Water Quality Monitoring for Pesticides in Upstate New York

2023 ANNUAL REPORT

(minor error corrections April 2025)

to the Bureau of Pesticides Management
New York State Department of Environmental Conservation

MOU 136274

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Executive Summary

This annual report covers the activities of Year 3 of our five-year MOU with NYS DEC to monitor potential mobilization of pesticides residues under normal label-compliant use in upstate New York, and includes interpretation of analytical results for samples collected through the end of Year 3.

Two key principles have undergirded our ongoing research program for DEC: 1) a primary emphasis on sites with greater than average vulnerability due to soil, aquifer, and topographic characteristics in combination with known or presumed pesticide use, and 2) maintaining strict landowner and location confidentiality to encourage participation.

Twice during 2023, Cornell personnel sampled 21 *categorical sites* which are a primary focus of the program. These sites were selected based on falling in one of *eight land use categories*: golf courses, sod farms, other managed turfgrass, greenhouses, outdoor nurseries, fruit/vegetable farms, vineyards, and utility/railroad rights-of-way. Each site has one to five sampling locations on their property including landowner domestic or irrigation wells, shallow Cornell-installed monitor wells, and in several cases groundwater-fed ponds. Sampling locations were classified as *within* (located within the pesticide use areas), *downgradient* (downhill from pesticide use areas), or *upgradient* (uphill of the landowner pesticide use area). Total collections in 2022 (our sampling ramp-up year) and 2023 (full sampling of the completed site roster) reached 204 samples, representing 75% of our cumulative sample load to date.

Complementing the categorical sites are 33 *long-term sites* sampled once per year. These sites are intended for long-term lower-intensity monitoring of tap-based sampling of landowner's well (typically one per site) selected for apparent vulnerability based on topography and nearby pesticide use. Some of these sites were first sampled in the initial years of our county-based sampling dating back to 2003, providing valuable longitudinal data. Following some initial sampling in 2022, the site roster was completed and fully sampled in 2023, thus reaching 38 samples collected (14% of total). Finally, our second year of sampling was completed for four *lakes* (Chautauqua, Canadarago, Little York and Waccabuc), with a total two-year sample load of 30 (11% of the total).

Analysis by the NY DEC laboratory of these samples for nearly 90 pesticides and pesticide degradation products thus resulted in over 23,600 individual tests. Of the tests performed on groundwater samples (categorical and long-term site wells), 99.1% were non-detects (Figure 1). Of the detections, 0.41% were very low level (0.01-0.1 µg/L), 0.35% were low-level (0.1-1 µg/L), and only 0.07% were moderately low level (>1 µg/L).

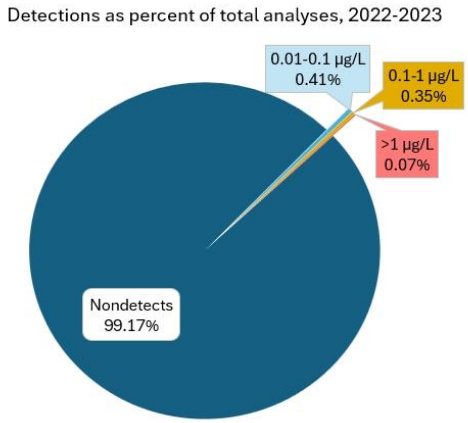

Figure 1. Detection rates among 2022-2023 groundwater samples.

There were *no exceedences* of any known pesticide groundwater standards among these detections, continuing the pattern of findings of our sampling program since its inception.

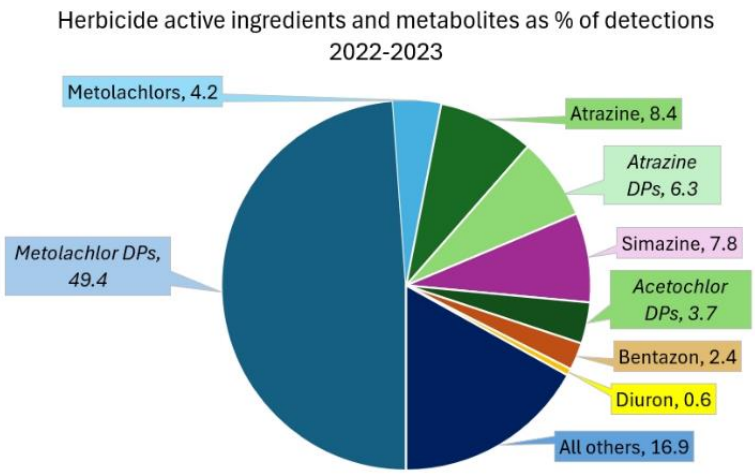

Figure 2. Breakdown of pesticides and degradations products (DPs) as percent of total detections.

