# Should karst settings receive special attention in New York pesticide registration?

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Underground stream emerges from limestone rock (J. B. Thacher State Park)

Contents

List of Figures

List of Tables

## Summary

Groundwater in karst carbonate terrain has a well-known high sensitivity to pollution, due to sinkholes and solution-widened fractures where surface water and its pollutants can rapidly reach the water table and wells. Groundwater and surface water in a karst area of northeastern Genesee County, NY were monitored for pesticides in 2010-2012, to accumulate field data to help determine if karst settings deserve special attention in New York's pesticide registration.

Besides short retention times between surface and wells, the area is at particular risk from agricultural herbicides because it receives significant amounts of agricultural stream runoff that recharges the aquifer seasonally. Three settings were monitored: an array of superfund monitor wells related to a 1970 solvent spill, together with nearby losing stream reaches that carry agricultural runoff from the south; sinkholes entering the carbonate rock, following a snowmelt event that occurred after local fields had been treated early with herbicides; and private drinking water wells drilled into the carbonate rock. All three sets of samples were analyzed for atrazine and selected other herbicides, anions, and cations. The set of samples from drinking water wells, one sample from the sinkhole set, and three samples representing springs and streams were also tested for a broader array of pesticides.

Groundwater in the 40-50 meters of carbonate rock at the superfund area had very similar seasonal nitrate and herbicide concentrations to the recharging stream reaches. Shale beneath the carbonate had much lower concentrations: no detectable residues of analyzed pesticides and less than half as much nitrate. Residues in the streams and carbonate peaked in June as high as 5 µg/L, after the common atrazine application season, and were all below detection limits by December.

Three of the ten sinkholes sampled had traces of atrazine, and a fourth had a concentration much higher than the 5.0 µg/L maximum of the ELISA method. The same sample tested at DEC's lab had a concentration over 10x the 3 µg/L drinking water standard for atrazine, 16 µg/L Metolachlor, and quantified metabolites of alachlor, metolachlor, and atrazine.

Just one of the drinking water wells in the carbonate had notable herbicide concentrations, up to 3 µg/L metolachlor. A few contained traces of herbicide metabolites. Overall, this sampling did not yield evidence of much exposure to pesticides via private drinking water from this type of rock. This is consistent with other upstate results outside the karst setting -- unlike on Long Island, pesticides rarely reach upstate private drinking water wells at concentrations anywhere near standards, in any aquifer type.

However, the bill of health is not entirely clean. It is clear from the superfund well sampling and non-pesticide incidents in Genesee County that contaminants in surface water do enter this karst ground water system quickly and that the ground water in this aquifer type is more like surface water in the seasonality of herbicide concentrations, which is related to seasonality of herbicide use and seasonality of hydrogeology which are at their "worst" together in the spring. The spring

2012 sinkhole sampling, the Oatka Creek concentration of atrazine above the drinking water standard in June 2010, and earlier USGS surface water sampling demonstrate that surface water can contain transient pesticide concentrations of concern.

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# 1. Purpose and Context

Pesticide contamination to groundwater can pose a risk to the health of individuals and municipalities that use groundwater as their primary source of drinking water. The best nearby example of this can be seen in Long Island (Storen and Stetz, 1984) where Aldicarb pesticide contamination in the aquifer required the addition of filter systems to hundreds of wells to ensure the safety of private water supplies. To help prevent this in the future, the NYSDEC evaluates proposed pesticide uses including timing and amount of pesticide allowed to be applied, using Long Island hydrogeologic conditions as a representative worst case for all of New York. Long Island is considered a worst-case scenario because of the permeable nature of the soil; low percentage of organic matter; shallow, unconfined water table conditions; and because of the importance of this groundwater as a drinking water source. The resulting rules encoded on pesticide labels are important to prevent recurrence of problems on Long Island; however they are based on an area that contains surficial aquifers with thick deposits of unconsolidated glacial sediments, thick soils and sometimes deep water tables. In contrast, large portions of New York State have geological settings with thin soils and shallow water tables. One geologic setting that is well known for its sensitivity to groundwater pollution is karst, which commonly contains sinkholes and solution-widened fractures where surface water can rapidly reach the water table. This report documents a project that monitored groundwater and associated surface water for pesticides in 2010-2012 in a karst area of eastern Genesee County near its corner with Livingston County and Monroe County. The project's objective was to accumulate field data to help determine if karst settings deserve special attention in pesticide registration, analogously to how sand and gravel aquifers of Long Island have received special attention.

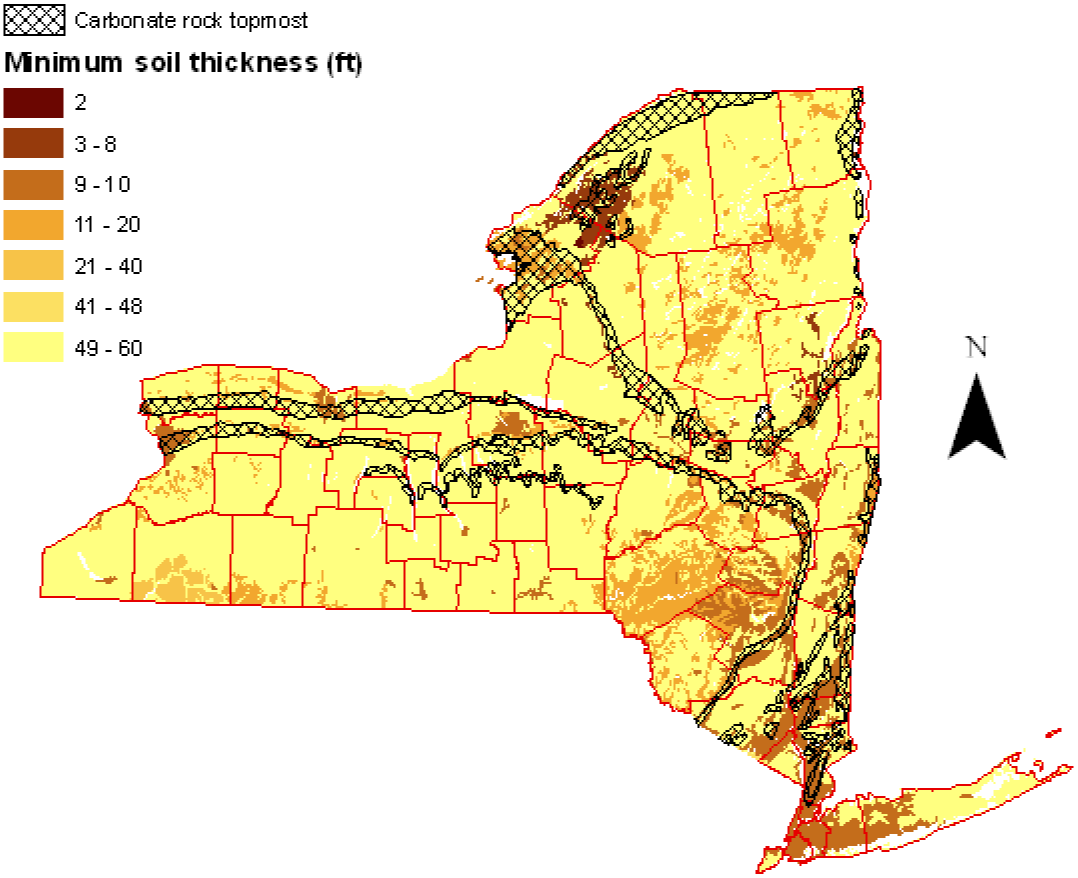

Figure 1: Carbonate rock and shallow soils in NY

## 1.1 Karst: A Sensitive Ground Water Type

New York has large areas where carbonate rock -- limestone or dolostone -- constitutes the uppermost geologic formation (Figure 1). This type of rock is subject to dissolution by acidic percolating waters which enlarge existing openings to create paths for rapid entry, transmission, and exit of water. It is not unusual for dissolution to create conduit and cave systems hosting underground streams, and surface sinkholes that capture overland flow and surface streams. Landscapes rich in sinkholes, caves, swallow holes (sinkholes that "swallow" streamflow), and other dissolution features are termed "karst" after the Kras region of Slovenia and Italy where these hydrogeological features were first documented systematically (Cvijić, 1893).

Carbonate rocks provide 15-20% of the ground water used by public supplies in the US, 5% of ground water used by public supplies in New York, and half of the total water supply in Austria and Slovenia (Maupin and Barber, 2005; COST 65, 1995). New York's carbonate groundwater dependence is lower than the average for the US or Europe, and thus our ground water protection programs focus on the more extensive unconsolidated sedimentary aquifers (NYS DEC, 1990) and give only case-by-case attention to carbonate systems. As part of special case treatment, New York considers springs emanating from karst aquifers to be "ground water under the influence of surface water" when tapped by public water supplies.

Near-surface carbonate ground water systems have inherent vulnerabilities to surface contamination different from unconsolidated sediments and consolidated sandstone and shale. Sinkholes, especially those with large surface catchments as a consequence of being fed by sinking streams, can quickly introduce pollutants into an aquifer (Vesper *et al.*, 2001). The open conduits in karst strata (Figure 2) provide no filtration, a service that users of unconsolidated aquifers rely upon to avoid using point-of-use water treatment. The large apertures of these conduits are capable of transporting a variety of surface pollutants (Vesper *et al.*, 2001; Crain, 2006), including bacteria (Wallace, 1993; Mahler *et al.*, 2000; Davis *et al.*, 2005), pesticides (Pasquarell and Boyer, 1996), and particulates (Atteia and Kozel, 1997). The complexity of flow directions and connectivity within conduit systems leads to uncertainty about which surface pollutant sources link to which well zones (White, 2002). In general, karst aquifers require protective attention that differs from other sorts of aquifers (Kemmerly, 1981; Hubbard and Balfour, 1993; Ray and O'Dell, 1993; Goodman *et al.*, 1994). The protection of New York State aquifers located in karst settings may require similar customized management measures.

**Figure 2: Emergence of flow conduits in limestone (J.B. Thacher State Park)**

Genesee County has had at least four karst-related ground water contamination cases that illustrate the vulnerability of this type of aquifer. In 1970, a trichloroethene (TCE) spill from a railroad car impacted the groundwater that was relied upon as a drinking water source by individual well water supplies of nearly 40 residences and businesses in Leroy and Caledonia, NY. The spill required temporary individual water treatment and eventually extension of a public water supply system into the area (US EPA, 1999; NYS DEC, 1997; Rust Environment & Infrastructure, 1996). The spill was exacerbated when spill responders attempted to dilute the spill plume in soil with water, causing the TCE to move farther in the subsurface through conduits and fractures.   A more recent (2004) Genesee County case involves nitrate and pathogen contamination of private wells north of the City of Batavia.  This case also highlights the role of shallow soils (Figure 1) atop carbonate rock in exacerbating spills.  Manure application on thin soils underlain by fractured limestone was interpreted to be the cause of the contamination.  These cases and others like them have led to changes in manure management advice to farmers from Cornell Cooperative Extension. The revised guidance cites NYS DEC requirements to be sensitive to the presence of karst features within or near fields, mandates setbacks and buffers, and requires incorporation of liquid manure when spread in the spring (Czymmek *et al.*, 2011).

Karst features are well documented and mapped within Genesee County (see Reddy and Kappel, 2010; Richards *et al*., 2010 for a review) but other New York areas with underlying carbonates have not been inventoried and detailed maps are not yet available.

If manure-borne nitrate and pathogens, or spilled solvents, can enter a conduit-laced zone of a carbonate aquifer, so can pesticides.   Furthermore, the short residence time characteristic of karst flow systems means that natural pesticide degradation processes may not have sufficient time to reduce pesticide concentrations as the water moves through the subsurface.  This scenario is in contrast to the majority of groundwater systems where long residence times afford opportunity for pesticide degradation. Thinly-soiled karst areas with shallow water tables may thus be the most sensitive subsurface geologic setting in which pesticide contamination can occur.  The potential problem is not necessarily limited to the "leacher" type of pesticide active ingredient. Investigations in the Barton Springs karst aquifer in Texas demonstrated that an aquifer with well-developed conduits transports sediment as well as solutes (Mahler *et al.*, 1999). Others have shown that normally immobile contaminants can travel freely if sorbed to transported sediments (McCarthy and Zachara, 1989; Richards *et al.*, 2007). The Texas aquifer researchers traced peak transport events for four pesticides and one solvent through the aquifer with lag times of just one week following storms (Mahler and Massei, 2007). In comparison, a stereotypical New York unconsolidated aquifer may take years or decades to flush a sudden pollutant loading to discharge points.

One reason why karst settings have not received much attention from New York's ground water managers is that no large population centers rely on this type of stratum for public water supplies.  Instead villages, hamlets, isolated businesses, and households are the primary carbonate aquifer users.  These small rural water users do not have the extensive protection, treatment, and frequent monitoring that accompany the largest public water supply systems.

## 1.2 Case analysis area: East-west bands of western NY

The dark green and striated pink areas on Figure 3 indicate where the respective Onondaga and Lockport formations of western NY are the uppermost rock.  These two formations are prominent in the landscape because their hard limestone or dolostone is resistant to erosion and thus forms vertical escarpments.  The western Onondaga escarpment and its eastern companion the Helderberg escarpment run across the state from Buffalo to Albany and extend southward into the Hudson Valley.  The Niagara (Lockport) escarpment begins near Syracuse and extends westward as far as the Wisconsin-Illinois border on the far side of Lake Michigan.  These two escarpments mark the northernmost extents where a carbonate formation is the uppermost rock in western New York.  Both formations continue south far beyond their marked southern boundary, buried beneath younger shale rock.

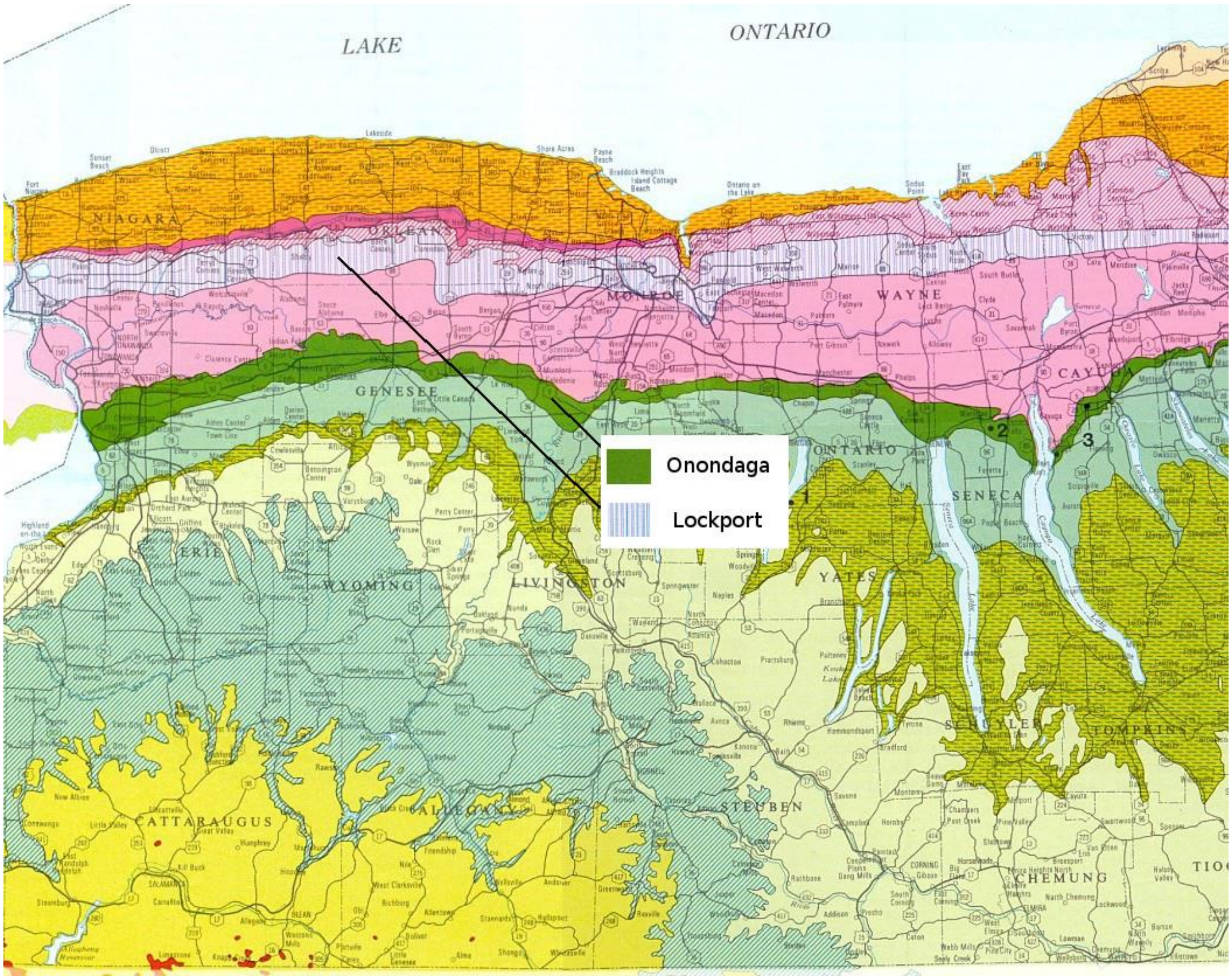

**Figure 3: Western NY uppermost rock**

(Figure 3 source: NYS Geology Map, Fisher *et al.*, 1970)

The Onondaga formation in Western NY lies atop a major "unconformity", representing a geologic time period when rocks older than the Onondaga were eroded away before the Onondaga began to be deposited.  Figure 4 shows the unconformity as a pale yellow interval between the dark green Onondaga and the older pink-represented Salina formation below.  The thick Onondaga sits atop the Salina formation’s much older and thinner Akron and Bertie dolostones, which are also carbonate rock.  Moderately thick shale (Camillus, Syracuse, and

Vernon members) underlies the Akron/Bertie, and finally the Lockport group's carbonate dolostones lay conformably beneath the younger shale. This report focuses on the Onondaga formation where documented water quality problems are more frequent than in the Lockport formation.

