn/forage rotation strip cropped land	1.7	6	3	0

2.3.5. Conclusions

The PSUR database was examined for Cortland County for the years 1997 to 2001. About 81% of the nearly 40,000 applicator records and 77% of the nearly 5,000 sales records were determined to be valid in terms of valid address location and EPA identification number. Between 17 and 19% of the total records present were “restricted use” pesticides of primary concern in targeting potential groundwater sampling. Of these data records, 88% were successfully geocoded, indicating that transference to and utilization in GIS-based approaches is feasible.

No significant correlations were found between PSUR application data and the pattern of trace (<0.1 µg/L) atrazine detections that occurred in 20 of 40 wells sampled. In contrast, a strong positive correlation was found between trace atrazine detections and a qualitative land use/topography risk assessment based on characteristics near the well and in the well’s estimated contributing area. It is inferred that the utility of the PSUR database for atrazine in Cortland County was limited by that fact that private (farmer- applied) atrazine use is not reported, leaving the PSUR database with an incomplete picture of atrazine applications in the county.

This limitation does not necessarily extend to other counties (where farmer vs. commercial applicator patterns may differ) and/or to other pesticides that may be less likely to be farmer-applied. It is anticipated that future work (with greater sensitivity due to newer equipment and more refined targeted analysis procedures at the NYS DEC laboratory) will result in more trace detections, allowing us to test correlations with PSUR-reported applications for a larger range of pesticides.

2.4. Statewide Assessment of Relative Groundwater Exposure

A risk-based selection process was developed for identifying and prioritizing other candidate counties in upstate NY for groundwater sampling in Year 2 and beyond. We have followed the GIS-based protocol first outlined in an earlier progress report, which overlays vulnerable aquifers, population dependence on groundwater and several indices of pesticide use. This procedure was 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 ground water 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.

2.4.1. Protocol Considerations

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, Schenectady, 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.

Not relying upon actual usage data, a Pennsylvania assessment (Petersen and others, 1996) and the NYS DOH Source Water Assessment Program (NYS DOH, 1999) employ land use data as a surrogate for pesticide use. They reasoned that because pesticide use is highly correlated with land

use types (little on forests and wetlands, more on suburban and agricultural land), area-wide assessments could rely on land use proximity to wells as a surrogate for actual pesticide use.

In New York, statewide uniform land use data are rare. The most consistent source reasonably representative of the last couple of decades is probably the USGS land cover data set, which is from the early 1990's.

For this process, the pesticide application estimates were divided by the areas of land assumed to be associated with pesticides. This improves two aspects compared to using the PSUR zip code data (a weight of total AI of restricted use pesticides) directly. Residue concentrations in ground water are sensitive to the AI weight applied per unit of land to which it is actually applied. (An alternative would have been to divide by the total land area of a zone. This would underestimate exposure in zones having a large proportion of forest or parkland and small developed or agricultural areas.)

2.4.2. 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 km², as shown in Figure 2.4.1 (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 km², as shown in Figure 2.4.1 (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 2.4.2).

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 km², as shown in Figure 2.4.3 (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 km², displayed as Figure 2.4.3 (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 2.4.4.

Combining commercial use, private sales, and land use

The commercial pesticide use per km² and pesticide sales per km² 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 2.4.4) to yield the combined pesticide use per km² in the combined *Restricted Use Pesticide Applied* map (Figure 2.4.5).

Finding Relative Potential Exposure Areas

Combining Combined Population Served and Combined Pesticide Use maps

For each ZCTA, population dependent on groundwater per km² was multiplied by combined pesticide use (lbs) per km² to find the value called "Relative Potential Exposure" per km². 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 2.4.6.

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 km². These exposure values were summed by county (Dissolve function) then normalized by the area of each county to result in a new Relative Potential Exposure per km² value. These are presented in Table 2.4.1, scaled between 0 and 1 (1.00 being the county with the greatest risk factor) to result in the final Scale Risk Factor (Table 2.4.1) and the *Relative Potential Exposure by County* map, Figure 2.4.7.