Detections (which were under 0.8% of total tests) were clearly dominated by herbicides and their metabolites (Figure 2), especially the degradation products of metolachlor (49% of detections) and the metolachlor parent compounds (4%). Atrazine and its degradates came next (15% of detections) followed by simazine (8%), acetochlor degradates (4%), bentazon (2%) and diuron (0.6%). All other classes of pesticides together represented only 17% of detections, the greatest among them being imidacloprid (4%), carbaryl (3%), and propiconazole (2%). Eleven other analytes had only one or two detections, cumulatively representing 8% of total detections.

In contrast, the lakes samples had greater detection frequencies but at similarly low levels. These detections were again dominated by herbicides, with detections of metolachlor OA (degradation product) detected in 37% of lake samples, atrazine in 30%, metolachlor ESA in 16%, and 2,4-D in 13%. S-metolachlor and imidacloprid were detected in 7% of lake samples, and mefentrifluconizole in 3%.

Significant effort is being invested in the ongoing development of analysis and synthesis of observed detection patterns as a function of both site (soil, aquifer, land use) and pesticide characteristics. Although, as expected, most detections occurred with pesticides with the weakest soil sorption strength (as reflected in Koc), a surprising number of pesticide detections occurred with moderately and strongly adsorbed pesticides. Similarly, detections occurred for analytes across the entire range of half-lives (representing relative persistence), although most were for analytes with longer half-lives. Land use categories (of categorical sites) had widely-ranging detection frequencies, although these were somewhat associated with the prevalent soil types associated with several land uses. Examination of detection patterns for sampling locations for categorical sites showed those within the application areas unsurprisingly had the greatest detection frequencies, while only the metabolites with the weakest sorption (smallest Koc) were found in downgradient wells. Relationships between detections and presumed site vulnerability (based on site soil textures or drainage class) also yielded counter-intuitive results. Sites with soils that tended to have preferential flowpaths were relatively more likely to have detections.

Given the size, scope and complexity of the database of detections and site/pesticide characteristics, the team invested heavily in improved approaches for analysis and synthesis. First was the development and initial publication of the Theoretical Groundwater Ubiquity Score (TGUS), which is an improvement of the long-used Groundwater Ubiquity Score (GUS). Both approaches use the ratio of half-life and Koc to predict leaching potential. The TGUS approach enables incorporation of site properties and modern detection limits for assessing the likelihood of detectable leaching within a specified period of leaching vulnerability, as well as testing which characteristics contribute most strongly to detectable leaching. The TGUS predicted 90% of the detects correctly. Finally, the team is supporting development of AI-based machine learning (here termed Interactive Machine Learning Detection Assessment, IMLDA) to help elucidate which site and pesticide characteristics can best predict detectable leaching. Development of all three assessment approaches is ongoing, as is the Year 4 sampling.

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1 Introduction

1.1 Purpose and context

The New York State Department of Environmental Conservation's (NYS DEC) Bureau of Pesticides Management has requested that Cornell's Soil and Water Group (in the Department of Biological & Environmental Engineering) identify and recruit a select array of groundwater well owners and lake cooperators, then sample groundwater and lake water for pesticide residues. This is the latest in a series of efforts since 2000 under the NYS Pesticide Sales and Use Reporting law, which has designated Cornell as an agent of New York's groundwater monitoring.

This work is part of an ongoing series of joint research ventures between the Cornell Soil and Water Group (SWG) and NYS DEC. This work contributes to New York's need to balance the economic and public health benefits of pesticide use versus the potential health and environmental costs of their residues spreading beyond the sites of pesticide use. NYS DEC is responsible for determining whether and under what conditions any given pesticide can be used in New York and, therefore, is highly interested in focused environmental sampling to ensure that unanticipated mobility of pesticide residues to water resources is not occurring as a consequence of allowed label-compliant pesticide use.