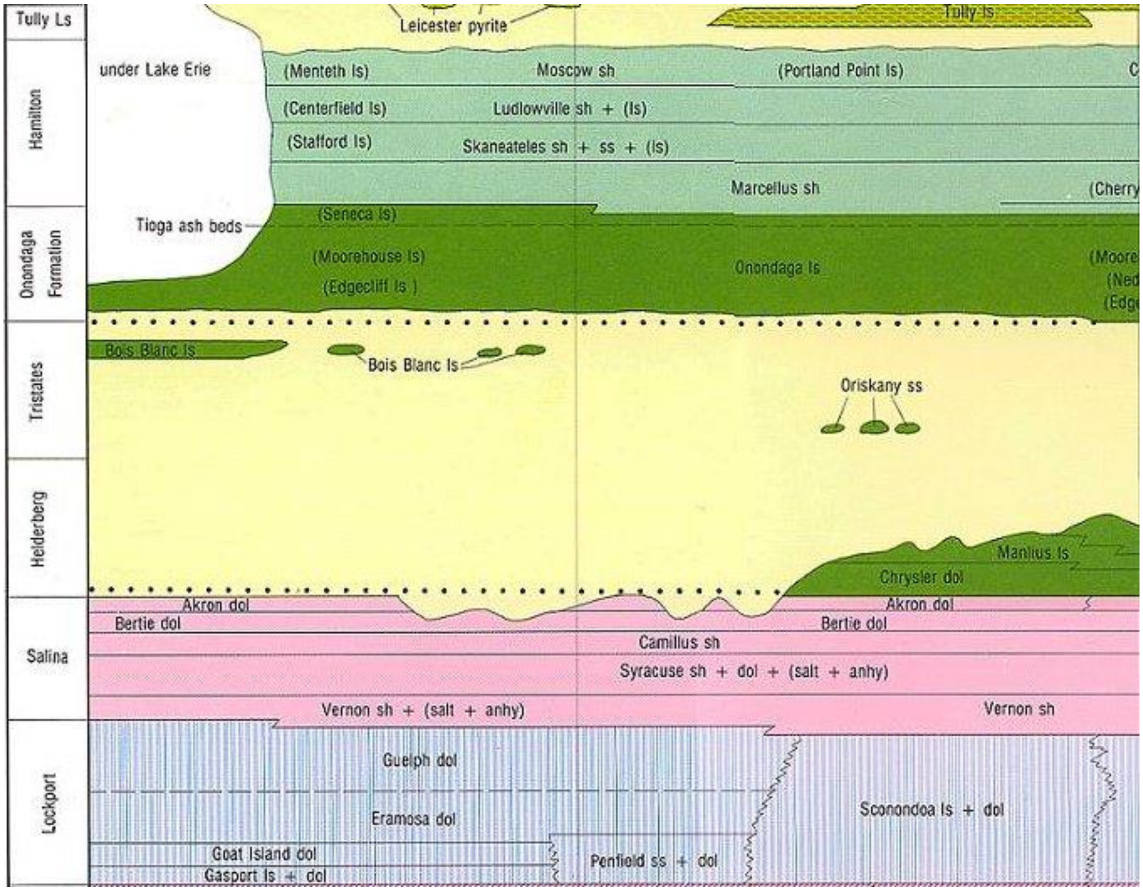

**Figure 4: Schematic of WNY geologic layering, Hamilton fm. to Lockport fm.**

(Source of Figure 4: Adapted from NYS Geology Map, Fisher *et al.*, 1970; yellow represents missing (eroded) layers.)

## 1.3 Objective

This project was designed to initiate a process to determine if it may be necessary to implement special pesticide use guidance in karstic terrain like that in Western NY. This objective was addressed by sampling wells, springs, streams, and sinkholes in a hydrogeologically well-characterized area that is representative of many karst terrains that occur in the state.

## 1.4 Sections of Report

Chapter 2 provides background about specific karst system vulnerability and about the project area's geology and hydrology.

Chapter 3 summarizes the project’s monitoring activity including sampling and analytical protocols.

Chapter 4 presents and interprets sampling results.

Appendices enumerate all sampling locations, samples, and analytical results.

# 2. Monitoring Area

**Figure 5: General sampling area in relation to carbonate in western NY**

(Stippled area represents where carbonate is the uppermost rock type.
Blue and green symbols represent the sampled region for two types
of sampling. The third type -- private wells -- were sampled confidentially
in the central stippled part of Genesee County.)

## 2.1 Three Monitoring Types

The monitoring area is located in Genesee County and small portions of Monroe and Livingston Counties where these two counties share boundaries with Genesee in the Le Roy and Caledonia areas (Figure 5). There were three areas monitored in different fashions:

1. Streams, swallow holes, and monitor wells in a band between Le Roy and Caldeonia -- sampled repeatedly between spring 2010 and fall 2011 to obtain a complete seasonal cycle;

2. Sinkholes that serve as outlets for enclosed surface drainages, and input focal points to the carbonate groundwater system -- sampled once during an April 2012 critical hydrological period following early herbicide application; and
3. Household drinking water wells tapping Onondaga limestone that had been sampled earlier in a 2009 project -- resampled once in spring 2012 shortly after the April critical period.

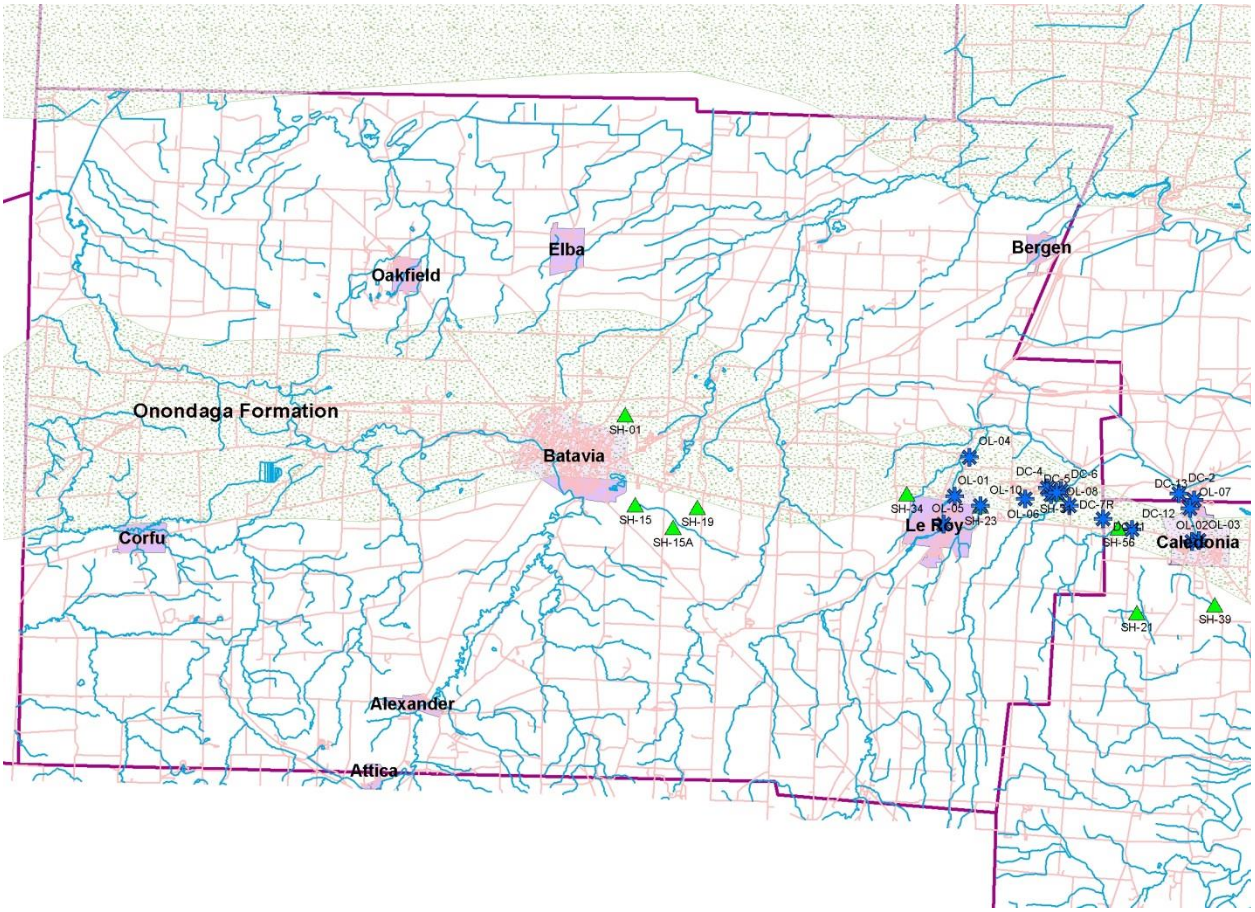

Figure 6: Sinkholes (triangles), monitor wells and streams (stars), and Onondaga formation (stippled; private well zone)

The Villages of Batavia, Leroy, and Caledonia NY (Figure 6) are part of the zone of the karstic limestone Onondaga formation (FM) that, as noted, is present as a narrow band across NY. The unique position of this formation at the base of the Alleghany plateau and its interception of northward flowing streams in western NY have made it especially sensitive to groundwater contamination. Highlands to the south provide extensive recharge areas and high water table gradients which cause this unit to intercept large groundwater fluxes. Streams draining heavily farmed areas farther south flow northward where they are sometimes intercepted by swallets or become losing streams as they flow over the limestone. The Onondaga formation thus receives -

- as point or line recharge -- surface runoff from agricultural and developed areas to the south. Transducers located in sinkholes in the eastern part of the study area indicate that the regional piezometric surface is close to the ground surface and can periodically rise into the soil zone and, in some places, above the ground (Richards and Rhinehart, 2006). This suggests that there are periods when manure and septic wastewater may be flushed over the land surface, bypassing any in-soil treatment and filtration. This problem is exacerbated by the thinness of soils that were left after glacial meltwaters from the ice-age retreat stripped away much of the overburden (Fairchild, 1909). The Onondaga FM in the study area is heavily fractured; a study by Fronk (2001) suggests that many fractures are quite wide (up to 0.1 m), certainly wide enough to transport particulates. In other parts of New York State, the Onondaga FM has been documented to contain extensive cave systems (Mylroie and Palmer, 1977; Matson, 1987; Palmer *et al.*, 1991; Rubin, 1995). Caves have not been observed in our study area; however numerous depressions interpreted to be sinkholes have been documented by Reddy and Kappell (2010) and Richards *et al.* (2010). Video logs of the Camillus and Akron/Bertie FM boreholes commonly show large voids in the subsurface. Rubble-filled features have also been interpreted from geophysical data collected by the consultants who are assessing the fate of a TCE plume in Le Roy.

Richards and Boehm (2012) identified numerous parts of Genesee and northwestern Livingston Counties having enclosed (endorheic) drainages. These have no surface outlet and instead drain into one or more sinkholes that enter the Onondaga formation. These enclosed basins typically contain streams that gather flow then terminate in a wetland at the lowest spot in the basin containing the sinkhole(s).

Reddy and Kappel (2010) refined the mapping of carbonate rock as the uppermost formation in Genesee County.

Note: There are several differences between this monitoring project and earlier monitoring in the Upstate Pesticides in Groundwater series:

- Most samples are from the ambient environment instead of drinking water systems;
- Some samples were from surface water;
- Samples were taken repeatedly from the same sites to reflect seasonal variability, instead of at a single time;
- All samples except a few collected in April and May 2012 were analyzed solely at a Cornell University lab rather than divided among Cornell and NYS DEC's pesticide lab; and
- Sample locations excepting the private wells are not confidential.

## 2.2 Geology

The general study area contains fractured Devonian and Silurian strata. At the base, and exposed in the northeastern part of the streams/monitor wells study area, are the Camillus shale, Falkirk

FM and the Akron/Bertie FM. Overlying these units is the Onondaga FM which consists of four members: Edgecliff, Clarence, Nedrow and Moorehouse. The uppermost Seneca member of the Onondaga FM elsewhere is not present in the study area and has been assumed to have been eroded away by the same glacial meltwater that stripped away much of the soil. Beds dip slightly towards the south with the result that the Onondaga formation both thickens and deepens as one journeys southward. Overlying these rocks to the south of the study area are the younger Marcellus shale, Stafford limestone, and Levanna shale. Pump tests by the NYSDEC (Craft, personal communication, 2009) suggest that these units are not very permeable and that the Stafford limestone is thus not a significant source of water. There are some local structures (e.g., minor folds) in the area that are believed to be due to subsidence (Fairchild, 1909). The Onondaga limestone is extensively fractured with joint sets that trend north, northeast and east-southeast. Mapping by Fronk (1991) indicates these joint sets change with stratigraphic position and are quite variable. Pump tests by Malcom Pirnie (Malcom Pirnie, 2005) suggest that the permeability in the Onondaga is low and dominated by fracture flow. Observations at Buttermilk Falls on Oatka Creek north of Le Roy and numerous quarry exposures show strong evidence of extensive fracture flow. Geochemical evidence has determined that this flow is a mixture of surface water and groundwater (Libby, 2010).

The few streams that exist in the area are fairly straight and parallel to fracture traces which may indicate their position is structurally controlled. This is also supported by the occurrence of sinkholes within stream valleys of Mud Creek and Oatka Creek in Genesee County. All of the northward-flowing tributaries east of the Town of Leroy disappear near NY Route 5, with the exception of Mud Creek. These streams presumably terminate in sinkholes and contribute surface water directly into the local aquifer. Mud Creek flows into a sinkhole just south of Gulf Road, at the former Lehigh Valley railway right of way. While this stream is not terminated at the sinkhole, flow measurements indicate that much of the flow in this creek is lost to this feature. The eastern part of the study area contains broken craggy relief with numerous depressions and hummocky ridges. Information on subsurface flow paths is scant, but, a TCE plume mapped for the NYDEC (Dunn Geos. Eng., 1992) suggests groundwater flows east-southeast from Leroy and discharges at the springs of Caledonia. This is also supported by water table contour information.

## 2.3 Flow paths of the stream and monitor well monitoring area

Several sinkhole systems exist in the study area, which intermittently receive surface drainage: Le Roy golf course sinkhole, Mud Creek sinkhole, Site 55 sinkhole, Waterfalls sinkhole, Cemetery sinkhole under Oatka Creek, and Site 56 sinkhole (Figure 7 below). Of these sites, the golf course sinkhole and Cemetery sinkhole receive drainage throughout the year, while the others receive drainage between November and late April, and occasionally during large storm events outside that interval. These input periods coincide with the period that water tables in the study area are at the highest and closest to the surface. Figure 7 also presents the probable subsurface flow direction in the study area; a major groundwater flow path apparently exists from Gulf Road (Mud Creek sinkhole) to the springs of Caledonia. This flowpath picks up agricultural runoff from tributaries that intersect the Mud Creek, Waterfalls, and Site 55 sinkholes. The path then surfaces near Mackay Spring and Big Spring in downtown Caledonia, where the discharged water flows to Oatka Creek via Spring Creek. Since the groundwater elevation increases to the west towards Oatka Creek, the possibility exists that this flowpath extends all the way to Oatka Creek at the Cemetery sinkhole, where the thesis by Libby (2010) has determined that a significant amount of flow is lost from the creek. If this is the case, this groundwater flowpath also picks up the runoff entering the golf course sinkhole.

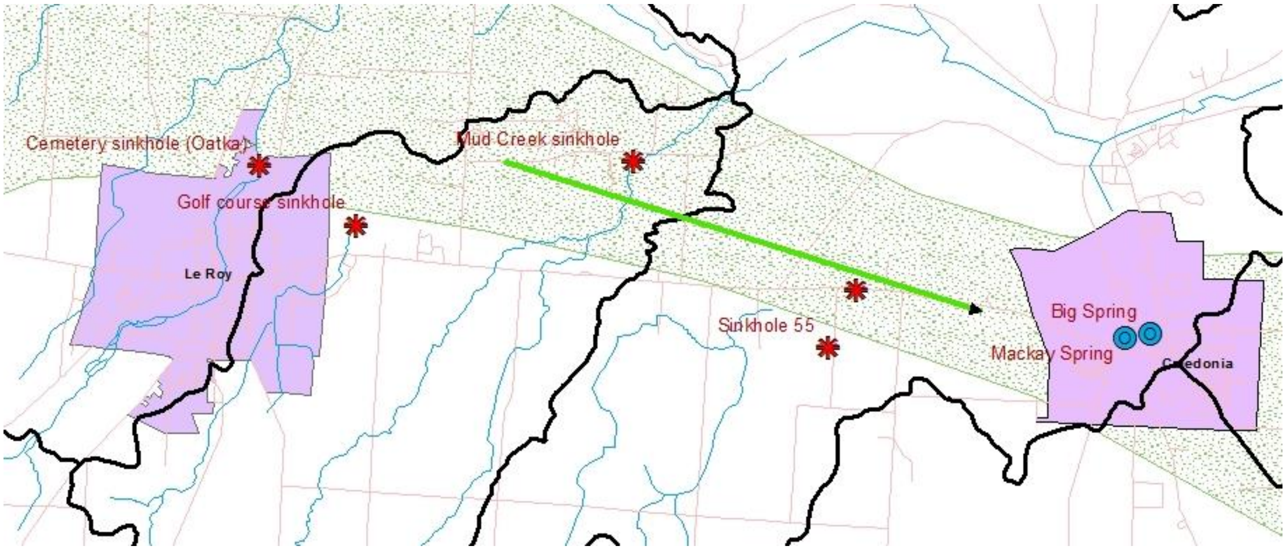

Figure 7: Sinkholes, probable subsurface flow path, and outflow springs

The cemetery sinkhole in Oatka Creek at the northern edge of the village of Le Roy drinks in much of the streamflow at times. Figure 8 shows the depleted streambed shortly before the first June 2010 sample collection in this study. This zone is just above Buttermilk Falls at which Oatka Creek falls over the edge of the Onondaga escarpment.