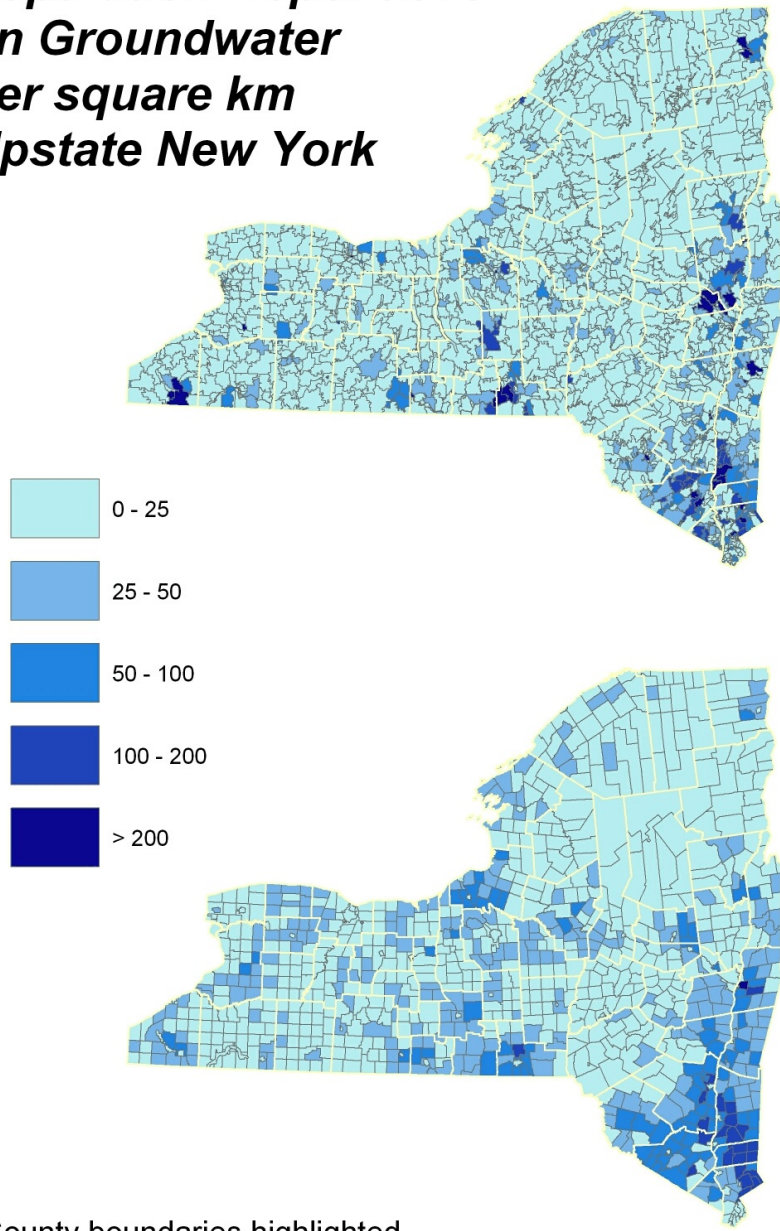
2.4.3. Exposure assessment results

The results are summarized numerically in Table 2.4.1 and graphically in Figure 2.4.7. It is noteworthy that Cortland County emerged from the screening process as one of the two counties with the highest potential pesticide exposure via ground water, based on the screening criteria used. Schenectady was the only county with a comparable risk score. Based on this process, Schenectady and, to a lesser extent, the second tier of downstate counties were the primary candidates for year 2 screening. The final stage of the selection process is assessment of local institutional capability and interest, which are deemed essential to a successful monitoring process. The results used from this protocol are being used to guide selection of candidate counties for subsequent survey work.

Table 2.4.1. New York counties with the greatest relative potential exposure, based on pesticide use and population dependence on groundwater. Counties ranked by score and grouped by score ranges.		
	County	Relative Potential Exposure
1	Cortland	1.000
2	Schenectady	0.998
3	Westchester	0.451
4	Rockland	0.418
5	Orange	0.372
6	Putnam	0.355
7	Albany	0.244
8	Erie	0.228
9	Greene	0.204
10	Saratoga	0.182

This initial mapping approach has been satisfactory to identify counties where there is a conjunction of higher spatial densities of population using ground water and higher spatial densities of restricted pesticide sales and use. Refinements will include incorporation of more than one year of PSUR data, focus on fewer pesticides than the entire list of restricted use products, and updated land use and water dependence data.

**Population Dependent
on Groundwater
per square km
Upstate New York**



Public Systems (by ZCTA)

Private Systems (by Municipality)