The current NYS DEC-Cornell MOU covers activities from 2021 through 2025 (Cornell Soil and Water Group, 2024), in which Cornell personnel and volunteers associated with lake sites collect targeted water samples for analysis of pesticide residues in groundwater and lakes in upstate New York (representing areas north or west of New York City). This 2023 annual report provides our results and analysis for samples collected through the end of 2023. In addition to the results for our three sampling site rosters, we present progress on the development of multiple improved conceptual frameworks for analyzing and synthesizing these results.

1.2 Voluntarism and confidentiality

The project relies on volunteer, confidential cooperators who allow Cornell to sample from wells and other environmental water access points on their properties. The privacy of the confidential cooperators is specifically protected under the provisions of Cornell's contract with NYS DEC, thus nothing about the identity or specific locations of confidential cooperators will be released to NYS DEC or the public (a cooperator can of course, declare their involvement). As a result, any release or publication of data (such as in reports, website and/or NYS DEC's analytical chemistry information system called EQuIS) will include only anonymized and location-blurred data to preserve anonymity.

In recent years the project has also relied on a small cadre of volunteers who carry out sampling of several lakes with Cornell's assistance. These lake sampling volunteers are prominent locally and part of the Citizen Statewide Lake Assessment Program (CSLAP), and

thus have less need for anonymity but have the choice about release of project data to the public. NYS DEC and Cornell are grateful to the confidential cooperators and lake sampling volunteers.

1.3 Prior work

The Cornell team has previously conducted sampling studies of upstate private wells in six counties (Figure 1.1; in chronological order: Cortland, Schenectady, Orange, Cayuga, Wayne and Genesee) for NYS DEC, yielding single-timepoint data for around 240 wells. Cornell later revisited selected wells in several counties with seasonal sampling for a year or longer. In addition to annual reports to NYS DEC describing this work (available at this link https://soilandwaterlab.cornell.edu/wp-content/uploads/static/dec-early/downloads.html) several peer-reviewed papers covering this work have been published (Richards et al., 2012; Sinkevich et al., 2005). One focus in Genesee County was sampling wells in a karst (carbonate bedrock) area, where groundwater in karst-related fissures is vulnerable to rapid contamination from the surface, including the entry of water via sinkholes in fields and streambeds.

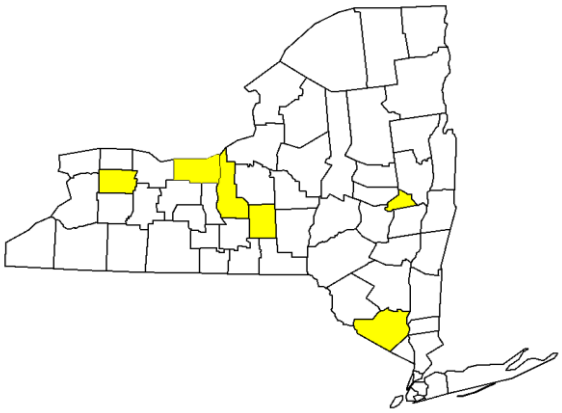

Figure 1.1. Counties sampled in earlier groundwater work

Figure 1.2. Lakes sampled previously by CSLAP volunteers with Cornell

In related work, our research group studies how the ubiquitous herbicide glyphosate moves in the environment, with most emphasis on migration to surface water from wetness-prone sites (Richards et al., 2018).

Our earlier NYS DEC/Cornell project (Cornell Soil and Water Group, 2017) also sampled four lakes in one round and later returned to two of the lakes (Lake Waccabuc, Sleepy Hollow Lake) in second rounds (Figure 1.2).

1.4 Project objectives, priorities, and coverage

As noted above, NYS DEC wants to ensure that excess levels of pesticides (or their degradation products) are not migrating from their sites of application to groundwater and other water resources. Given that our prior years of work with NYS DEC had sampling sites that were primarily (although not exclusively) influenced by nearby field crop systems (corn and/or soybeans) and their herbicides, the primary focus of the current 2021-2025 project is on other land uses that involve differing pesticides and cultural practices.

These sites – termed *categorical sites* since their selection was based on categories of land use and corresponding pesticide use. These are multi-well sites where the priority is to sample upgradient, downgradient, and in some cases, within the area of application. Existing wells (or in some cases, groundwater-fed springs or ponds) are supplemented with shallow monitor wells installed by the Cornell team. These categorical sites are sampled twice annually and represent about 80% of the annual project sampling load.