Figure 8: Swallow-hole depleted flow in Oatka Creek below Le Roy, June 2010

Piezometric data collected in well clusters associated with the Lehigh Valley Superfund site (the aforementioned railroad car TCE spill) show that groundwater flow is generally downward through the Onondaga to the Akron/Bertie Group below the unconformity at the base of the Onondaga. Thus, in this eastward trending groundwater flowpath, flow moves progressively from the Nedrow to the Morehouse to the Edgecliff to the Akron/Bertie FMs. Based on the hydrogeologic characteristics of the stratigraphic units in the study area and the depth and distribution of screened intervals of monitor wells in the study area, the wells in the study area sample three hydrostratigraphic intervals: 1) the Onondaga FM where flow is downward and constrained within secondary fractures; 2) the Akron Bertie Group which is believed to be the dominant eastward bearing flow zone by virtue of the piezometric and videolog data; and 3) the Camillus shale which contains very large voids and is also a dominant flowzone (Dunn Geoscience Engineering, 1992). Flow in the Camillus has an upward vertical component suggesting its source water comes from deeper. Mackay Spring, one of the important springs in Caledonia, is located at the base of the Edgecliff FM and receives water from the Akron-Bertie interval. An unpublished spring survey along Oatka Creek determined 29 active springs along

Oatka Creek at the base of the escarpment (Richards, *et al.*, 2012). These springs receive their water from the Onondaga hydrostratigraphic interval, implying some leakage of groundwater from the escarpment northward directly into Oatka Creek. A secondary flow system thus exists where groundwater can move northward from the study area. This secondary flow system is well developed at the base of Circular Hill Road and where Mud Creek enters Oatka Creek. This groundwater flow system is not considered to be important from a mass flow perspective as flow measurements suggest it is much smaller than the springs at Caledonia (Richards *et al.*, 2012). The Eastward trending groundwater flowpath is thus considered to be the dominant groundwater flowpath in the study area.

Based on the previous work we can make the following statements about the study area:

- The dominant groundwater flowpath is eastward from Leroy to Caledonia. This flowpath picks up discharge from most of the sinkholes in the study area.
- The setting is at high risk for groundwater contamination because of its thin soil, shallow water table, evidence of solution-widened fractures, and numerous sinkholes.
- The study area receives significant amounts of agricultural runoff from the south and west.
- The study area is thus an excellent candidate for determining if pesticide use poses a risk in this type of setting to the extent that additional pesticide BMP measures need to be taken for karst terrains.

## 2.4 Sampling sites within the streams, swallow hole, and monitor wells area

This area contains an array of superfund monitor wells from the 1970 TCE spill. (The wells are 1990's vintage.) Figure 9 shows a blend of surface water sampling sites (OL-*n*) and superfund monitor well clusters (DC-*n*). Site OL-01 is the Machpelah Cemetery swallow hole on Oatka Creek in Le Roy. Moving eastward, the Quarry site OL-06 is downgradient from Oatka Creek and fills rapidly in spring when water levels in the monitor wells also rise. Flow continues eastward toward the group of monitor well sites DC-2, DC-4, DC-5, and DC-6 which are near the solvent spill near Gulf Road. Farther downgradient sites to the east, DC-7R, DC-11, and DC-12, follow the originally expected solvent plume toward Caledonia where well DC-13 is the easternmost and most downgradient. Surface water sites OL-02 and OL-03 represent the Mackay and Big Springs in Caledonia, respectively.

A few other sites were sampled occasionally. Stream sites OL-05 and OL-04 are on Oatka Creek above and below the Cemetery sinkhole, OL-07 is in Spring Creek below the springs area (downstream of OL-02 and OL-03), OL-08 represents a large swallow hole on Mud Creek, and OL-10 is a swallow hole at the terminus (within the LeRoy Country Club) of a stream draining the eastern side of Le Roy.

Figure 10 shows a vertical section of this flowpath based on the monitor well logs and topographic maps. Different grays identify the upper Onondaga (lightest), then the lower Onondaga limestone and Scajaquada dolostone bracketing the unconformity (medium), and finally the lowest Camillus shale (darkest). Table 1 describes the rock layers and Table 2 correlates wells with layers. In Table 2, letter suffices A through D represent wells in a cluster with successively deeper screened intervals.

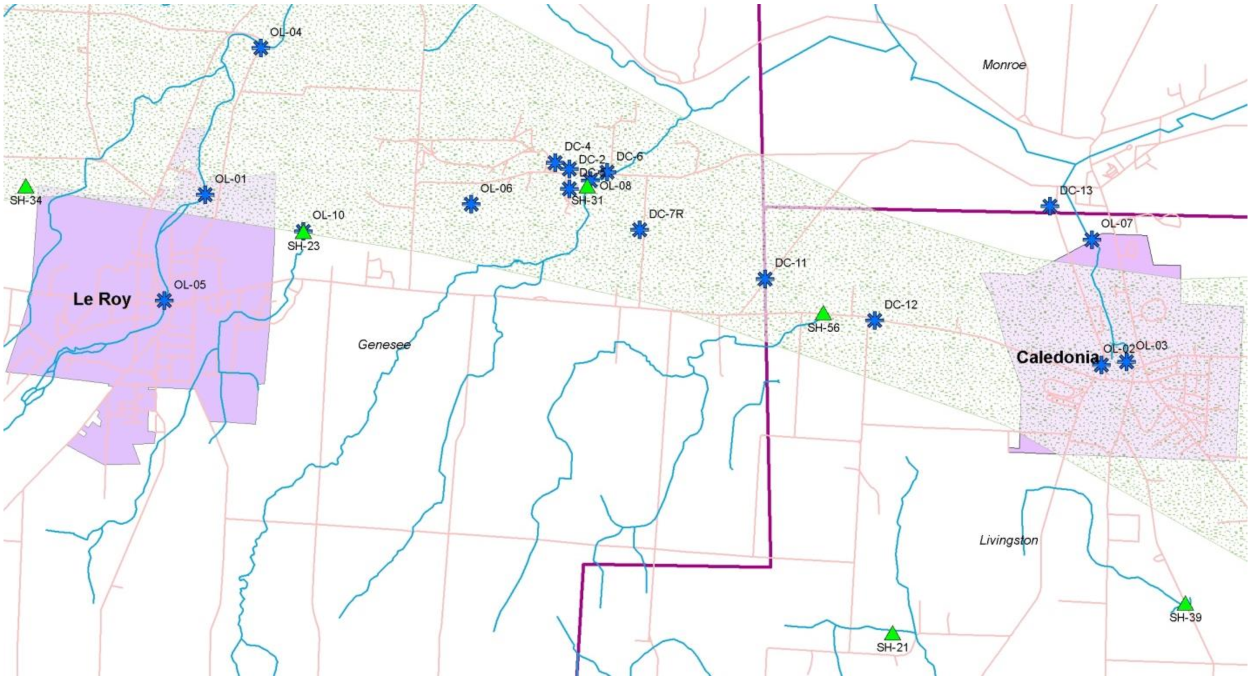

Figure 9: Monitoring sites of the Superfund area

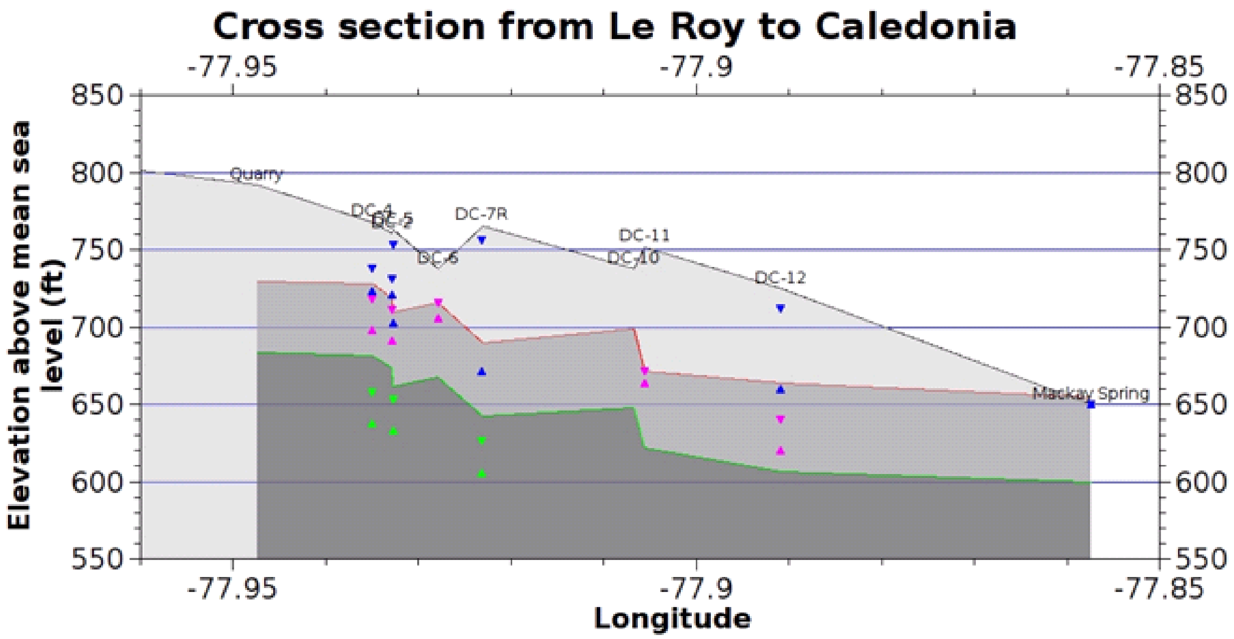

Figure 10: Three vertical zones of the Le Roy - Caledonia section

**Table 1: Geologic formation details (from newest to oldest rock)**

| Member | Group or formation | Deposition Period | Rock type |
|---|---|---|---|
| Nedrow | Onondaga | Middle Devonian | Limestone |
| Clarence | Onondaga | Middle Devonian | Limestone |
| Edgecliff | Onondaga | Middle Devonian | Limestone |
| (unconformity) | | | |
| Bois Blanc | Tristates | Early Devonian | Dolostone |
| (unconformity) | | | |
| Scajaquada | Salina | Late Silurian | Dolostone |
| Falkirk | Salina | Late Silurian | Dolostone |
| Camillus | Salina | Late Silurian | Shale |

**Table 2: Sampling locations correlated with rock**

| Site | Type | Surf Elev (ft) | Elev top screen (ft) | Elev bot screen (ft) | Rock in screened interval (*italic* indicates carbonate) | Layer in Fig 10 |
|---|---|---|---|---|---|---|
| DC-2A | Well | 761 | 761 | 721 | *Clarence* | surface |
| DC-2B | Well | 761 | 711 | 691 | *Bois Blanc, Scajaquada, Falkirk* | middle |
| DC-4A | Well | 768 | 738 | 723 | *Clarence, Edgecliff* | surface |
| DC-4B | Well | 768 | 718 | 698 | *Bois Blanc, Scajaquada, Falkirk* | middle |
| DC-4C | Well | 768 | 658 | 638 | Camillus | bottom |
| DC-5A | Well | 763 | 753 | 703 | *Nedrow, Clarence, Edgecliff* | surface |
| DC-5B | Well | 763 | 703 | 683 | *Edgecliff, Bois Blanc, Scajaquada, Falkirk* | |
| DC-5C | Well | 763 | 653 | 633 | Camillus | bottom |
| DC-6A | Well | 738 | 738 | 708 | *Clarence, Edgecliff* | middle |
| DC-7RA | Well | 766 | 756 | 671 | *Nedrow, Clarence, Edgecliff, Falkirk* | surface |
| DC-7RC | Well | 766 | 664 | 642 | Camillus | bottom |
| DC-11A | Well | 752 | 680 | 656 | *Clarence, Edgecliff, Bois Blanc* | middle |
| DC-12A | Well | 725 | 712 | 660 | Nedrow, *Clarence, Edgecliff* | surface |
| DC-13A | Well | 650 | 640 | 625 | Camillus | bottom |
| OL-01 | Stream (Oatka Cr) | 810 | | | Enters *Clarence* | surface |
| OL-02 | Spring (Mackay) | 650 | | | Emerges from *Edgecliff* | middle |
| OL-03 | Spring/ stream (Big Spring) | 650 | | | Emerges from *Edgecliff* | middle |
| OL-04 | Stream (Oatka Cr) | | | | Clarence? | surface |
| OL-05 | Stream (Oatka Cr.) | | | | (Above karst area) | surface |
| OL-06 | Quarry | 790 | 790 (rim) | 720?? (floor) | Base in *Edgecliff*? | surface, middle |
| OL-07 | Stream (Spring Cr) | | | | | bottom |
| OL-08 | Stream (Mud Cr.) | | | | | surface |
| OL-09 | Snow | | | | | |
| OL-10 | Stream | | | | | |

(Well data in Tables 1 and 2 are based on well logs in Rust Environment & Infrastructure, 1997.)

## 2.5 Spring 2012 sinkhole sampling sites

As discussed above there are numerous locations in the Genesee/Livingston Onondaga FM karst area where liquid in a stream channel disappears into a sinkhole instead of remaining in a surface watercourse channel. The water eventually re-emerges in springs if it is not intercepted by wells. Typically such a stream dead-ends into a wetland which covers the sinkhole entry to a solution-enhanced subsurface path. Brockport College personnel had studied many enclosed topographic basins recently and chose ten from which to collect water samples from streams near their disappearance. Table 3 enumerates the selected list. Figures 6 and 9 showed the sampled locations as green stars.

The timing of the samples was intentional and took advantage of unusual spring weather. Unseasonably warm temperatures in March and April 2012 dried out fields and enabled farms to prepare for planting in April, a few weeks earlier than usual. Some farmers applied herbicides early according to local observers. Then temperatures plunged briefly and a snowstorm dropped 61mm of water-equivalent snow at Rochester Airport in the April 21-24 period. The snow melted quickly when temperatures rose to 17C during daytimes of April 25-26. Rapid surface and shallow subsurface runoff would have carried recently applied soluble chemicals (such as atrazine) toward streams including the ones which disappear into sinkholes.

This sequence of a runoff event shortly after herbicide application has a quantitatively low probability, but qualitatively was not unusual for this region. Eckhardt *et al.* (2000) described how a 50 mm/2 hour storm in June 1998 mobilized peak concentrations of 29 µg/L metolachlor and 10 µg/L atrazine in small tributaries to Cayuga Lake. Phillips *et al.* (2000) reported atrazine concentrations in tributaries to reservoirs used by LeRoy and Perry, NY reaching 8-11 and 21 µg/L respectively during June 1998 storms.

Extensive aldicarb contamination of wells in eastern Long Island probably was influenced by cool spring temperatures combined with April insecticide applications at the planting of potatoes. Cooler air and soil temperatures during this time of year encourage liquid flow through soil by inhibiting evaporation. Limited leaf area reduces transpiration and uptake of systemic crop protection chemicals. Cooler temperatures also slow biodegradation and chemical degradation of the pesticide active ingredients. Shorter daytimes provide less opportunity for photo degradation. In general this time of year is favorable to pesticide mobility. It also is a unison season for herbicide application, and in the earlier Long Island case a time for unison insecticide application.

Near-sinkhole samples were collected during the snowmelt event of April 25 and 26.

Table 3: Spring 2012 sinkhole sampling sites

| ID | General location | Surf elev (ft) |
|---|---|---|
| SH-01 | west of Genesee Community College, Batavia | 890 |
| SH-15 | Route 63, southeast of Batavia | 875 |
| SH-15A | Townline Road, Batavia | 925 |
| SH-19 | Fargo Road, Stafford | 920 |
| SH-21 | Railroad line, Caledonia | 730 |
| SH-23 | Le Roy golf course sinkhole (same as OL-10) | 810 |
| SH-31 | Gulf Road, Le Roy | 740 |
| SH-34 | Quinlan Road, Le Roy | 865 |
| SH-39 | Middle Rd, Caledonia | 660 |
| SH-56 | Rte 5 Limerock | 745 |

(Source: Richards and Boehm (2012) except elevations, which were read from USGS topographic maps.)

## 2.6 Spring 2012 private drinking water well resampling sites

In 2009 a survey of pesticide concentrations in 40 Genesee County wells was carried out in an earlier project in this series. A subset of these wells was selected for resampling in spring 2012, via renewed agreements with the landowners (Table 4). Many private drinking water wells in Genesee County penetrate the same rock. Not all of the owners know that their wells tap limestone – the sites sampled in 2009 were compared to known aquifer presence and thicknesses to select a subset for resampling. Their geochemical data, especially calcium and magnesium, were also compared to geochemical data in known carbonate wells.

Another well definitely in carbonate had a second sample in 2009 following the discovery of an elevated metolachlor concentration, then a third sample in 2010.

The locations of these wells are confidential by agreement with the land owners, thus only the general vicinity is disclosed in this report to regulators.