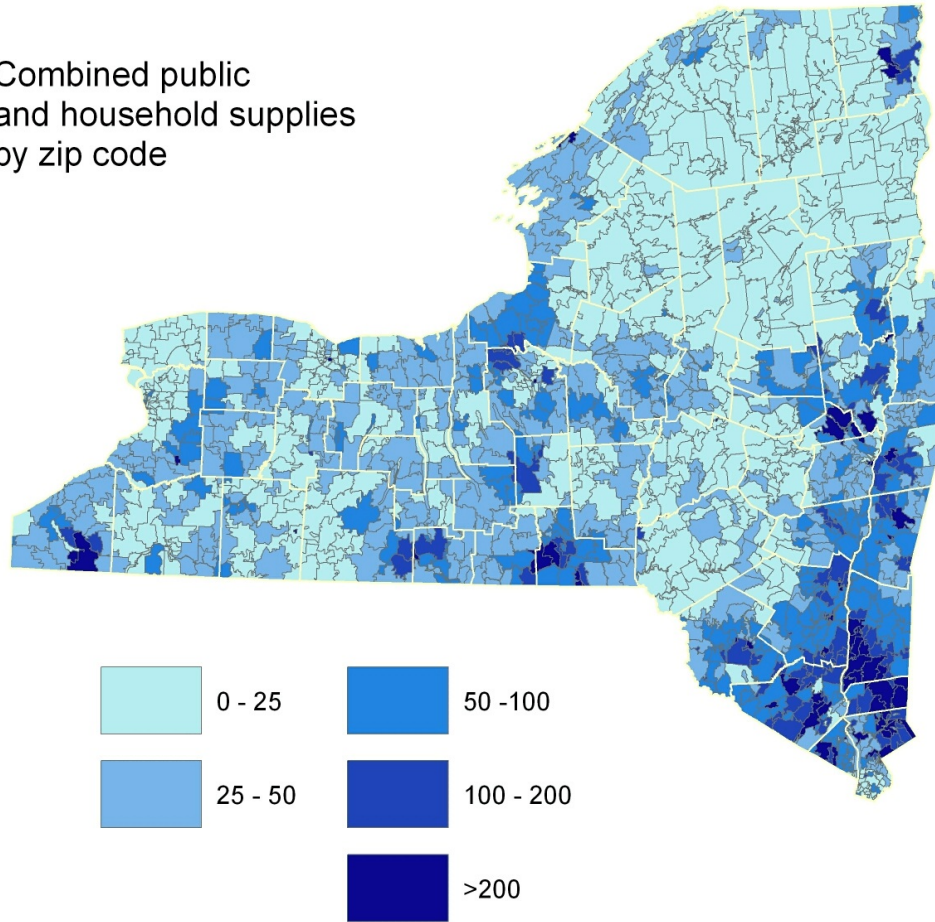
County boundaries highlighted

Figure 2.4.1. Population dependence on public (top) and private (bottom) groundwater supplies.

Population Dependent on Groundwater per square km

Upstate New York

Combined public
and household supplies
by zip code



County boundaries highlighted

Figure 2.4.2. Combined population dependence on public and private groundwater supplies.