Supplementing these are *long-term sites* primarily representing single wells which are sampled annually. In a number of cases, these are sites that have been carried over from prior sampling projects – some dating 20 years since we first sampled them – and thus provide a longer timespan of sampling record. These represent ~15% of the annual sampling load.

Finally, representing about 5% of the annual sampling load are four lakes that are sampled annually or semiannually at inlet, outlet and mid-lake positions.

In terms of overall progress, Year 1 (2021) was mainly preparation for the project including building a geographic database and developing a recruitment strategy. In 2022 we recruited most of our categorical groundwater cooperators and lake volunteers, installed additional shallow wells where needed at the categorical sites, and began sampling at categorical and lake sites. Recruitment of the long-term sites, a lower priority, began in 2023 and sampling of them began alongside the second year of sampling of categorical and lake sites. By the end of 2023, the project recruited all of its final cooperator roster. Initial analytical data interpretation began with the return of pesticide results for 2022 samples from the NYS DEC Air Toxics Laboratory in early 2023.

The upstate project has reached 28 counties (Figure 1.3), with an intentionally diverse coverage that allows monitoring of a broad range of conditions that could affect the environmental fate of pesticides. We do not expect to encounter many cases of upstate conditions as vulnerable to groundwater contamination as much of Long Island has proven to be. The sensitivity of modern lab techniques guarantees that we will detect some residues – especially breakdown products – of certain popular chemicals at very low levels, as we did in earlier work. The 2022 results included the herbicide metolachlor's breakdown products at several sites, at concentrations far below levels of concern. These earliest findings confirm that many of our monitoring points and sampling techniques are working as intended.

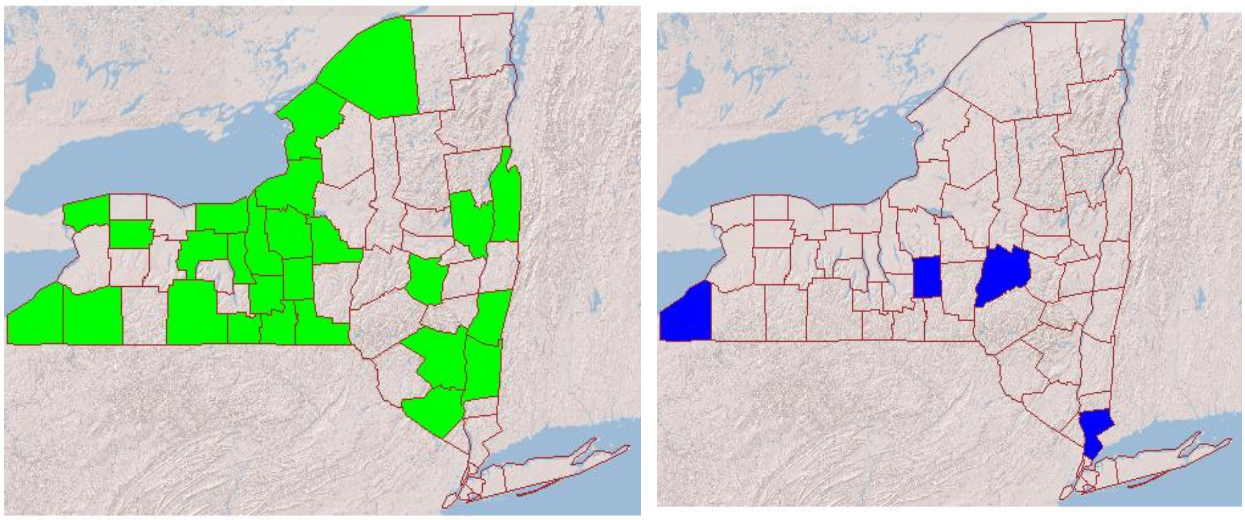

Figure 1.3. Upstate NY counties with groundwater well sampling sites (green) and lake sampling sites (blue).

1.5 Pesticide use in 2022

The many pesticide products registered for use in New York contain a variety of *active ingredients* (AIs). There were around 600 different restricted-use active ingredients reported in 2022 to the New York State Pesticide Sales and Use Reporting system (NYS DEC, 1996) as used by commercial pesticide applicators or sold to farmers (who do not have to report their own use). The most-used AIs (Figure 1.4) should be familiar.

For environmental fate assessment, we are more interested in the fate of the active ingredients rather than the specific product formulations, and cumulative use data helps to determine which active ingredients should be measured in groundwater and lake water.