Table 4: Spring 2012 private drinking water well resampling sites

| Well number | Years sampled | Comment | Mailing zip code |
|---|---|---|---|
| GC-06 | 2009, 2012 | North of Onondaga escarpment, possible influence of carbonate, 30 ft deep. | 14482 (Le Roy) |
| GC-07 | 2009, 2010 | Definite carbonate, well uncased to 140 ft depth (through Onondaga, into unconformity?). Well had 2-3 µg/L metolachlor in two 2009 samplings. High nitrate > 10 mg N/L. | 14482 (Le Roy) |
| GC-14 | 2009, 2012 | Carbonate, 45 ft deep. | 14036 (Corfu) |
| GC-19 | 2009, 2012 | Probable carbonate | 14020 (Batavia) |
| GC-25 | 2009, 2012 | Probable carbonate | 14020 (Batavia) |
| GC-27 | 2009, 2012 | Probable carbonate | 14020 (Batavia) |
| GC-66 | 2009, 2012 | Shale | 14020 (Batavia) |
| GC-81 | 2012 | Opportunistic well near GC-06, almost certainly older carbonate | 14482 (Le Roy) |

# 3. Sampling and Analysis in Three Types of Area

## 3.1 Sampling times

Samples were collected along the Le Roy – Caledonia section from streams, springs, monitor wells, and a quarry several times between June 2010 and September 2011. Samples were collected from sinkholes entering the Onondaga limestone during late April 2012, following a snowmelt event that occurred after local fields had been treated early with herbicides. This was opportunistic. Drinking water wells that had been sampled in June 2009 were resampled in early May 2012.

All three sets of samples were analyzed for atrazine and selected other pesticides, anions, and cations. The set of samples from drinking water wells, one sample from the sinkhole set, and three samples representing springs and streams were also tested for a wider array of pesticides, at increased sensitivity compared to the 2009 samples.

## 3.2 Sample collection and handling

Stream and spring samples were collected via grab sampling from shore, in a flowing part of the cross section and below the surface. (The "spring" samples are actually in flowing water in streams tens to hundreds of feet downstream from the spring emergence.) The sampling device used by Cornell personnel in June 2010 was a HDPE bottle on a long handle, which was filled and dumped several times before drawing the actual sample and pouring into the final sample bottles. Brockport University personnel, who did all other stream sampling, also used 500ml acid-washed bottles to obtain grab samples. Sample containers were Nalgene or equivalent HDPE types.

Spring 2012 sinkhole samples were similar to surface water grab samples, in very shallow water upstream from where it sinks into the subsurface, using a container rinsed several times in the flow before a final filling.

Spring 2012 drinking water well samples were collected by Cornell personnel into acid-washed (certified precleaned) HDPE bottles from the owners' taps, prior to any onsite treatment. Typically this is an outdoor tap. The tap is opened and allowed to run for at least three minutes to bring water into the well from the surrounding aquifer. The bottles were rinsed twice with flowing liquid, and finally the bottles were filled and sealed allowing airspace for expansion during freezing.

Brockport personnel collected all monitor well samples, using a PVC bailer. The bailer was rinsed twice with well water before it was refilled and used to fill sample containers. Unfortunately, it was not possible to purge the monitor wells before sampling because water withdrawn from them is technically hazardous waste due to the 1970 railroad solvent spill.

Samples were generally chilled onsite, then frozen after return to home bases in Brockport or Ithaca. The Brockport samples were re-frozen for longer-term storage in Ithaca. No preservatives were added. A small amount of each sample was vacuum filtered through 0.45 micron Millipore membrane filters at Brockport, then refrigerated until analysis.

## 3.3 Analytical methods

Most lab analyses reported here were performed at the Cornell Biological and Environmental Engineering, Soil and Water Group lab. Anions (nitrate, chloride, and sulfate) were determined by ion chromatography using a Dionex IC-2000 with anion column. Most anion aliquots were diluted 5x or 10x to reduce the interference of high sulfate with nitrate detection. Lower detection limits were typically 0.5 ppm for nitrate as nitrogen, 8 ppm for chloride, and 2 ppm for sulfate as sulfur. (Individual sample detection limits take into account dilution.) Formal MDL tests with the same apparatus and EPA methodology yielded nitrate-nitrogen detection limits of 0.2-0.5 ppm, better than the estimated limits applied in this report.

Note that samples processed by the IC are filtered during analysis to protect the column.

Unfiltered cation aliquots were tested via inductively coupled plasma atomic emission spectroscopy (ICP-AES; Thermo Jarrel Ash, 61E Trace Analyzer). Cation aliquots did not require dilution. Detection limits for cations are typically 1 ppm, and are determined on a case by case basis according to the coefficient of variation computed from three replicate analyses from the same vial; data are only reported as detects if the CV is under 5%.

Pesticide concentrations were determined using Strategic Diagnostics Incorporated (SDI) ELISA kits for atrazine, metolachlor, and alachlor. For all three kits the manufacturer specified a MDL of 0.05 ppb and quantification limit of 0.1 ppb; values between the detection and quantification limits are reported as "trace". Except for one sample reported as ">5 ppb", the methods' upper bound of 5 ppb was not exceeded thus no dilution was necessary. (The available volume of that sample was too small to permit diluted re-analysis.) ELISA analyses were performed in duplicate and the average reported. The SDI ELISA method has a built-in quality assurance procedure in the form of five criteria that must be satisfied. (Note: The Strategic Diagnostics Inc. company's water quality division was sold to the Modern Water PLC company in 2011 during this project; technical notes are still attributed to the earlier manufacturer.)

The following paragraphs are adapted from metadata provided by Peter Furdyna of the NYS DEC Division of Air Laboratory (now responsible for pesticides), with the analyte list and reporting limits summarized in Table 5:

> *Water samples from Cornell were submitted to the NYSDEC Pesticides Laboratory (now operated by Division of Air Resources) in July 2012. 47 pesticide and herbicide compounds (including some environmental breakdown products) were analyzed by*

*direct injection followed by UPLC/MS-MS. Additionally, Dithiopyr was analyzed using the Quechers extraction technique followed by gas chromatography/mass spectrometry (GC/MS). Quality control consisted of analyzing reagent blanks, method blanks (DI water), matrix spikes, and matrix spike duplicates. All target chemicals were spiked for QC analyses. Spike levels were 1 pbb in most cases, excepting 5 ppb and 10 ppb for dithiopyr and AMPA (a glyphosate breakdown product) respectively.*

*Spike recovery information is as follows: For UPLC/MS-MS direct injection pesticide samples, recoveries ranged from 12% to 151%. Dithiopyr spiked at 5 ppb and analyzed via GC/MS recovered at 125%-158%. AMPA spiked at 10 ppb had UPLC/MS-MS recoveries ranging from81% to 102%.*

**Table 5: Method reporting limits of pesticide/herbicide analyses run by the NYS DEC laboratory.**

| **Analyte** | **Reporting Limit** | **Method Code*** | **Analyte** | **Reporting Limit** | **Method Code*** |
|---|---|---|---|---|---|
| ***Base Neutral Parent Chemicals*** | | | ***Base Neutral Metabolites & Sulfentrazone*** | | |
| Aldicarb | <0.1µg/L | U | 3-Hydroxy Carbofuran | <0.1µg/L | U |
| Atrazine | <0.1µg/L | U | Aldicarb Sulfone | <0.2µg/L | U |
| Azinphos Methyl | <0.1µg/L | U | Aldicarb Sulfoxide | <0.1µg/L | U |
| Azoxystrobin | <0.2µg/L | U | De Ethyl Atrazine | <0.1µg/L | U |
| Carbaryl | <0.1µg/L | U | De Isopropyl Atrazine | <0.1µg/L | U |
| Carbendazim | <0.1µg/L | U | Hydroxy Atrazine | <0.1µg/L | U |
| Carbofuran | <0.1µg/L | U | Sulfentrazone | <0.2µg/L | U |
| Chlorosulfuron | <0.1µg/L | U | | | |
| Clethodim | <0.1µg/L | U | ***Acid Metabolites & Acid Herbicides*** | | |
| Cyprodynil | <0.1µg/L | U | 2,4-D | <0.1µg/L | U |
| Diazinon | <0.1µg/L | U | Alachlor - OA | <0.1µg/L | U |
| Dimethoate | <0.1µg/L | U | Alachlor - ESA | <0.1µg/L | U |
| Dithiopyr | <1µg/L | G | Clopyralid | <0.2µg/L | U |
| Diuron | <0.1µg/L | U | Dicamba | <0.1µg/L | U |
| Fluazafop-p-butyl | <0.2µg/L | U | MCPA | <0.1µg/L | U |
| Halofenozide | <0.1µg/L | U | MCPP | <0.1µg/L | U |
| Imazalil | <0.2µg/L | U | Metolachlor ESA | <0.1µg/L | U |
| Imidacloprid | <0.1µg/L | U | Metolachlor OA | <0.1µg/L | U |
| Malathion | <0.2µg/L | U | | | |
| Metalaxyl | <0.1µg/L | U | ***Special Analytes*** | | |
| Methomyl | <0.1µg/L | U | AMPA | <1µg/L | U |
| Metolachlor | <0.2µg/L | U | Captan | unstable | |
| Metsulfuron Methyl | <0.1µg/L | U | | | |
| Nicosulfuron | <0.1µg/L | U | | | |
| Oxamyl | <0.1µg/L | U | | | |
| Oxydemeton Methyl | <0.1µg/L | U | | | |
| Propamocarb | <0.1µg/L | U | | | |
| Propoxur | <0.1µg/L | U | | | |
| Prosulfuron | <0.1µg/L | U | | | |
| Simazine | <0.1µg/L | U | | | |
| Tebuconazole | <0.1µg/L | U | | | |
| Tebufenozide | <0.1µg/L | U | | | |
| Thiacloprid | <0.1µg/L | U | | | |
| Thiamethoxam | <0.1µg/L | U | | | |
| Thifensulfuron Methyl | <0.1µg/L | U | | | |
| Thiodicarb | <0.1µg/L | U | | | |

* Method codes: U - UPLC/MS-MS; G - GC/SIM-MS.

# 4. Results and Interpretation

## 4.1 Superfund wells and nearby surface waters

Table 6 and Figure 11 provide an overview of herbicide and nitrate analytical results by layer of the earlier Figure 10. (See Appendix A for detailed results.) Detected amounts and traces were similar in the top two layers. The bottom shale has much lower concentrations: no detectable residues of either pesticide and less than half as much nitrate.

Table 6: Atrazine, metolachlor, and nitrate patterns by vertical layer

| **Atrazine** | **Layer** | **# nd <0.05** | **# trace <0.1** | **# detect >=0.1** |
|---|---|---|---|---|
| | top | 17 | 2 | 3 |
| | middle | 12 | 6 | 1 |
| | bottom | 9 | 0 | 0 |
| **Metolachlor** | **Layer** | **# nd < 0.05** | **# trace < 0.1** | **# detect >=0.1** |
| | top | 7 | 4 | 2 |
| | middle | 6 | 3 | 2 |
| | bottom | 6 | 0 | 0 |
| **Nitrate-N (mg/L)** | **Layer** | **Min** | **Mean** | **Max** |
| | top | 0.1 | 1.7 | 4.4 |
| | middle | 0.1 | 1.5 | 3.9 |
| | bottom | 0.1 | 0.6 | 1.5 |

Figure 11 indicates that the top two layers also exhibit similar seasonality of concentrations. Residues peaked in June after the common atrazine application season, and were all below detection limits by December.

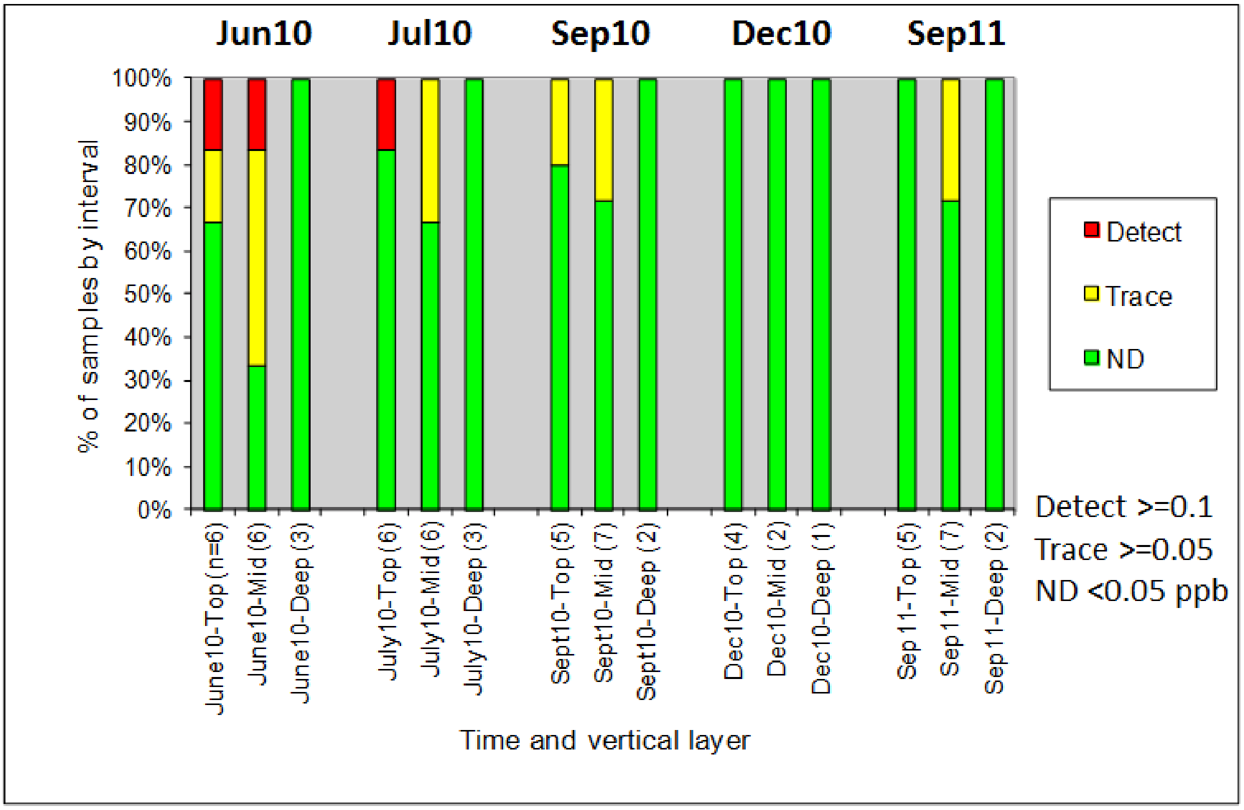

Figure 11: Seasonality of atrazine detections

The similar seasonality of the two upper layers indicates that there is close coupling between their transport times and recharge quality. Recharge – autogenic, or allogenic from swallowed stream water – apparently penetrates to the depth of the middle zone, 75 - 125 feet below the land surface except at the eastern extremity, quickly. This consistency of seasonality is due to the solution-enhanced fractures that allow easy and rapid access of surface water to both layers. Seasonality in sand and gravel aquifers this deep would be far less.

## 4.2 Sinkholes during a critical period

Three of the ten sinkholes sampled had traces of atrazine, and a fourth, SH-01, had a concentration much higher than the 5.0 µg/L limit of the ELISA test when using undiluted samples (Table 7). The SH-01 sample tested at DEC's lab had a concentration over 10x the 3.0 drinking water standard for Atrazine, 16 µg/L Metolachlor, and quantified metabolites of alachlor, metolachlor, and atrazine. The surface catchment of SH-01 is almost all farmland and possibly is under the control of a single farmer. The results for SH-01 illustrate how local point recharge to limestone can contain herbicide concentrations greatly above a drinking water standard if there is a critical hydrological event shortly after an application period. This finding is identical to that in spring stormwater sampling by USGS in 1998, cited earlier. The much lower results for the other sinkholes indicate great spatial variability, likely resulting from different farmer preferences in the catchment and different fractions of land treated before the event.

Table 7: Analytical results from April 2012 sinkhole samples

| lab | parameter | SH-01 | SH-15 | SH-15A | SH-19 | SH-21 | SH-23 | SH-31 | SH-34 | SH-39 | SH-56 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| CORNELL | Atrazine | >10.3 | nd | nd | nd | trace <0.1 | nd | trace <0.1 | nd | nd | trace <0.1 |
| CORNELL | Calcium | 27.3 | 29.4 | 41.1 | 42.1 | 56.2 | 26.0 | 41.2 | 31.7 | 43.3 | 38.0 |
| CORNELL | Chloride | 12.0 | 26.5 | 42.8 | 5.1 | 14.8 | 20.0 | 42.2 | 39.9 | 54.8 | 30.7 |
| CORNELL | Potassium | 1.7 | 1.5 | 1.8 | 1.2 | 12.1 | 1.0 | 4.0 | 2.3 | 3.6 | 6.0 |
| CORNELL | Magnesium | 3.8 | 7.5 | 10.8 | 14.1 | 30.6 | 8.6 | 16.9 | 18.1 | 27.1 | 20.1 |
| CORNELL | Sodium | 1.3 | 10.1 | 18.3 | 1.3 | 19.3 | 7.2 | 14.9 | 16.8 | 20 | 11.3 |
| CORNELL | Nitrate-N | 1.1 | nd | nd | nd | 5.9 | 0.6 | 9.2 | nd | 1.5 | 4.4 |
| CORNELL | Sulfur (ICP) | 1.5 | 2.7 | 3.2 | 5.2 | 13.1 | 3.1 | 7.1 | 4.1 | 6.4 | 8.5 |
| CORNELL | Sulfate (IC) | 5.4 | 9.6 | 9.2 | 15.1 | 11.5 | 9.9 | 21 | 29.6 | 19.3 | 24.6 |
| NYSDEC | Alachlor - OA | 0.13 | | | | | | | | | |
| NYSDEC | Alachlor - ESA | 0.22 | | | | | | | | | |
| NYSDEC | Atrazine | 40.8 | | | | | | | | | |
| NYSDEC | De Ethyl Atrazine | 3.42 | | | | | | | | | |
| NYSDEC | De Isopropyl Atrazine | 0.88 | | | | | | | | | |
| NYSDEC | Hydroxy Atrazine | 1.0 | | | | | | | | | |
| NYSDEC | Metolachlor | 16.3 | | | | | | | | | |
| NYSDEC | Metolachlor ESA | 2.89 | | | | | | | | | |
| NYSDEC | Metolachlor OA | 2.55 | | | | | | | | | |
| NYSDEC | (all other analytes) | nd | | | | | | | | | |

## 4.3 Private wells and other sites, DEC

The monitor well and surface water sampling results illustrated that herbicides penetrate quickly into the limestone aquifer. It is possible that other parts of the karst zone have less pronounced seasonality. Table 7 shows repeated samples from a farm drinking water well tapping the Onondaga formation a few miles west of Le Roy. It had been sampled twice in a prior pesticide monitoring project in this series. An additional sample in 2010 had nearly identical results: notable metolachlor and nitrate, plus minor amounts of atrazine.