Restricted Use Pesticide Applied (Active Ingredients) Upstate New York

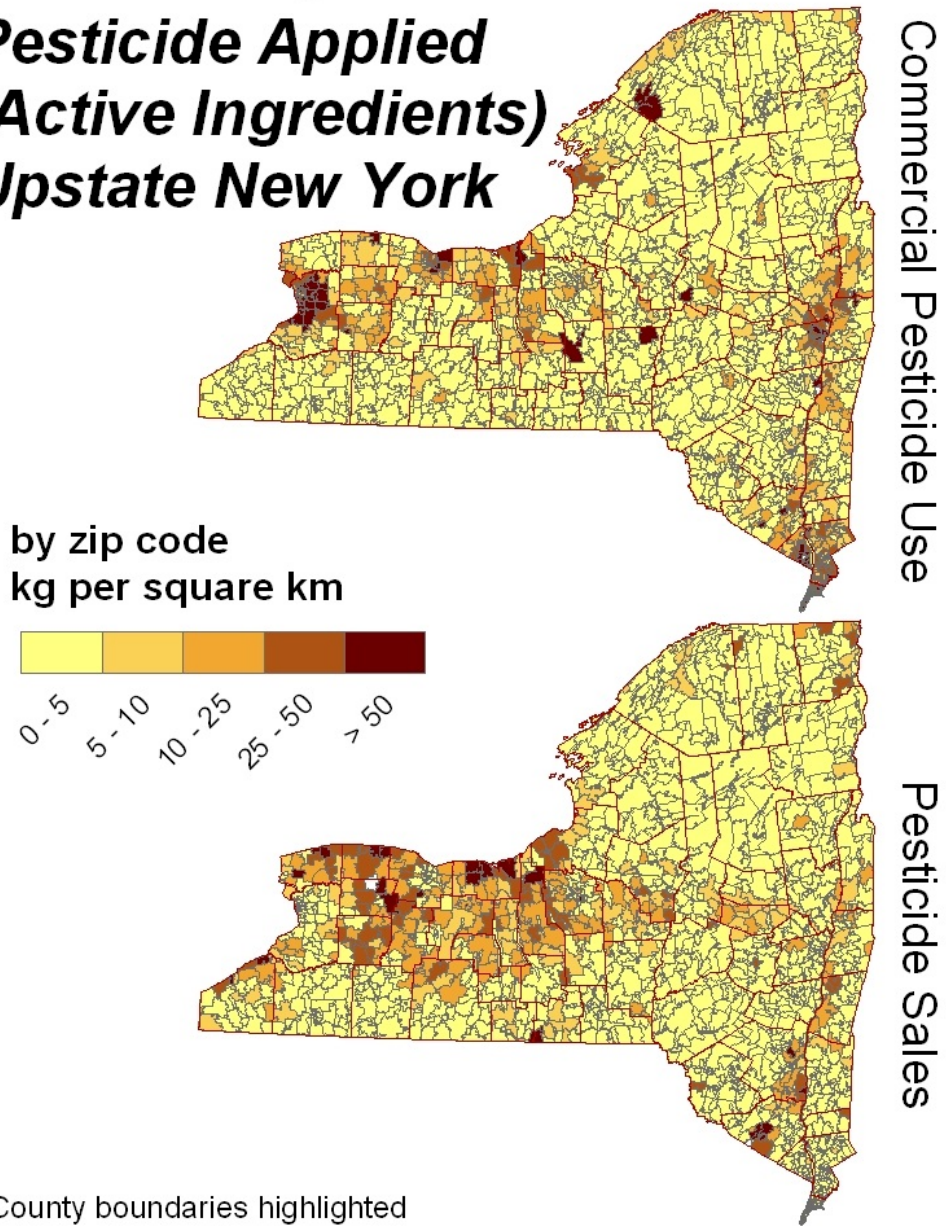


Figure 2.4.3. Commercial pesticide (restricted use active ingredients) applications (top) and pesticide sales (bottom) by zip code.

Likelihood of Pesticide Use Upstate New York

Fraction of Agricultural, Commercial,
Industrial, and Residential Land Uses

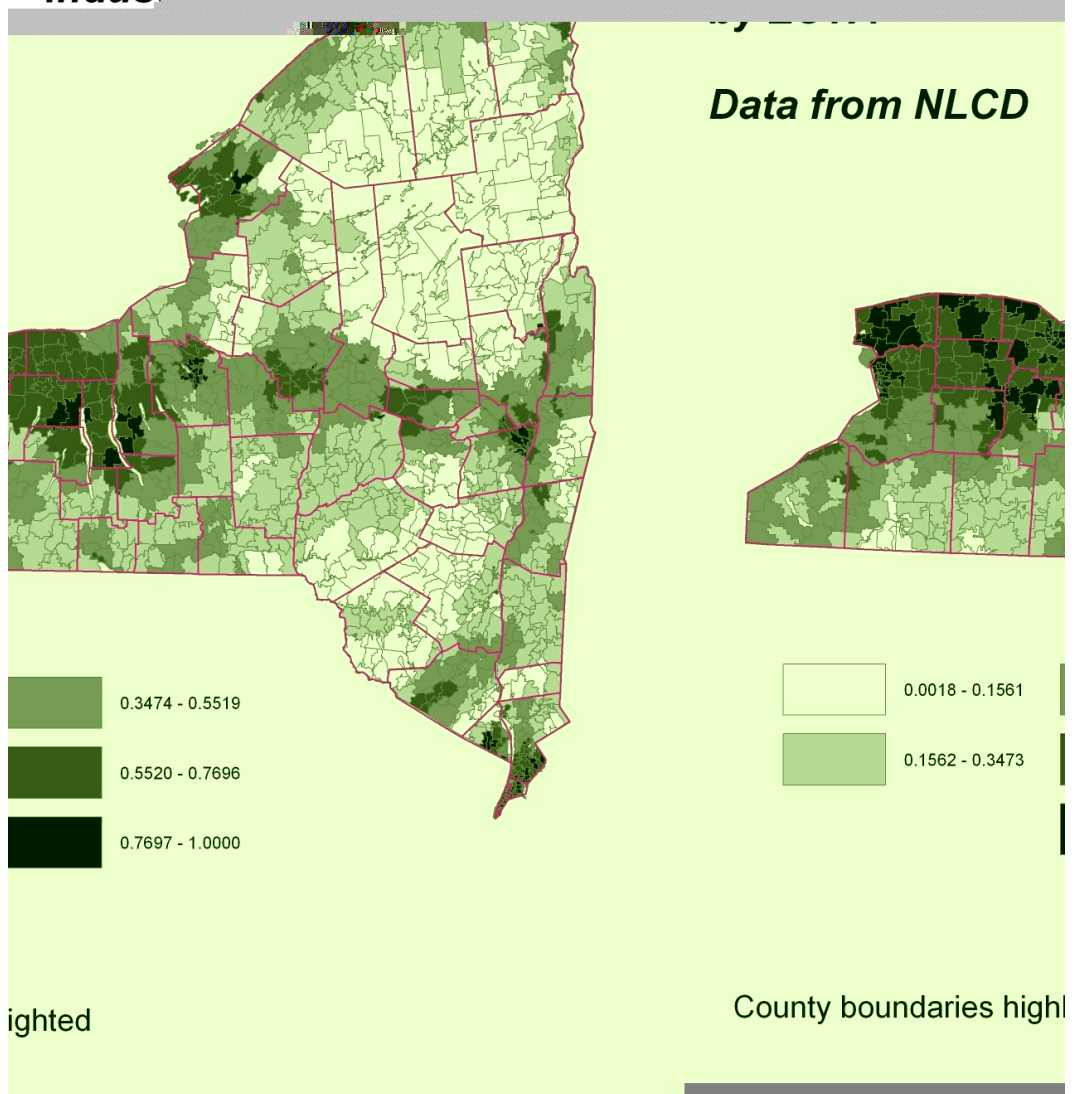
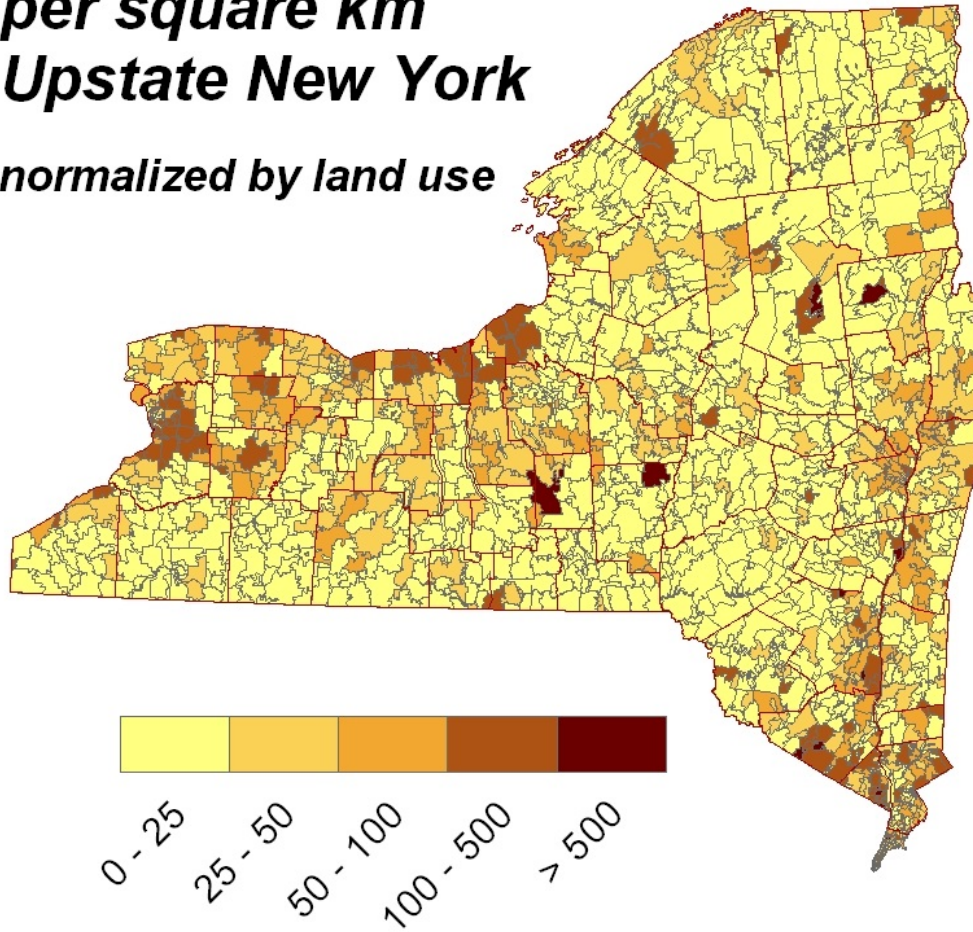


Figure 2.4.4. Likelihood of pesticide use based on land use.