Table 8: Analytical results, Genesee County private well GC-07

| **Date** | **6/2/09** | **8/11/09 (as GC-79)** | **6/23/10** |
|---|---|---|---|
| ELISA metolachlor (ppb) | 2.6 | 3.0 | 2.9 |
| ELISA atrazine (ppb) | nd | trace <0.1 | 0.2 |
| ELISA alachlor (ppb) | | | trace <0.1 |
| UPLC-MSMS metolachlor (ppb) | 3.7 | 2.0 | (not analyzed) |
| Nitrate-N (mg/L) | 15 | 13 | 12.7 |

(UPLC-MSMS analysis by NYS DEC Pesticide Lab. All other analysis by Cornell University.)

DEC's lab resumed accepting samples before the end of the project and was able to test 2012 samples from private drinking water wells. The site GC-07 which was sampled in 2009 in the earlier Genesee County project of this series had been resampled shortly after we found the original 3 µg/L metolachlor via ELISA; the resample showed a similar concentration. DEC's lab had found values consistent with these. In 2010 this site again showed metolachlor around 3.0.

The remaining Genesee drinking water wells identified in Table 4 above were sampled in 2012 about one week after the sinkholes were sampled. The OL-01 and OL-02 surface water sites were sampled on the same trip to provide a link to the superfund area sampling in 2010-2011. As in 2009, the sampled drinking water wells were all clear of atrazine down to the 0.05 µg/L ELISA method detection limit. However three of seven wells contained a metolachlor metabolite above DEC's reporting limit 0.1 µg/L. The OL-01 and OL-02 samples contained the same metabolite and traces of atrazine via ELISA (under 0.1 µg/L which would not be detectable at the DEC lab). The surface water atrazine results were consistent with the 2010-2011 superfund zone samplings and these two sites also contained the metolachlor metabolite found in three wells. None of the detected concentrations has significance for drinking water thus the homeowners were not cautioned about using their well water. However, the presence of the metolachlor metabolite does indicate that the wells are downgradient from herbicide-treated areas which might at some other season or year yield higher concentrations.

Table 9: Analytical results from private wells and reference surface water, early May 2012 (one well June 2010)

| **lab** | **parameter** | **GC-06** | **GC-14** | **GC-19** | **GC-25** | **GC-27** | **GC-66** | **GC-81** | **GC-07 (2010)** | **OL-01 Oatka Creek** | **OL-02 Mackay Spring** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| CORNELL | Alachlor | | | | | | | | trace | | |
| CORNELL | Atrazine | nd | nd | nd | nd | nd | nd | nd | 0.2 | trace | trace |
| CORNELL | Metolachlor | | | | | | | | 2.9 | | |
| | | | | | | | | | | | |
| *CORNELL* | *Atrazine (2009-2011 range)* | *nd* | *nd* | *nd* | *nd* | *nd* | *nd* | | *nd-trace* | *nd-3.2* | *nd-trace* |
| | | | | | | | | | | | |
| CORNELL | Calcium | 53.2 | 72.1 | 52.9 | 78.8 | 63.0 | 62.5 | 150.5 | 41.2 | 27.5 | 140.3 |

| **lab** | **parameter** | **GC-06** | **GC-14** | **GC-19** | **GC-25** | **GC-27** | **GC-66** | **GC-81** | **GC-07 (2010)** | **OL-01 Oatka Creek** | **OL-02 Mackay Spring** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| CORNELL | Chloride | 31.3 | 118.3 | 39.2 | 260.3 | 48.3 | 25.4 | 31.9 | 111.0 | 42.7 | 54.2 |
| CORNELL | Potassium | 3.4 | 2.1 | 2.0 | 5.7 | 1.2 | 2.7 | 2.5 | 2.5 | 3.0 | 4.8 |
| CORNELL | Magnesium | 41.3 | 48.4 | 36.9 | 47.7 | 33.7 | 46.5 | 39.3 | 14.5 | 12.2 | 22.7 |
| CORNELL | Sodium | 9.9 | 25.9 | 8.7 | 69.0 | 8.6 | 7.6 | 11.1 | 18.9 | 16.4 | 20.2 |
| CORNELL | Nitrate-N | 2.1 | nd | nd | nd | 0.8 | nd | 2.6 | 12.7 | 1.4 | interf* |
| CORNELL | Sulfur (ICP) | 58.7 | 19.6 | 15.2 | 19.2 | 21.1 | 26.3 | 89.7 | 6.8 | 6.5 | 91.3 |
| CORNELL | Sulfate (IC) | 151.5 | 54.5 | 43.8 | 43.1 | 59.3 | 71.3 | 227.5 | 37.9 | 19.8 | 228.9 |
| *CORNELL* | *Nitrate-N (2010-2011 range)* | | | | | | | | *13-15* | *nd-3.6* | *nd-1.8* |
| NYSDEC | 2,4-D | nd | nd | nd | nd | nd | nd | nd | | nd | nd |
| NYSDEC | 3 Hydroxy Carbofuran | nd | nd | nd | nd | nd | nd | nd | | nd | nd |
| NYSDEC | Alachlor - OA | nd | nd | nd | nd | nd | nd | nd | | nd | nd |
| NYSDEC | Alachlor - ESA | nd | nd | nd | nd | nd | nd | nd | | nd | nd |
| NYSDEC | Aldicarb | nd | nd | nd | nd | nd | nd | nd | | nd | nd |
| NYSDEC | Aldicarb Sulfone | nd | nd | nd | nd | nd | nd | nd | | nd | nd |
| NYSDEC | Aldicarb Sulfoxide | nd | nd | nd | nd | nd | nd | nd | | nd | nd |
| NYSDEC | AMPA | nd | nd | nd | nd | nd | nd | nd | | nd | nd |
| NYSDEC | Atrazine | nd | nd | nd | nd | nd | nd | nd | | nd | nd |
| NYSDEC | Azinphos Methyl | nd | nd | nd | nd | nd | nd | nd | | nd | nd |
| NYSDEC | Azoxystrobin | nd | nd | nd | nd | nd | nd | nd | | nd | nd |
| NYSDEC | Carbaryl | nd | nd | nd | nd | nd | nd | nd | | nd | nd |
| NYSDEC | Carbendazim | nd | nd | nd | nd | nd | nd | nd | | nd | nd |
| NYSDEC | Carbofuran | nd | nd | nd | nd | nd | nd | nd | | nd | nd |
| NYSDEC | Chlorosulfuron | nd | nd | nd | nd | nd | nd | nd | | nd | nd |
| NYSDEC | Clethodim | nd | nd | nd | nd | nd | nd | nd | | nd | nd |
| NYSDEC | Clopyralid | nd | nd | nd | nd | nd | nd | nd | | nd | nd |
| NYSDEC | Cyprodynil | nd | nd | nd | nd | nd | nd | nd | | nd | nd |
| NYSDEC | De Ethyl Atrazine | nd | nd | nd | nd | nd | nd | nd | | nd | nd |
| NYSDEC | De Isopropyl Atrazine | nd | nd | nd | nd | nd | nd | nd | | nd | nd |
| NYSDEC | Diazinon | nd | nd | nd | nd | nd | nd | nd | | nd | nd |
| NYSDEC | Dicamba | nd | nd | nd | nd | nd | nd | nd | | nd | nd |
| NYSDEC | Dimethoate | nd | nd | nd | nd | nd | nd | nd | | nd | nd |
| NYSDEC | Dithiopyr | nd | nd | nd | nd | nd | nd | nd | | nd | nd |
| NYSDEC | Diuron | nd | nd | nd | nd | nd | nd | nd | | nd | nd |
| NYSDEC | Fluazafop-p-butyl | nd | nd | nd | nd | nd | nd | nd | | nd | nd |
| NYSDEC | Halofenozide | nd | nd | nd | nd | nd | nd | nd | | nd | nd |
| NYSDEC | Hydroxy Atrazine | nd | nd | nd | nd | nd | nd | nd | | nd | nd |
| NYSDEC | Imazalil | nd | nd | nd | nd | nd | nd | nd | | nd | nd |
| NYSDEC | Imidacloprid | nd | nd | nd | nd | nd | nd | nd | | nd | nd |
| NYSDEC | Malathion | nd | nd | nd | nd | nd | nd | nd | | nd | nd |
| NYSDEC | MCPA | nd | nd | nd | nd | nd | nd | nd | | nd | nd |

| lab | parameter | GC-06 | GC-14 | GC-19 | GC-25 | GC-27 | GC-66 | GC-81 | GC-07 (2010) | OL-01 Oatka Creek | OL-02 Mackay Spring |
|---|---|---|---|---|---|---|---|---|---|---|---|
| NYSDEC | MCPP | nd | nd | nd | nd | nd | nd | nd |  | nd | nd |
| NYSDEC | Metalaxyl | nd | nd | nd | nd | nd | nd | nd |  | nd | nd |
| NYSDEC | Methomyl | nd | nd | nd | nd | nd | nd | nd |  | nd | nd |
| NYSDEC | Metolachlor | nd | nd | nd | nd | nd | nd | nd |  | nd | nd |
| NYSDEC | Metolachlor ESA | 0.2 | nd | nd | nd | 0.5 | nd | 0.1 |  | 0.8 | 0.8 |
| NYSDEC | Metolachlor OA | nd | nd | nd | nd | nd | nd | nd |  | 0.3 | nd |
| NYSDEC | Metsulfuron Methyl | nd | nd | nd | nd | nd | nd | nd |  | nd | nd |
| NYSDEC | Nicosulfuron | nd | nd | nd | nd | nd | nd | nd |  | nd | nd |
| NYSDEC | Oxamyl | nd | nd | nd | nd | nd | nd | nd |  | nd | nd |
| NYSDEC | Oxydemeton Methyl | nd | nd | nd | nd | nd | nd | nd |  | nd | nd |
| NYSDEC | Propamocarb | nd | nd | nd | nd | nd | nd | nd |  | nd | nd |
| NYSDEC | Propoxur | nd | nd | nd | nd | nd | nd | nd |  | nd | nd |
| NYSDEC | Prosulfuron | nd | nd | nd | nd | nd | nd | nd |  | nd | nd |
| NYSDEC | Simazine | nd | nd | nd | nd | nd | nd | nd |  | nd | nd |
| NYSDEC | Sulfentrazone | nd | nd | nd | nd | nd | nd | nd |  | nd | nd |
| NYSDEC | Tebuconazole | nd | nd | nd | nd | nd | nd | nd |  | nd | nd |
| NYSDEC | Tebufenozide | nd | nd | nd | nd | nd | nd | nd |  | nd | nd |
| NYSDEC | Thiacloprid | nd | nd | nd | nd | nd | nd | nd |  | nd | nd |
| NYSDEC | Thiamethoxam | nd | nd | nd | nd | nd | nd | nd |  | nd | nd |
| NYSDEC | Thifensulfuron Methyl | nd | nd | nd | nd | nd | nd | nd |  | nd | nd |
| NYSDEC | Thiodicarb | nd | nd | nd | nd | nd | nd | nd |  | nd | nd |

* high sulfate masking low nitrate

## 4.4 Discussion

Sampling for pesticides in the karst area in Genesee County and the LeRoy corner of Livingston and Monroe Counties has not yielded evidence of much exposure to pesticides via private drinking water from this type of rock. One drinking water well had elevated (but below standard) concentrations of one herbicide in three samplings, and three of seven wells had minor amounts of an environmental breakdown product of the same herbicide. This is consistent with other upstate results outside the karst setting -- unlike on Long Island, pesticides rarely reach upstate private drinking water wells at concentrations anywhere near standards, in any aquifer type.

However, the bill of health is not entirely clean. It is clear from the superfund well sampling and non-pesticide incidents in Genesee County that contaminants in surface water do enter this karst ground water system quickly and that the ground water in this aquifer type is more like surface water in the seasonality of herbicide concentrations, which is related to seasonality of herbicide use and seasonality of hydrogeology which are at their "worst" together in the spring. The spring 2012 sinkhole sampling, the OL-01 (Oatka Creek) concentration of atrazine above the drinking water standard in June 2010, and earlier USGS surface water sampling demonstrate that surface water can contain transient pesticide concentrations of concern.

Potential follow up:

- There is not (yet) a case for special pesticide label wording in New York about karst settings.
- Cornell Cooperative Extension does include this aspect in its training about nutrient management for relevant regions of New York (Czymmek *et al.*, 2011).
- Continue sampling selected private or monitor wells in karst areas, emphasizing the spring herbicide season. It would be helpful if the location could be disclosed.
- Continue sampling surface water at sites above swallow holes that recharge karst aquifers, also emphasizing the spring herbicide season. Oatka Creek at LeRoy should be a suitable site.

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Mikki Smith and Jamye Babocsi, SUNY Brockport students, did most sampling.

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Shree Giri of Cornell BEE performed all ICP cations analyses. Cornell students Austin Merboth and Christopher Perry, and Portugese student Carla Sofia Ferreira assisted in analytical work.

# Appendix A: Analytical results arrayed by site, depth, and time

## Table 10: Analytical results arranged by layer and time

| | | Onondaga formation | | | | | | Older carbonate | | | | | | | | | Oldest shale | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **parameter** | **date** | OL-01 | DC-4A | DC-2A | DC-5A | DC-7RA | DC-12A | DC-4B | DC-2B | DC-5B | DC-6A | DC-11A | DC-12B | DC-13A | OL-02 | OL-03 | DC-4C | DC-5C | DC-7RC | OL-07 |
| Atrazine | 06/09/2010 | 3.2 | nd | nd | nd | trace | nd | nd | nd | nd | 0.6 | trace | | trace | trace | | nd | nd | nd | |
| (µg/l) | 07/26/2010 | | nd | nd | nd | 0.1 | nd | nd | nd | | nd | trace | | trace | nd | nd | nd | nd | nd | |
| | 09/08/2010 | trace | | nd | nd | | nd | nd | nd | nd | nd | trace | nd | nd | trace | trace | nd | nd | | trace |
| | 12/30/2010 | nd | | nd | nd | | nd | | nd | nd | | | | | nd | nd | | nd | | |
| | 09/09/2011 | trace | nd | nd | nd | | | nd | nd | nd | nd | | | | | | nd | nd | | |
| | 09/14/2011 | | | | | | nd | | | | | | trace | | trace | trace | | | | |
| | 09/21/2011 | | | | | | | | | | | | | trace | | | | | | trace |
| | 05/03/2012 | trace | | | | | | | | | | | | | trace | nd | | | | |
| Chloride | 06/09/2010 | 30.7 | 6.9 | 4.9 | 13.5 | 59.9 | 78.0 | 9.7 | 39.6 | 39.0 | 46.3 | 64.2 | | 45.9 | 54.8 | | 21.9 | 24.0 | 37.9 | |
| (mg/l) | 07/26/2010 | | 12.6 | 4.5 | 8.4 | 91.5 | 80.3 | 20.8 | 6.5 | | 10.3 | 85.2 | | 65.6 | 62.3 | 39.2 | 25.0 | 49.8 | 24.8 | |
| | 09/08/2010 | 72.5 | | 1.8 | 33.3 | | 165.3 | 12.3 | 30.3 | 31.1 | 15.0 | 65.0 | 41.6 | 52.2 | 61.8 | 64.5 | 20.6 | 23.1 | | 60.2 |
| | 12/30/2010 | 49.5 | | 5.5 | 32.2 | | 14.4 | | 8.6 | 23.6 | | | | | 32.3 | 57.7 | | 13.1 | | |
| | 09/09/2011 | 61.8 | 6.5 | 3.3 | 14.5 | | | 12.5 | 29.3 | 26.1 | 42.7 | | | | | | 17.6 | 19.3 | | |
| | 09/14/2011 | | | | | | 140.9 | | | | | 56.5 | 37.8 | | 53.5 | 51.7 | | | | |
| | 09/21/2011 | | | | | | | | | | | | | 43.3 | | | | | | 53.2 |
| | 05/03/2012 | 42.7 | | | | | | | | | | | | | 54.2 | 55.7 | | | | |
| Metolachlor | 06/09/2010 | 2.5 | trace | nd | nd | nd | trace | nd | nd | nd | 0.5 | 0.1 | | nd | trace | | nd | nd | nd | |
| (µg/l) | 07/26/2010 | | trace | nd | nd | trace | nd | nd | trace | | nd | trace | | nd | nd | nd | nd | nd | nd | |
| Nitrate-N | 06/09/2010 | 3.6 | 0.5 | 1.5 | nd | 1.2 | 3.8 | nd | 0.6 | 0.6 | 3.9 | 2.1 | | 2.5 | 1.7 | | nd | nd | 1.4 | |
| (mg/l) | 07/26/2010 | | 0.0 | 1.6 | 0.0 | 2.8 | 4.4 | 0.1 | 0.6 | | 0.8 | 2.5 | | 3.6 | 1.8 | 0.8 | 0.3 | 0.6 | 0.8 | |
| | 09/08/2010 | nd | | 1.6 | 0.8 | | 3.5 | nd | 0.5 | nd | 0.6 | 1.1 | 1.6 | 2.2 | 0.8 | nd | nd | 0.4 | | 1.1 |
| | 12/30/2010 | 2.5 | | 1.1 | 1.1 | | 6.2 | | 1.0 | 0.5 | | | | | 1.8 | 2.5 | | 2.5 | | |
| | 09/09/2011 | nd | nd | nd | nd | | | nd | nd | nd | nd | | | | | | nd | nd | | |
| | 09/14/2011 | | | | | | 3.7 | | | | | 0.2 | 1 | | nd | nd | | | | |
| | 09/21/2011 | | | | | | | | | | | | | 0.6 | | | | | | nd |
| | 05/03/2012 | 1.3 | | | | | | | | | | | | | | | | | | |
| Sulfate | 06/09/2010 | 20.8 | 92.4 | 18.8 | 49.0 | 97.0 | 29.1 | 167.6 | 77.2 | 56.1 | 15.5 | 256.8 | | 130.4 | 246.3 | | 234.5 | 164.1 | 372.5 | |
| (mg/l) | 07/26/2010 | | 76.0 | 19.8 | 90.7 | 124.5 | 23.6 | 147.8 | 86.5 | | 14.0 | 232.3 | | 123.7 | 201.4 | 227.1 | 34.1 | 92.9 | 280.3 | |
| | 09/08/2010 | 24.8 | | 17.6 | 55.2 | | 35.8 | 172.0 | 81.4 | 46.7 | 23.3 | 282.3 | 95.2 | 142.3 | 292.8 | 363.3 | 208.5 | 129.5 | | 271.1 |
| | 12/30/2010 | 24.0 | | 7.0 | 57.5 | | 20.1 | | 57.6 | 95.9 | | | | | 232.3 | 358.6 | | 130.5 | | |
| | 09/09/2011 | 32.7 | 86.2 | 29.6 | 58.3 | | | 173.9 | 73.7 | 47.2 | 48.2 | | | | | | 210.4 | 131.6 | | |
| | 09/14/2011 | | | | | | 37.3 | | | | | 286.0 | 83.9 | | 285.5 | 340.8 | | | | |
| | 09/21/2011 | | | | | | | | | | | | | 150.0 | | | | | | 264.6 |
| | 05/03/2012 | 19.8 | | | | | | | | | | | | | 228.9 | 296.6 | | | | |