***Kg Restricted Use
Pesticide Applied
(Active Ingredients)
per square km
Upstate New York
normalized by land use***

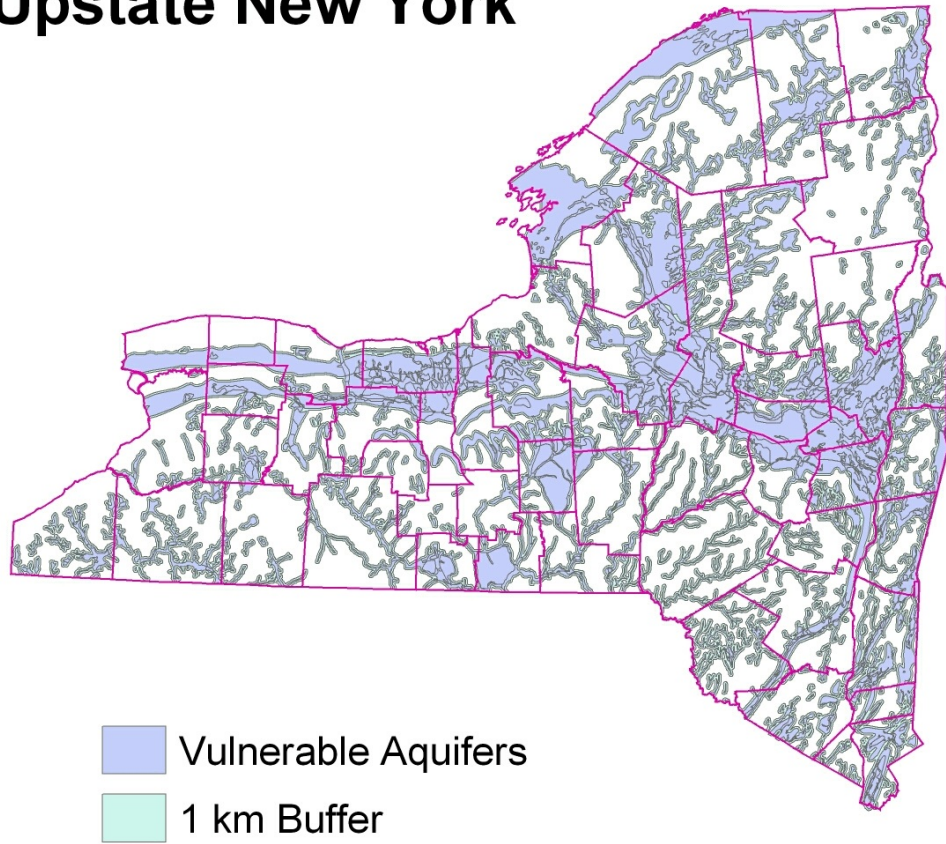


County boundaries highlighted

Figure 2.4.5. Pesticide applications (restricted use active ingredients) normalized by land use.

Carbonate and Surficial Aquifers

Upstate New York



County boundaries highlighted

Figure 2.4.6. Carbonate rock and surficial aquifers, including 1 km buffer zone.

Combination of Pesticide Use and Population Dependent on Groundwater

Upstate New York

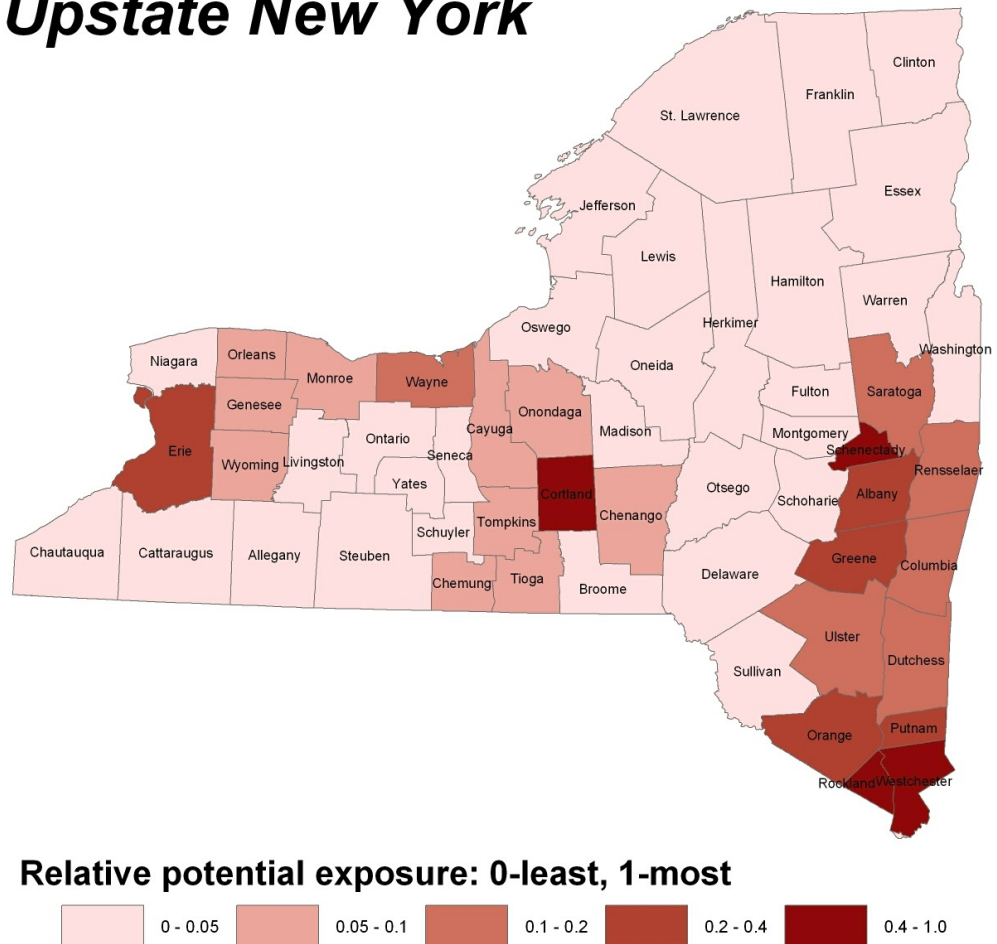


Figure 2.4.7. Relative potential exposure to pesticides in groundwater by county, based on population groundwater dependence and pesticide use. Scaled 0 to 1 (county with greatest exposure index = 1.00).

3. DISCUSSION and ONGOING WORK

This first year project provided a number of useful insights. Experience gained in landowner recruitment is being applied in Year 2 work in Schenectady County. The active participation of the Cortland County Soil & Water Conservation District was invaluable throughout the project and showed the importance of local involvement in the process. Furthermore, the groundwater risk model shown in Section 2 was adapted for use in site identification in Year 2 work underway in Schenectady County.

The unexpectedly elevated detection limits experienced by the NYS DEC laboratories – due in part to interference from organics associated with shallow groundwater and to the wide range of analytes preventing optimization for particular classes – constrain the overall results to confirming that major contamination was not found in the sampled wells for the analytes listed as “general pesticides” in Table 2.1.3; the same conclusions are not tenable with the acid herbicides and carbamates due to the elevated detection limits for those compounds. However, the fact that all ELISA assay results showed that levels of atrazine (and related triazines, given the cross-reactivity of the ELISA assay) were below the 0.1 µg/L limit of quantitation – a level that is 1/30th of the 3 µg/L drinking water standard – gives a high level of certainty that atrazine and related compounds are not present at levels of concern in the wells sampled. With many of the wells sampled in close proximity to corn culture and with all wells selected because they were judged to be relatively vulnerable to contamination, the fact that atrazine detections were so low is reassuring. We anticipate substantially improved detection limits in Year 2 due to more focused analyte targets and submission of multiple larger volume samples.

Nitrate concentrations ranged up to 12.2 mg/L, with a mean of 3.7 ± 3.4 mg/L. Of the 40 wells sampled, three had levels in excess of the 10 mg/L drinking water standard, and nine had levels between 5 and 10 mg/L. Among wells where at least one of the ELISA runs found possible traces of atrazine (as indicated by “<0.1” in Table 2.1.5), mean nitrate levels were 5.5 ± 3.4 mg/L. In contrast, wells where atrazine was not detected (“nd”) in both runs had mean nitrate levels of 2.0 ± 2.4 mg/L. All 12 wells with nitrate-N levels in excess of 5 mg/L had corn fields in near proximity. However, close proximity to corn fields was not a guarantee of elevated nitrate-N levels. In fact, a correlation test of well nitrate concentrations in Section 1 vs. the land-use atrazine risk index used in Section 3 (which used presence of corn culture as a predictor) showed no clear correlation (coefficient of +0.43) between the two data sets.

The results used from the statewide exposure assessment protocol were and are being used to guide selection of candidate counties for subsequent survey work. It was noteworthy that Cortland County emerged from the statewide screening process as one of the two most counties with the greatest potential exposure, based on the screening criteria used. Schenectady was the only county with a comparable score. Based on this process, Schenectady was selected as the candidate for year 2 work. It is recognized that both approaches used for determining pesticide use distributions have limitations. The PSUR pesticide database does not contain direct records of agricultural pesticide applications if applied personally by the farmer (reflected only in the sales database at the zip code level), nor does it record applications by homeowners, and thus does not represent the total picture of the geographic distribution of pesticide applications. The alternative land use approach is

restricted to conjectures of “probable” or “average” use, and depends on assumptions about actual crops and crop rotations. The land use approach is practically limited in this case to agricultural uses. We will continue to evaluate the utility of these approaches.

4. ACKNOWLEDGMENTS

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6. APPENDICES

- A) Landowner Information Handout**
- B) Sampling Protocol**
- C) Sample Information Log Sheet**
- D) Landowner Reporting Form**

A) Landowner information handout (distributed on Cornell letterhead)

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

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

Why? Some areas of NY State - notably Long Island - have had several decades of groundwater monitoring for pesticides. Drinking water wells on Long Island became contaminated as a result of intensive agricultural and suburban use of pesticides on sandy soils and aquifers that allowed the pesticides to leach downward into the groundwater. Conditions in upstate New York are different, and it has long been assumed that there is little probability of groundwater becoming contaminated in the same way. However, little actual sampling of upstate wells has been carried out to confirm this. The NY Department of Environmental Conservation (DEC) wants to confirm the quality of upstate drinking water and as a first step has asked Cornell to carry out a limited, voluntary sampling of drinking water wells in selected areas of Cortland County. Cortland County was chosen because of its location and range of soil and water resources. The goal is to get an accurate "snapshot" of well water quality in areas of the county, 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 and otherwise), relatively shallow groundwater levels, soils that allow leaching, degree of hillslope, etc. While pesticide contamination of groundwater is unlikely, is more likely to occur in wells in these situations as compared to areas where pesticides are rarely used or where the soil resists pesticide leaching. We are trying to locate a range of settings and well types, but due to program constraints can only sample a limited number of wells.