# Appendix B: Sites and Samples Taken

### Table 11: Sites Sampled

| sitecode | sitetype | description | top depth (ft) | bottom depth (ft) | latitude | longitude |
|---|---|---|---|---|---|---|
| DC-2A | monitor well | well cluster member in shallow Onondaga Fm. | 10 | 41 | 42.9926 | -77.9335 |
| DC-2B | monitor well | well cluster member in older carbonate | 50 | 70 | 42.9926 | -77.9335 |
| DC-4A | monitor well | well cluster member in shallow Onondaga Fm. | 31 | 46 | 42.9932 | -77.9355 |
| DC-4B | monitor well | well cluster member in older carbonate | 50 | 70 | 42.9932 | -77.9355 |
| DC-4C | monitor well | well cluster member in deep shale | 110 | 130 | 42.9932 | -77.9355 |
| DC-5A | monitor well | well cluster member in shallow Onondaga Fm. | 10 | 60 | 42.9906 | -77.9334 |
| DC-5B | monitor well | well cluster member in older carbonate | 60 | 80 | 42.9906 | -77.9334 |
| DC-5C | monitor well | well cluster member in deep shale | 110 | 130 | 42.9906 | -77.9334 |
| DC-5D | monitor well | well cluster member in deep shale | 145 | 165 | 42.9906 | -77.9334 |
| DC-6A | monitor well | well cluster member in older carbonate | 10 | 30 | 42.9924 | -77.9283 |
| DC-6B | monitor well | well cluster member in older carbonate | 35 | 55 | 42.9924 | -77.9283 |
| DC-7RA | monitor well | well cluster member in shallow Onondaga Fm. | 10 | 95 | 42.9867 | -77.9236 |
| DC-7RB | monitor well | well cluster member in older carbonate | 103 | 123 | 42.9867 | -77.9236 |
| DC-7RC | monitor well | well cluster member in deep shale | 140 | 160 | 42.9867 | -77.9236 |
| DC-11A | monitor well | well cluster member in older carbonate | 72 | 94 | 42.9822 | -77.9061 |
| DC-11B | monitor well | well cluster member in deep shale | 140 | 160 | 42.9822 | -77.9061 |
| DC-12A | monitor well | well cluster member in shallow Onondaga Fm. | 13 | 65 | 42.9784 | -77.8909 |
| DC-12B | monitor well | well cluster member in older carbonate | 85 | 105 | 42.9784 | -77.8909 |
| DC-12C | monitor well | well cluster member in deep shale | 115 | 135 | 42.9784 | -77.8909 |
| DC-12D | monitor well | well cluster member in deep shale | 139 | 159 | 42.9784 | -77.8909 |
| DC-13A | monitor well | well cluster member in older carbonate | 10 | 25 | 42.9905 | -77.8674 |
| DC-13B | monitor well | well cluster member in deep shale | 40 | 58 | 42.9905 | -77.8674 |
| OL-01 | stream | Oatka Creek, cemetery sinkhole | | | 42.9887 | -77.9833 |
| OL-02 | spring | Mackay Spring, base of older carbonate | | | 42.9747 | -77.8596 |
| OL-03 | spring | Big Spring, park bridge, base of older carbonate | | | 42.9751 | -77.8562 |
| OL-04 | stream | Oatka Creek at North Street Rd. bridge | | | 43.0037 | -77.9764 |
| OL-05 | stream | Oatka Creek at Rte NY 5 bridge | | | 42.9779 | -77.9884 |
| OL-06 | quarry | Base of quarry on Gulf Rd. | | | 42.9887 | -77.9468 |
| OL-07 | stream | Spring Creek, railroad bridge, in shale | | | 42.9873 | -77.8615 |
| OL-08 | stream | Mud Creek at railway r.o.w. cross | | | 42.9915 | -77.9306 |
| OL-09 | snow | In Le Roy | | | | |
| OL-10 | stream | Golf course sinkhole @Unnamed stream at Le Roy Country Club | | | 42.9854 | -77.9697 |
| SH-01 | sinkhole | west of Gensess  County College | | | 43.015 | -78.155 |
| SH-15 | sinkhole | Rte 63, Batavia | | | 42.981 | -78.148 |
| SH-15A | sinkhole | Townline Rd, Batavia | | | 42.973 | -78.128 |
| SH-19 | sinkhole | Fargo Rd, Stafford | | | 42.981 | -78.116 |
| SH-21 | sinkhole | Railroad line, Caledonia (De Noon Rd) | | | 42.947 | -77.887 |
| SH-23 | sinkhole | Le Roy Golf Course sinkhole, same as OL-10 | | | 42.9854 | -77.9697 |
| SH-31 | sinkhole | Gulf Road, Le Roy sinkhole (Mud Creek), same as OL-08 | | | 42.991 | -77.931 |
| SH-34 | sinkhole | Quinlan Road, Le Roy | | | 42.989 | -78.008 |
| SH-39 | sinkhole | Middle Rd, Caledonia | | | 42.951 | -77.847 |
| SH-56 | sinkhole | Rte 5, Limerock | | | 42.979 | -77.898 |

### Table 12: Samples Collected

| sitecode | sitetype | description | sample date |
|---|---|---|---|
| OL-01s1 | stream sediment | Oatka Creek, cemetery, above sinkhole | 6/23/2010 |
| OL-01s2 | stream sediment | Oatka Creek, cemetery, above sinkhole | 6/23/2010 |
| OL-03s1 | spring sediment | Big Spring, upstream from park bridge | 6/23/2010 |
| OL-02s1 | spring sediment | Mackay Spring, same as water sample | 6/23/2010 |
| OL-02s2 | spring sediment | Mackay Spring, same as water sample | 9/14/2011 |
| OL-03s2 | spring sediment | Big Spring, upstream from park bridge? | 9/14/2011 |
| OL-07s | stream sediment | Spring Creek, railroad bridge, in shale | 9/21/2011 |
| DC-2A | monitor well | well cluster member in shallow Onondaga Fm. | 6/9/2010 |
| DC-2A | monitor well | well cluster member in shallow Onondaga Fm. | 7/26/2010 |
| DC-2A | monitor well | well cluster member in shallow Onondaga Fm. | 9/8/2010 |
| DC-2A | monitor well | well cluster member in shallow Onondaga Fm. | 12/30/2010 |
| DC-2A | monitor well | well cluster member in shallow Onondaga Fm. | 9/9/2011 |
| DC-2B | monitor well | well cluster member in older carbonate | 6/9/2010 |
| DC-2B | monitor well | well cluster member in older carbonate | 7/26/2010 |
| DC-2B | monitor well | well cluster member in older carbonate | 9/8/2010 |
| DC-2B | monitor well | well cluster member in older carbonate | 12/30/2010 |
| DC-2B | monitor well | well cluster member in older carbonate | 9/9/2011 |
| DC-4A | monitor well | well cluster member in shallow Onondaga Fm. | 6/9/2010 |
| DC-4A | monitor well | well cluster member in shallow Onondaga Fm. | 7/26/2010 |
| DC-4A | monitor well | well cluster member in shallow Onondaga Fm. | 9/9/2011 |
| DC-4B | monitor well | well cluster member in older carbonate | 6/9/2010 |
| DC-4B | monitor well | well cluster member in older carbonate | 7/26/2010 |
| DC-4B | monitor well | well cluster member in older carbonate | 9/8/2010 |
| DC-4B | monitor well | well cluster member in older carbonate | 9/9/2011 |
| DC-4C | monitor well | well cluster member in deep shale | 6/9/2010 |
| DC-4C | monitor well | well cluster member in deep shale | 7/26/2010 |
| DC-4C | monitor well | well cluster member in deep shale | 9/8/2010 |
| DC-4C | monitor well | well cluster member in deep shale | 9/9/2011 |
| DC-5A | monitor well | well cluster member in shallow Onondaga Fm. | 6/9/2010 |
| DC-5A | monitor well | well cluster member in shallow Onondaga Fm. | 7/26/2010 |
| DC-5A | monitor well | well cluster member in shallow Onondaga Fm. | 9/8/2010 |
| DC-5A | monitor well | well cluster member in shallow Onondaga Fm. | 12/30/2010 |
| DC-5A | monitor well | well cluster member in shallow Onondaga Fm. | 9/9/2011 |
| DC-5B | monitor well | well cluster member in older carbonate | 6/9/2010 |
| DC-5B | monitor well | well cluster member in older carbonate | 9/8/2010 |
| DC-5B | monitor well | well cluster member in older carbonate | 12/30/2010 |
| DC-5B | monitor well | well cluster member in older carbonate | 9/9/2011 |
| DC-5C | monitor well | well cluster member in deep shale | 6/9/2010 |
| DC-5C | monitor well | well cluster member in deep shale | 7/26/2010 |
| DC-5C | monitor well | well cluster member in deep shale | 9/8/2010 |
| DC-5C | monitor well | well cluster member in deep shale | 12/30/2010 |
| DC-5C | monitor well | well cluster member in deep shale | 9/9/2011 |
| DC-5D | monitor well | well cluster member in deep shale | 12/30/2010 |
| DC-6A | monitor well | well cluster member in older carbonate | 6/9/2010 |
| DC-6A | monitor well | well cluster member in older carbonate | 7/26/2010 |
| DC-6A | monitor well | well cluster member in older carbonate | 9/8/2010 |
| DC-6A | monitor well | well cluster member in older carbonate | 9/9/2011 |
| DC-6B | monitor well | well cluster member in older carbonate | 9/9/2011 |
| DC-7RA | monitor well | well cluster member in shallow Onondaga Fm. | 6/9/2010 |
| DC-7RA | monitor well | well cluster member in shallow Onondaga Fm. | 7/26/2010 |

| sitecode | sitetype | description | sample date |
|---|---|---|---|
| DC-7RB | monitor well | well cluster member in older carbonate | 9/14/2011 |
| DC-7RC | monitor well | well cluster member in deep shale | 6/9/2010 |
| DC-7RC | monitor well | well cluster member in deep shale | 7/26/2010 |
| DC-11A | monitor well | well cluster member in older carbonate | 6/9/2010 |
| DC-11A | monitor well | well cluster member in older carbonate | 7/26/2010 |
| DC-11A | monitor well | well cluster member in older carbonate | 9/8/2010 |
| DC-11A | monitor well | well cluster member in older carbonate | 9/14/2011 |
| DC-11B | monitor well | well cluster member in deep shale | 9/14/2011 |
| DC-12A | monitor well | well cluster member in shallow Onondaga Fm. | 6/9/2010 |
| DC-12A | monitor well | well cluster member in shallow Onondaga Fm. | 7/26/2010 |
| DC-12A | monitor well | well cluster member in shallow Onondaga Fm. | 9/8/2010 |
| DC-12A | monitor well | well cluster member in shallow Onondaga Fm. | 12/30/2010 |
| DC-12A | monitor well | well cluster member in shallow Onondaga Fm. | 9/14/2011 |
| DC-12B | monitor well | well cluster member in older carbonate | 9/8/2010 |
| DC-12B | monitor well | well cluster member in older carbonate | 9/14/2011 |
| DC-12C | monitor well | well cluster member in deep shale | 12/30/2010 |
| DC-12D | monitor well | well cluster member in deep shale | 12/30/2010 |
| DC-13A | monitor well | well cluster member in older carbonate | 6/9/2010 |
| DC-13A | monitor well | well cluster member in older carbonate | 7/26/2010 |
| DC-13A | monitor well | well cluster member in older carbonate | 9/8/2010 |
| DC-13A | monitor well | well cluster member in older carbonate | 9/21/2011 |
| DC-13B | monitor well | well cluster member in deep shale | 9/21/2011 |
| OL-01 | stream | Oatka Creek, Cemetery sinkhole | 6/9/2010 |
| OL-01 | stream | Oatka Creek, Cemetery sinkhole | 6/23/2010 |
| OL-01 | stream | Oatka Creek, Cemetery sinkhole | 9/8/2010 |
| OL-01 | stream | Oatka Creek, Cemetery sinkhole | 12/30/2010 |
| OL-01 | stream | Oatka Creek, Cemetery sinkhole | 9/9/2011 |
| OL-01 | stream | Oatka Creek, Cemetery sinkhole | 5/3/2012 |
| OL-02 | spring | Mackay Spring, base of older carbonate | 6/9/2010 |
| OL-02 | spring | Mackay Spring, base of older carbonate | 6/23/2010 |
| OL-02 | spring | Mackay Spring, base of older carbonate | 7/26/2010 |
| OL-02 | spring | Mackay Spring, base of older carbonate | 9/8/2010 |
| OL-02 | spring | Mackay Spring, base of older carbonate | 12/30/2010 |
| OL-02 | spring | Mackay Spring, base of older carbonate | 9/14/2011 |
| OL-02 | spring | Mackay Spring, base of older carbonate | 5/3/2012 |
| OL-03 | spring | Big Spring, park bridge, base of older carbonate | 6/23/2010 |
| OL-03 | spring | Big Spring, park bridge, base of older carbonate | 7/26/2010 |
| OL-03 | spring | Big Spring, park bridge, base of older carbonate | 9/8/2010 |
| OL-03 | spring | Big Spring, park bridge, base of older carbonate | 12/30/2010 |
| OL-03 | spring | Big Spring, park bridge, base of older carbonate | 9/14/2011 |
| OL-03 | spring | Big Spring, park bridge, base of older carbonate | 5/3/2012 |
| OL-04 | stream | Oatka Creek at North Street Rd. bridge | 6/9/2010 |
| OL-05 | stream | Oatka Creek at Rte NY 5 bridge | 6/9/2010 |
| OL-06 | quarry | Base of quarry on Gulf Rd. | 7/26/2010 |
| OL-06 | quarry | Base of quarry on Gulf Rd. | 9/8/2010 |
| OL-07 | stream | Spring Creek, railroad bridge, in shale | 9/8/2010 |
| OL-07 | stream | Spring Creek, railroad bridge, in shale | 9/21/2011 |

| sitecode | sitetype | description | sample date |
|---|---|---|---|
| OL-08 | stream | Mud Creek at railway r.o.w. cross | 12/30/2010 |
| OL-09 | snow | In Le Roy | 12/30/2010 |
| OL-10 | stream | Golf course sinkhole @Unnamed stream at Le Roy Country Club | 12/30/2010 |
| SH-01 | sinkhole | west of GCC | 4/25/2012 |
| SH-15 | sinkhole |  | 4/25/2012 |
| SH-15A | sinkhole |  | 4/25/2012 |
| SH-19 | sinkhole |  | 4/25/2012 |
| SH-21 | sinkhole |  | 4/26/2012 |
| SH-23 | sinkhole | Golf Course sinkhole (same as OL-10) | 4/25/2012 |
| SH-31 | sinkhole |  | 4/26/2012 |
| SH-34 | sinkhole | Quinlan Road | 4/25/2012 |
| SH-39 | sinkhole | Middle Rd Caledonia | 4/26/2012 |
| SH-56 | sinkhole | Rte 5 Limerock | 4/26/2012 |