When? We would like to collect samples at a time that is convenient for you. We are particularly interested in sampling during May. The actual sampling would take about 30 minutes.

How? Samples will be collected by Cornell University personnel using a pre-established operating procedure, as shown below. Samples will be taken from landowners' existing plumbing systems if present, or from other existing wells. Personnel would also like to collect any information about the well (depth, age, if it ever goes dry).

Sampling procedure:

- 1) Use new, certified precleaned 950mL (32 oz) amber glass sample containers.
- 2) 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 filters).
- 3) Rinse and dump each sample bottle three times with the water being sampled.

- 4) Fill three sample bottles completely, cap tightly and place bottles in ice chest.
- 5) Return samples to laboratory for preservation and analysis.

What happens to the samples? Each sample will be analyzed at Cornell for nitrate (since nitrate often is found when agricultural pesticides are present in groundwater). We may also analyze for one or more pesticides, depending on the likely pesticide use in the area. Samples will be shipped to NY DEC for a complete pesticide scan. (Because of program limitations, if a site has multiple wells, we would send DEC only a single representative sample from the group.)

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 any pesticide concentrations determined by Cornell and NYS DEC (the DEC data will take longer). In the event that traces of pesticides are found, we will report 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 SWCD. The SWCD would notify relevant county agencies - most likely the Department of Health - to help safeguard the health of people consuming water from the well(s) by taking appropriate remedial and/or preventative measures.

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

- 4) Any published reports about this study will summarize data on a general basis so that the location and concentrations of particular well(s)/land cannot be determined from the report.

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

What's next? If you have been identified as a candidate landowner and are interested in having your well sampled (again, at no cost to you) or have more questions you'd like to ask first, respond to the Cortland County Soil & Water Conservation District. You will be contacted by Cornell University personnel to arrange a convenient sampling time.

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/D). Replicates A and B (large 1000 mL bottles) will be for DEC submission; C and D (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) Surveying Upstate NY Well Water for Pesticide Contamination

Department of Biological & Environmental Engineering, Cornell University
NY Water Resources Institute
Cortland 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 _____ Type _____

Location _____

GPS _____

Water system information (pump, storage, treatment; point of sampling)

Area information (apparent upgradient topography and land use)

[D) EXAMPLE WELL OWNER REPORT]

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

You are receiving this mailing because you participated in the voluntary sampling of drinking water wells in selected areas of Cortland County carried out by Cornell University's Department of Biological & Environmental Engineering, in cooperation with the Cortland County Soil & Water Conservation District. **These results are confidential and are provided without cost to landowners.** Cornell is required to retain a confidential list of all landowner contact information and exact well locations. Your sample code number: ____ Tests run on the well water samples included:

1) Atrazine Atrazine – a common herbicide used for weed control in corn – was tested for at Cornell because of its wide use in agriculture and its ability to move and persist in groundwater supplies. We used a very sensitive test able to quantify atrazine at levels down to 1/30th of the drinking water concentration limit. At most, only traces of atrazine were detected in about half of the samples but at levels that were too low to accurately measure. This was heartening news, because we assumed that atrazine, with relatively high mobility and wide usage, was the most likely pesticide to appear on groundwater in the area.

The result for the water from your well sample was:

- no detectable atrazine
- very low (trace) levels of atrazine detected. Concentrations were below the 0.1 micrograms per liter limit of the test used (less than one tenth of one part per billion (ppb) and far below the US drinking water limit for atrazine of 3 micrograms per liter (3 ppb).

2) Nitrate-nitrogen We tested for nitrate because some researchers suggest that nitrate and pesticide residues may appear together in wells. The drinking water limit for nitrate-nitrogen (NO₃-N) is 10 milligrams per liter (10 parts per million (ppm)), based on levels that protect the health of infants under one year old. Of the wells we sampled in the county, 7.5% had levels slightly in excess of the 10 ppm drinking water standard, and another 22.5% had levels between 5 and 10 ppm.

The result for the water from your well sample was:

- low to moderate: ____ ppm. If levels are in excess of 5 mg/L you may want to consider occasional monitoring of your well.
- high: ____ ppm. This level was in excess of the drinking water standard. *As a result, we would like to retest the water at your convenience to confirm this result.*

In addition, samples were shipped to NY DEC for a broad scan of over 100 insecticides and herbicides. After a long delay, NY DEC tests were run, with the result that no pesticides were detected in any samples tested. However, these results were not as useful as hoped because many of the tests used were not as sensitive as the atrazine scan run at Cornell.

Please contact us with any question or concerns.

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