# Appendix C: All Analytical Results

### Table 13: All analyses: anions (mg/l)

| sitecode | group | sampdate | Chloride | Nitrate-N | Sulfate |
|---|---|---|---|---|---|
| OL-09 | | 12/30/2010 | 57.20 | 0.90 | 2.90 |
| SH-01 | | 4/25/2012 | 12.00 | 1.10 | 5.40 |
| SH-15 | | 4/25/2012 | 26.50 | | 9.60 |
| SH-15A | | 4/25/2012 | 42.80 | | 9.20 |
| SH-19 | | 4/25/2012 | 5.10 | | 15.10 |
| SH-21 | | 4/26/2012 | 14.80 | 5.90 | 11.50 |
| SH-23 | | 4/25/2012 | 20.00 | 0.60 | 9.90 |
| SH-31 | | 4/26/2012 | 42.20 | 9.20 | 21.00 |
| SH-34 | | 4/25/2012 | 39.90 | | 29.60 |
| SH-39 | | 4/26/2012 | 54.80 | 1.50 | 19.30 |
| SH-56 | | 4/26/2012 | 30.70 | 4.40 | 24.60 |
| DC-2A | 1-shallow carbonate | 6/9/2010 | 4.93 | 1.52 | 18.90 |
| DC-2A | 1-shallow carbonate | 7/26/2010 | 4.52 | 1.63 | 19.80 |
| DC-2A | 1-shallow carbonate | 9/8/2010 | 1.90 | 1.60 | 17.60 |
| DC-2A | 1-shallow carbonate | 12/30/2010 | 5.50 | 1.20 | 7.00 |
| DC-2A | 1-shallow carbonate | 9/9/2011 | 3.40 | | 29.70 |
| DC-4A | 1-shallow carbonate | 6/9/2010 | 6.94 | 0.51 | 92.40 |
| DC-4A | 1-shallow carbonate | 7/26/2010 | 12.69 | 0.08 | 76.10 |
| DC-4A | 1-shallow carbonate | 9/9/2011 | 6.50 | | 86.30 |
| DC-5A | 1-shallow carbonate | 6/9/2010 | 13.60 | 0.11 | 49.00 |
| DC-5A | 1-shallow carbonate | 7/26/2010 | 8.46 | 0.08 | 90.80 |
| DC-5A | 1-shallow carbonate | 9/8/2010 | 33.40 | 0.80 | 55.20 |
| DC-5A | 1-shallow carbonate | 12/30/2010 | 32.30 | 1.10 | 57.50 |
| DC-5A | 1-shallow carbonate | 9/9/2011 | 14.60 | | 58.40 |
| DC-7RA | 1-shallow carbonate | 6/9/2010 | 59.90 | 1.28 | 97.00 |
| DC-7RA | 1-shallow carbonate | 7/26/2010 | 91.60 | 2.81 | 124.50 |
| DC-12A | 1-shallow carbonate | 6/9/2010 | 78.01 | 3.81 | 29.10 |
| DC-12A | 1-shallow carbonate | 7/26/2010 | 80.40 | 4.43 | 23.60 |
| DC-12A | 1-shallow carbonate | 9/8/2010 | 165.30 | 3.50 | 35.90 |
| DC-12A | 1-shallow carbonate | 12/30/2010 | 14.40 | 6.30 | 20.20 |
| DC-12A | 1-shallow carbonate | 9/14/2011 | 140.90 | 3.70 | 37.40 |
| OL-01 | 1-shallow carbonate | 6/9/2010 | 30.77 | 3.70 | 20.80 |
| OL-01 | 1-shallow carbonate | 6/23/2010 | 52.02 | 1.36 | 21.50 |
| OL-01 | 1-shallow carbonate | 9/8/2010 | 72.60 | | 24.90 |
| OL-01 | 1-shallow carbonate | 12/30/2010 | 49.50 | 2.50 | 24.00 |
| OL-01 | 1-shallow carbonate | 9/9/2011 | 61.90 | | 32.80 |
| OL-01 | 1-shallow carbonate | 5/3/2012 | 42.70 | 1.40 | 19.80 |
| OL-04 | 1-shallow carbonate | 6/9/2010 | 31.13 | 3.68 | 20.80 |
| OL-05 | 1-shallow carbonate | 6/9/2010 | 28.43 | 3.39 | 17.80 |
| OL-06 | 1-shallow carbonate | 7/26/2010 | 3.91 | 0.10 | 39.80 |
| OL-06 | 1-shallow carbonate | 9/8/2010 | 2.20 | | 46.70 |
| OL-08 | 1-shallow carbonate | 12/30/2010 | 51.50 | 3.00 | 29.30 |
| OL-10 | 1-shallow carbonate | 12/30/2010 | 61.60 | 2.00 | 28.70 |
| DC-2B | 2-middle carbonate | 6/9/2010 | 39.66 | 0.66 | 77.20 |
| DC-2B | 2-middle carbonate | 7/26/2010 | 6.60 | 0.69 | 86.50 |
| DC-2B | 2-middle carbonate | 9/8/2010 | 30.40 | 0.60 | 81.40 |
| DC-2B | 2-middle carbonate | 12/30/2010 | 8.70 | 1.00 | 57.60 |
| DC-2B | 2-middle carbonate | 9/9/2011 | 29.40 | | 73.80 |
| DC-4B | 2-middle carbonate | 6/9/2010 | 9.71 | 0.04 | 167.70 |
| DC-4B | 2-middle carbonate | 7/26/2010 | 20.80 | 0.12 | 147.80 |

| sitecode | group | sampdate | Chloride | Nitrate-N | Sulfate |
|---|---|---|---|---|---|
| DC-4B | 2-middle carbonate | 9/8/2010 | 12.30 |  | 172.00 |
| DC-4B | 2-middle carbonate | 9/9/2011 | 12.50 |  | 173.90 |
| DC-5B | 2-middle carbonate | 6/9/2010 | 39.01 | 0.62 | 56.10 |
| DC-5B | 2-middle carbonate | 9/8/2010 | 31.10 |  | 46.70 |
| DC-5B | 2-middle carbonate | 12/30/2010 | 23.60 | 0.60 | 95.90 |
| DC-5B | 2-middle carbonate | 9/9/2011 | 26.10 |  | 47.30 |
| DC-6A | 2-middle carbonate | 6/9/2010 | 46.38 | 3.91 | 15.60 |
| DC-6A | 2-middle carbonate | 7/26/2010 | 10.32 | 0.89 | 14.10 |
| DC-6A | 2-middle carbonate | 9/8/2010 | 15.10 | 0.70 | 23.40 |
| DC-6A | 2-middle carbonate | 9/9/2011 | 42.80 |  | 48.20 |
| DC-6B | 2-middle carbonate | 9/9/2011 | 49.20 |  | 61.90 |
| DC-7RB | 2-middle carbonate | 9/14/2011 | 28.30 | 0.50 | 142.30 |
| DC-11A | 2-middle carbonate | 6/9/2010 | 64.21 | 2.14 | 256.80 |
| DC-11A | 2-middle carbonate | 7/26/2010 | 85.26 | 2.57 | 232.30 |
| DC-11A | 2-middle carbonate | 9/8/2010 | 65.00 | 1.10 | 282.40 |
| DC-11A | 2-middle carbonate | 9/14/2011 | 56.50 | 0.30 | 286.00 |
| DC-12B | 2-middle carbonate | 9/8/2010 | 41.60 | 1.70 | 95.30 |
| DC-12B | 2-middle carbonate | 9/14/2011 | 37.90 | 1.00 | 83.90 |
| DC-13A | 2-middle carbonate | 6/9/2010 | 45.96 | 2.58 | 130.40 |
| DC-13A | 2-middle carbonate | 7/26/2010 | 65.65 | 3.68 | 123.80 |
| DC-13A | 2-middle carbonate | 9/8/2010 | 52.20 | 2.20 | 142.30 |
| DC-13A | 2-middle carbonate | 9/21/2011 | 43.40 | 0.70 | 150.00 |
| OL-02 | 2-middle carbonate | 6/9/2010 | 54.87 | 1.77 | 246.30 |
| OL-02 | 2-middle carbonate | 6/23/2010 | 61.38 | 2.54 | 253.00 |
| OL-02 | 2-middle carbonate | 7/26/2010 | 62.39 | 1.83 | 201.40 |
| OL-02 | 2-middle carbonate | 9/8/2010 | 61.90 | 0.80 | 292.80 |
| OL-02 | 2-middle carbonate | 12/30/2010 | 32.40 | 1.90 | 232.30 |
| OL-02 | 2-middle carbonate | 9/14/2011 | 53.50 |  | 285.50 |
| OL-02 | 2-middle carbonate | 5/3/2012 | 54.20 |  | 228.90 |
| OL-03 | 2-middle carbonate | 6/23/2010 | 59.22 | 2.53 | 237.80 |
| OL-03 | 2-middle carbonate | 7/26/2010 | 39.27 | 0.88 | 227.20 |
| OL-03 | 2-middle carbonate | 9/8/2010 | 64.50 |  | 363.30 |
| OL-03 | 2-middle carbonate | 12/30/2010 | 57.80 | 2.50 | 358.60 |
| OL-03 | 2-middle carbonate | 9/14/2011 | 51.70 |  | 340.90 |
| OL-03 | 2-middle carbonate | 5/3/2012 | 55.80 |  | 296.70 |
| DC-4C | 3-deep shale | 6/9/2010 | 21.98 | 0.06 | 234.60 |
| DC-4C | 3-deep shale | 7/26/2010 | 25.06 | 0.37 | 34.10 |
| DC-4C | 3-deep shale | 9/8/2010 | 20.60 |  | 208.60 |
| DC-4C | 3-deep shale | 9/9/2011 | 17.60 |  | 210.40 |
| DC-5C | 3-deep shale | 6/9/2010 | 24.08 | 0.44 | 164.20 |
| DC-5C | 3-deep shale | 7/26/2010 | 49.85 | 0.62 | 92.90 |
| DC-5C | 3-deep shale | 9/8/2010 | 23.10 | 0.40 | 129.60 |
| DC-5C | 3-deep shale | 12/30/2010 | 13.20 | 2.50 | 130.60 |
| DC-5C | 3-deep shale | 9/9/2011 | 19.30 |  | 131.70 |
| DC-5D | 3-deep shale | 12/30/2010 | 18.90 | 0.70 | 392.20 |
| DC-7RC | 3-deep shale | 6/9/2010 | 37.91 | 1.46 | 372.50 |
| DC-7RC | 3-deep shale | 7/26/2010 | 24.84 | 0.81 | 280.30 |
| DC-11B | 3-deep shale | 9/14/2011 | 45.50 |  | 203.00 |
| DC-12C | 3-deep shale | 12/30/2010 | 28.30 | 2.20 | 99.30 |
| DC-12D | 3-deep shale | 12/30/2010 | 49.20 | 1.10 | 225.10 |
| DC-13B | 3-deep shale | 9/21/2011 | 38.60 |  | 108.70 |
| OL-07 | 3-deep shale | 9/8/2010 | 60.20 | 1.10 | 271.10 |
| OL-07 | 3-deep shale | 9/21/2011 | 53.20 |  | 264.70 |

**Table 14: All analyses: cations (mg/l)**

| sitecode | group | sampdate | Ca | Na |
|---|---|---|---|---|
| SH-01 | | 4/25/2012 | 27.30 | 1.30 |
| SH-15 | | 4/25/2012 | 29.40 | 10.10 |
| SH-15A | | 4/25/2012 | 41.10 | 18.30 |
| SH-19 | | 4/25/2012 | 42.10 | 1.30 |
| SH-21 | | 4/26/2012 | 56.20 | 19.30 |
| SH-23 | | 4/25/2012 | 26.00 | 7.20 |
| SH-31 | | 4/26/2012 | 41.20 | 14.90 |
| SH-34 | | 4/25/2012 | 31.70 | 16.80 |
| SH-39 | | 4/26/2012 | 43.30 | 20.00 |
| SH-56 | | 4/26/2012 | 38.00 | 11.30 |
| DC-2A | 1-shallow carbonate | 6/9/2010 | 15.70 | 0.76 |
| DC-2A | 1-shallow carbonate | 7/26/2010 | 27.60 | 1.80 |
| DC-2A | 1-shallow carbonate | 9/8/2010 | 56.60 | 1.00 |
| DC-2A | 1-shallow carbonate | 12/30/2010 | 14.66 | 0.46 |
| DC-2A | 1-shallow carbonate | 9/9/2011 | 78.10 | 2.10 |
| DC-4A | 1-shallow carbonate | 6/9/2010 | 18.90 | 2.21 |
| DC-4A | 1-shallow carbonate | 7/26/2010 | 39.90 | 6.10 |
| DC-4A | 1-shallow carbonate | 9/9/2011 | 93.80 | 5.20 |
| DC-5A | 1-shallow carbonate | 6/9/2010 | 19.40 | 2.20 |
| DC-5A | 1-shallow carbonate | 7/26/2010 | 34.20 | 9.70 |
| DC-5A | 1-shallow carbonate | 9/8/2010 | 75.00 | 14.70 |
| DC-5A | 1-shallow carbonate | 12/30/2010 | 71.69 | 19.01 |
| DC-5A | 1-shallow carbonate | 9/9/2011 | 70.70 | 6.30 |
| DC-7RA | 1-shallow carbonate | 6/9/2010 | 34.00 | 6.49 |
| DC-7RA | 1-shallow carbonate | 7/26/2010 | 50.70 | 26.80 |
| DC-12A | 1-shallow carbonate | 6/9/2010 | 21.20 | 12.67 |
| DC-12A | 1-shallow carbonate | 7/26/2010 | 20.50 | 30.10 |
| DC-12A | 1-shallow carbonate | 9/8/2010 | 94.40 | 58.90 |
| DC-12A | 1-shallow carbonate | 12/30/2010 | 62.51 | 5.65 |
| DC-12A | 1-shallow carbonate | 9/14/2011 | 89.00 | 41.90 |
| OL-01 | 1-shallow carbonate | 6/9/2010 | 16.90 | 5.13 |
| OL-01 | 1-shallow carbonate | 6/23/2010 | 18.88 | 7.87 |
| OL-01 | 1-shallow carbonate | 9/8/2010 | 40.00 | 26.10 |
| OL-01 | 1-shallow carbonate | 12/30/2010 | 48.43 | 19.59 |
| OL-01 | 1-shallow carbonate | 9/9/2011 | 56.50 | 25.40 |
| OL-01 | 1-shallow carbonate | 5/3/2012 | 27.50 | 16.40 |
| OL-04 | 1-shallow carbonate | 6/9/2010 | 15.40 | 5.24 |
| OL-05 | 1-shallow carbonate | 6/9/2010 | 13.00 | 4.79 |
| OL-06 | 1-shallow carbonate | 7/26/2010 | 24.90 | 1.50 |
| OL-06 | 1-shallow carbonate | 9/8/2010 | 31.20 | 1.10 |
| OL-08 | 1-shallow carbonate | 12/30/2010 | 53.89 | 11.74 |
| OL-10 | 1-shallow carbonate | 12/30/2010 | 52.38 | 12.79 |
| DC-2B | 2-middle carbonate | 6/9/2010 | 27.10 | 5.29 |
| DC-2B | 2-middle carbonate | 7/26/2010 | 37.20 | 17.40 |
| DC-2B | 2-middle carbonate | 9/8/2010 | 79.00 | 10.50 |
| DC-2B | 2-middle carbonate | 12/30/2010 | 27.20 | 4.07 |
| DC-2B | 2-middle carbonate | 9/9/2011 | 75.10 | 11.40 |
| DC-4B | 2-middle carbonate | 6/9/2010 | 41.80 | 1.75 |
| DC-4B | 2-middle carbonate | 7/26/2010 | 54.70 | 2.60 |
| DC-4B | 2-middle carbonate | 9/8/2010 | 108.70 | 4.00 |
| DC-4B | 2-middle carbonate | 9/9/2011 | 104.60 | 5.20 |
| DC-5B | 2-middle carbonate | 6/9/2010 | 21.90 | 6.15 |
| DC-5B | 2-middle carbonate | 9/8/2010 | 68.60 | 14.70 |
| DC-5B | 2-middle carbonate | 12/30/2010 | 84.76 | 14.45 |
| DC-5B | 2-middle carbonate | 9/9/2011 | 70.40 | 16.80 |
| DC-6A | 2-middle carbonate | 6/9/2010 | 13.20 | 6.90 |
| DC-6A | 2-middle carbonate | 7/26/2010 | 16.60 | 4.70 |
| DC-6A | 2-middle carbonate | 9/8/2010 | 54.90 | 7.90 |
| DC-6A | 2-middle carbonate | 9/9/2011 | 85.80 | 14.90 |
| DC-6B | 2-middle carbonate | 9/9/2011 | 56.70 | 28.00 |
| DC-7RB | 2-middle carbonate | 9/14/2011 | 108.40 | 11.60 |
| DC-11A | 2-middle carbonate | 6/9/2010 | 68.80 | 8.81 |
| DC-11A | 2-middle carbonate | 7/26/2010 | 95.00 | 28.50 |
| DC-11A | 2-middle carbonate | 9/8/2010 | 161.60 | 23.30 |
| DC-11A | 2-middle carbonate | 9/14/2011 | 162.10 | 22.30 |
| DC-12B | 2-middle carbonate | 9/8/2010 | 71.10 | 12.30 |
| DC-12B | 2-middle carbonate | 9/14/2011 | 89.70 | 13.20 |

| | | | | |
|---|---|---|---|---|
| DC-13A | 2-middle carbonate | 6/9/2010 | 33.50 | 5.90 |
| DC-13A | 2-middle carbonate | 7/26/2010 | 60.80 | 24.80 |
| DC-13A | 2-middle carbonate | 9/8/2010 | 102.10 | 17.30 |
| DC-13A | 2-middle carbonate | 9/21/2011 | 116.20 | 17.50 |
| OL-02 | 2-middle carbonate | 6/9/2010 | 66.90 | 7.45 |
| OL-02 | 2-middle carbonate | 6/23/2010 | 73.46 | 8.46 |
| OL-02 | 2-middle carbonate | 7/26/2010 | 88.10 | 21.80 |
| OL-02 | 2-middle carbonate | 9/8/2010 | 156.80 | 21.20 |
| OL-02 | 2-middle carbonate | 12/30/2010 | 113.01 | 13.93 |
| OL-02 | 2-middle carbonate | 9/14/2011 | 173.10 | 21.90 |
| OL-02 | 2-middle carbonate | 5/3/2012 | 140.30 | 20.20 |
| OL-03 | 2-middle carbonate | 6/23/2010 | 68.51 | 8.23 |
| OL-03 | 2-middle carbonate | 7/26/2010 | 109.20 | 14.70 |
| OL-03 | 2-middle carbonate | 9/8/2010 | 202.90 | 23.30 |
| OL-03 | 2-middle carbonate | 12/30/2010 | 132.43 | 18.05 |
| OL-03 | 2-middle carbonate | 9/14/2011 | 186.80 | 21.40 |
| OL-03 | 2-middle carbonate | 5/3/2012 | 166.40 | 21.20 |
| DC-4C | 3-deep shale | 6/9/2010 | 49.20 | 1.02 |
| DC-4C | 3-deep shale | 7/26/2010 | 41.60 | 3.70 |
| DC-4C | 3-deep shale | 9/8/2010 | 105.60 | 2.60 |
| DC-4C | 3-deep shale | 9/9/2011 | 111.50 | 2.70 |
| DC-5C | 3-deep shale | 6/9/2010 | 28.80 | 2.31 |
| DC-5C | 3-deep shale | 7/26/2010 | 34.40 | 3.00 |
| DC-5C | 3-deep shale | 9/8/2010 | 273.90 | 46.40 |
| DC-5C | 3-deep shale | 12/30/2010 | 49.12 | 3.89 |
| DC-5C | 3-deep shale | 9/9/2011 | 73.30 | 6.30 |
| DC-5D | 3-deep shale | 12/30/2010 | 108.87 | 6.04 |
| DC-7RC | 3-deep shale | 6/9/2010 | 86.70 | 4.83 |
| DC-7RC | 3-deep shale | 7/26/2010 | 106.50 | 8.80 |
| DC-11B | 3-deep shale | 9/14/2011 | 119.90 | 17.30 |
| DC-12C | 3-deep shale | 12/30/2010 | 74.28 | 10.10 |
| DC-12D | 3-deep shale | 12/30/2010 | 69.59 | 10.92 |
| DC-13B | 3-deep shale | 9/21/2011 | 98.00 | 15.10 |
| OL-07 | 3-deep shale | 9/8/2010 | 151.50 | 21.00 |
| OL-07 | 3-deep shale | 9/21/2011 | 160.40 | 21.00 |

**Table 15: Pesticide analytical results**

| sitecode | group | sitetype | parameter* | sampdate | result** |
|---|---|---|---|---|---|
| SH-01 | | sinkhole | Metolachlor ESA (DEC) | 4/25/2012 | 2.89 |
| SH-01 | | sinkhole | Metolachlor (DEC) | 4/25/2012 | 16.3 |
| SH-01 | | sinkhole | Atrazine (DEC) | 4/25/2012 | 40.79 |
| SH-01 | | sinkhole | Metolachlor OA (DEC) | 4/25/2012 | 2.54 |
| SH-01 | | sinkhold | Atrazine | 4/25/2012 | above maximum 5 |
| SH-15 | | sinkhole | Atrazine | 4/25/2012 | nd |
| SH-15A | | sinkhole | Atrazine | 4/25/2012 | nd |
| SH-19 | | sinkhole | Atrazine | 4/25/2012 | nd |
| SH-21 | | sinkhole | Atrazine | 4/26/2012 | trace |
| SH-23 | | sinkhole | Atrazine | 4/25/2012 | nd |
| SH-31 | | sinkhole | Atrazine | 4/26/2012 | trace |
| SH-34 | | sinkhole | Atrazine | 4/25/2012 | nd |
| SH-39 | | sinkhole | Atrazine | 4/26/2012 | nd |
| SH-56 | | sinkhole | Atrazine | 4/26/2012 | trace |
| DC-2A | 1-shallow carbonate | monitor well | Atrazine | 6/9/2010 | nd |
| DC-2A | 1-shallow carbonate | monitor well | Metolachlor | 6/9/2010 | nd |
| DC-2A | 1-shallow carbonate | monitor well | Metolachlor | 7/26/2010 | nd |
| DC-2A | 1-shallow carbonate | monitor well | Atrazine | 7/26/2010 | nd |
| DC-2A | 1-shallow carbonate | monitor well | Atrazine | 9/8/2010 | nd |
| DC-2A | 1-shallow carbonate | monitor well | Atrazine | 12/30/2010 | nd |
| DC-2A | 1-shallow carbonate | monitor well | Atrazine | 9/9/2011 | nd |
| DC-4A | 1-shallow carbonate | monitor well | Metolachlor | 6/9/2010 | trace |
| DC-4A | 1-shallow carbonate | monitor well | Atrazine | 6/9/2010 | nd |
| DC-4A | 1-shallow carbonate | monitor well | Atrazine | 7/26/2010 | nd |
| DC-4A | 1-shallow carbonate | monitor well | Metolachlor | 7/26/2010 | trace |
| DC-4A | 1-shallow carbonate | monitor well | Atrazine | 9/9/2011 | nd |
| DC-5A | 1-shallow carbonate | monitor well | Metolachlor | 6/9/2010 | nd |
| DC-5A | 1-shallow carbonate | monitor well | Atrazine | 6/9/2010 | nd |
| DC-5A | 1-shallow carbonate | monitor well | Atrazine | 7/26/2010 | nd |
| DC-5A | 1-shallow carbonate | monitor well | Metolachlor | 7/26/2010 | nd |
| DC-5A | 1-shallow carbonate | monitor well | Atrazine | 9/8/2010 | nd |
| DC-5A | 1-shallow carbonate | monitor well | Atrazine | 12/30/2010 | nd |
| DC-5A | 1-shallow carbonate | monitor well | Atrazine | 9/9/2011 | nd |
| DC-7RA | 1-shallow carbonate | monitor well | Metolachlor | 6/9/2010 | nd |
| DC-7RA | 1-shallow carbonate | monitor well | Atrazine | 6/9/2010 | trace |
| DC-7RA | 1-shallow carbonate | monitor well | Metolachlor | 7/26/2010 | trace |
| DC-7RA | 1-shallow carbonate | monitor well | Atrazine | 7/26/2010 | 0.15 |
| DC-12A | 1-shallow carbonate | monitor well | Atrazine | 6/9/2010 | nd |
| DC-12A | 1-shallow carbonate | monitor well | Metolachlor | 6/9/2010 | trace |
| DC-12A | 1-shallow carbonate | monitor well | Metolachlor | 7/26/2010 | nd |
| DC-12A | 1-shallow carbonate | monitor well | Atrazine | 7/26/2010 | nd |
| DC-12A | 1-shallow carbonate | monitor well | Atrazine | 9/8/2010 | nd |
| DC-12A | 1-shallow carbonate | monitor well | Atrazine | 12/30/2010 | nd |
| DC-12A | 1-shallow carbonate | monitor well | Atrazine | 9/14/2011 | nd |
| OL-01 | 1-shallow carbonate | stream | Atrazine | 6/9/2010 | 3.29 |
| OL-01 | 1-shallow carbonate | stream | Metolachlor | 6/9/2010 | 2.54 |
| OL-01 | 1-shallow carbonate | stream | Metolachlor | 6/23/2010 | 0.35 |
| OL-01 | 1-shallow carbonate | stream | Atrazine | 6/23/2010 | 0.41 |
| OL-01 | 1-shallow carbonate | stream | Atrazine | 9/8/2010 | trace |
| OL-01 | 1-shallow carbonate | stream | Atrazine | 12/30/2010 | nd |
| OL-01 | 1-shallow carbonate | stream | Atrazine | 9/9/2011 | trace |
| OL-01 | 1-shallow carbonate | stream | Metolachlor ESA (DEC) | 5/3/2012 | 0.83 |
| OL-01 | 1-shallow carbonate | stream | Atrazine | 5/3/2012 | trace |
| OL-01 | 1-shallow carbonate | stream | Atrazine (DEC) | 5/3/2012 | nd |
| OL-01 | 1-shallow carbonate | stream | Metolachlor OA (DEC) | 5/3/2012 | 0.3 |
| OL-01 | 1-shallow carbonate | stream | Metolachlor (DEC) | 5/3/2012 | nd |
| OL-04 | 1-shallow carbonate | stream | Atrazine | 6/9/2010 | 3.45 |
| OL-04 | 1-shallow carbonate | stream | Metolachlor | 6/9/2010 | 2.66 |
| OL-05 | 1-shallow carbonate | stream | Metolachlor | 6/9/2010 | 2.17 |
| OL-05 | 1-shallow carbonate | stream | Atrazine | 6/9/2010 | 2.98 |
| OL-06 | 1-shallow carbonate | quarry | Metolachlor | 7/26/2010 | nd |

| | | | | | |
|---|---|---|---|---|---|
| OL-06 | 1-shallow carbonate | quarry | Atrazine | 7/26/2010 | nd |
| OL-06 | 1-shallow carbonate | quarry | Atrazine | 9/8/2010 | nd |
| OL-08 | 1-shallow carbonate | stream | Atrazine | 12/30/2010 | nd |
| OL-10 | 1-shallow carbonate | stream | Atrazine | 12/30/2010 | nd |
| DC-2B | 2-middle carbonate | monitor well | Metolachlor | 6/9/2010 | nd |
| DC-2B | 2-middle carbonate | monitor well | Atrazine | 6/9/2010 | nd |
| DC-2B | 2-middle carbonate | monitor well | Atrazine | 7/26/2010 | nd |
| DC-2B | 2-middle carbonate | monitor well | Metolachlor | 7/26/2010 | trace |
| DC-2B | 2-middle carbonate | monitor well | Atrazine | 9/8/2010 | nd |
| DC-2B | 2-middle carbonate | monitor well | Atrazine | 12/30/2010 | nd |
| DC-2B | 2-middle carbonate | monitor well | Atrazine | 9/9/2011 | nd |
| DC-4B | 2-middle carbonate | monitor well | Metolachlor | 6/9/2010 | nd |
| DC-4B | 2-middle carbonate | monitor well | Atrazine | 6/9/2010 | nd |
| DC-4B | 2-middle carbonate | monitor well | Metolachlor | 7/26/2010 | nd |
| DC-4B | 2-middle carbonate | monitor well | Atrazine | 7/26/2010 | nd |
| DC-4B | 2-middle carbonate | monitor well | Atrazine | 9/8/2010 | nd |
| DC-4B | 2-middle carbonate | monitor well | Atrazine | 9/9/2011 | nd |
| DC-5B | 2-middle carbonate | monitor well | Atrazine | 6/9/2010 | nd |
| DC-5B | 2-middle carbonate | monitor well | Metolachlor | 6/9/2010 | nd |
| DC-5B | 2-middle carbonate | monitor well | Atrazine | 9/8/2010 | nd |
| DC-5B | 2-middle carbonate | monitor well | Atrazine | 12/30/2010 | nd |
| DC-5B | 2-middle carbonate | monitor well | Atrazine | 9/9/2011 | nd |
| DC-6A | 2-middle carbonate | monitor well | Metolachlor | 6/9/2010 | 0.54 |
| DC-6A | 2-middle carbonate | monitor well | Atrazine | 6/9/2010 | 0.63 |
| DC-6A | 2-middle carbonate | monitor well | Atrazine | 7/26/2010 | nd |
| DC-6A | 2-middle carbonate | monitor well | Metolachlor | 7/26/2010 | nd |
| DC-6A | 2-middle carbonate | monitor well | Atrazine | 9/8/2010 | nd |
| DC-6A | 2-middle carbonate | monitor well | Atrazine | 9/9/2011 | nd |
| DC-6B | 2-middle carbonate | monitor well | Atrazine | 9/9/2011 | nd |
| DC-7RB | 2-middle carbonate | monitor well | Atrazine | 9/14/2011 | nd |
| DC-11A | 2-middle carbonate | monitor well | Metolachlor | 6/9/2010 | 0.1 |
| DC-11A | 2-middle carbonate | monitor well | Atrazine | 6/9/2010 | trace |
| DC-11A | 2-middle carbonate | monitor well | Metolachlor | 7/26/2010 | trace |
| DC-11A | 2-middle carbonate | monitor well | Atrazine | 7/26/2010 | trace |
| DC-11A | 2-middle carbonate | monitor well | Atrazine | 9/8/2010 | trace |
| DC-12B | 2-middle carbonate | monitor well | Atrazine | 9/8/2010 | nd |
| DC-12B | 2-middle carbonate | monitor well | Atrazine | 9/14/2011 | trace |
| DC-13A | 2-middle carbonate | monitor well | Metolachlor | 6/9/2010 | nd |
| DC-13A | 2-middle carbonate | monitor well | Atrazine | 6/9/2010 | trace |
| DC-13A | 2-middle carbonate | monitor well | Atrazine | 7/26/2010 | trace |
| DC-13A | 2-middle carbonate | monitor well | Metolachlor | 7/26/2010 | nd |
| DC-13A | 2-middle carbonate | monitor well | Atrazine | 9/8/2010 | nd |
| DC-13A | 2-middle carbonate | monitor well | Atrazine | 9/21/2011 | trace |
| OL-02 | 2-middle carbonate | spring | Metolachlor | 6/9/2010 | trace |
| OL-02 | 2-middle carbonate | spring | Atrazine | 6/9/2010 | trace |
| OL-02 | 2-middle carbonate | spring | Metolachlor | 6/23/2010 | nd |
| OL-02 | 2-middle carbonate | spring | Atrazine | 6/23/2010 | trace |
| OL-02 | 2-middle carbonate | spring | Metolachlor | 7/26/2010 | nd |
| OL-02 | 2-middle carbonate | spring | Atrazine | 7/26/2010 | nd |
| OL-02 | 2-middle carbonate | spring | Atrazine | 9/8/2010 | trace |
| OL-02 | 2-middle carbonate | spring | Atrazine | 12/30/2010 | nd |
| OL-02 | 2-middle carbonate | spring | Atrazine | 9/14/2011 | trace |
| OL-02 | 2-middle carbonate | spring | Atrazine | 5/3/2012 | trace |
| OL-02 | 2-middle carbonate | spring | Atrazine (DEC) | 5/3/2012 | nd |
| OL-02 | 2-middle carbonate | spring | Metolachlor OA (DEC) | 5/3/2012 | nd |
| OL-02 | 2-middle carbonate | spring | Metolachlor ESA (DEC) | 5/3/2012 | 0.82 |
| OL-02 | 2-middle carbonate | spring | Metolachlor (DEC) | 5/3/2012 | nd |
| OL-03 | 2-middle carbonate | spring | Atrazine | 6/23/2010 | nd |
| OL-03 | 2-middle carbonate | spring | Metolachlor | 6/23/2010 | nd |
| OL-03 | 2-middle carbonate | spring | Metolachlor | 7/26/2010 | nd |
| OL-03 | 2-middle carbonate | spring | Atrazine | 7/26/2010 | nd |

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| OL-03 | 2-middle carbonate | spring | Atrazine | 9/8/2010 | trace |
| OL-03 | 2-middle carbonate | spring | Atrazine | 12/30/2010 | nd |
| OL-03 | 2-middle carbonate | spring | Atrazine | 9/14/2011 | trace |
| OL-03 | 2-middle carbonate | spring | Atrazine | 5/3/2012 | nd |
| DC-4C | 3-deep shale | monitor well | Metolachlor | 6/9/2010 | nd |
| DC-4C | 3-deep shale | monitor well | Atrazine | 6/9/2010 | nd |
| DC-4C | 3-deep shale | monitor well | Atrazine | 7/26/2010 | nd |
| DC-4C | 3-deep shale | monitor well | Metolachlor | 7/26/2010 | nd |
| DC-4C | 3-deep shale | monitor well | Atrazine | 9/8/2010 | nd |
| DC-4C | 3-deep shale | monitor well | Atrazine | 9/9/2011 | nd |
| DC-5C | 3-deep shale | monitor well | Metolachlor | 6/9/2010 | nd |
| DC-5C | 3-deep shale | monitor well | Atrazine | 6/9/2010 | nd |
| DC-5C | 3-deep shale | monitor well | Atrazine | 7/26/2010 | nd |
| DC-5C | 3-deep shale | monitor well | Metolachlor | 7/26/2010 | nd |
| DC-5C | 3-deep shale | monitor well | Atrazine | 9/8/2010 | nd |
| DC-5C | 3-deep shale | monitor well | Atrazine | 12/30/2010 | nd |
| DC-5C | 3-deep shale | monitor well | Atrazine | 9/9/2011 | nd |
| DC-5D | 3-deep shale | monitor well | Atrazine | 12/30/2010 | nd |
| DC-7RC | 3-deep shale | monitor well | Atrazine | 6/9/2010 | nd |
| DC-7RC | 3-deep shale | monitor well | Metolachlor | 6/9/2010 | nd |
| DC-7RC | 3-deep shale | monitor well | Metolachlor | 7/26/2010 | nd |
| DC-7RC | 3-deep shale | monitor well | Atrazine | 7/26/2010 | nd |
| DC-11B | 3-deep shale | monitor well | Atrazine | 9/14/2011 | trace |
| DC-12C | 3-deep shale | monitor well | Atrazine | 12/30/2010 | nd |
| DC-12D | 3-deep shale | monitor well | Atrazine | 12/30/2010 | nd |
| DC-13B | 3-deep shale | monitor well | Atrazine | 9/21/2011 | trace |
| OL-07 | 3-deep shale | stream | Atrazine | 9/8/2010 | trace |
| OL-07 | 3-deep shale | stream | Atrazine | 9/21/2011 | trace |

* (DEC) = analysis by DEC lab, all other analyses via ELISA at Cornell.

** nd = not detected at 0.1 µg/l (DEC) or 0.05 µg/l (Cornell), trace = detected between 0.05 and 0.1 µg/l but not quantified (Cornell only).