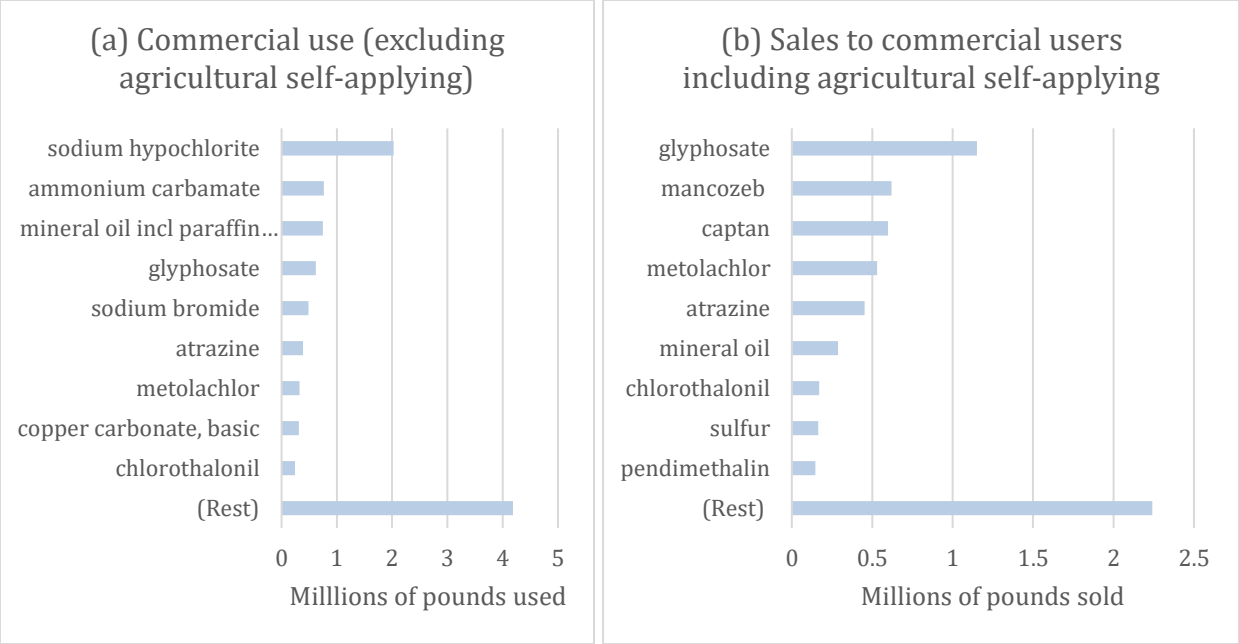

Figure 1.4. NYS reported pesticide commercial use (left, excludes farmer use) and sales (right)

1.6 This report

This report to NYS DEC is an annual compilation of all project results to date in the current 2021-2025 five-year program. It is focused on results, synthesis, and interpretation. An alternative view of this annual report will be available on the project's website (https://soilandwaterlab.cornell.edu/wp-content/uploads/static/dec-web/), where embedded links to detailed supplementary material are available.

The remainder of this report is organized as follows:

Section 2: Sites and Protocols
Section 3: Analytical Results
Section 4: Synthesis and Interpretation Approaches
Section 5: Ongoing Work and Considerations

2 Sites and Protocols

2.1 Design, approach, and recruiting

As noted in section 1.3, the project plan specifies three types of sampling sites (categorical, long-term, and lakes), detailed below.

As per NYSDEC's recommended site targeting strategy, the majority of our categorical groundwater sites (~85%) are in vulnerable aquifer areas, such as soils on stream alluvium, glacial outwash, lacustrine sands, and beach deposits, all of which have greater intrinsic leaching potential than do other landscapes. Relatively mobile pesticides applied in these contexts would have a greater chance of leaching into groundwater. Conversely, about 15% of sites are *presumptively* (based on traditional soil physical theory) less vulnerable locations for leaching of pesticides, with overlying soils including glacial till, lacustrine clay/silt, or organic soil muckland, which are less hydraulically conductive or more retentive of contaminants.

During site selection, we avoided organic farm operations as categorical sites due to the non-use of pesticides. Conversely, our long-term site roster does include organic farms bordered by neighboring land uses where pesticides are applied and potentially transported into the sampled site's well water.

As stated earlier, our overall site targeting strategy is based on the logical assumption that if water quality is good in these vulnerable settings, we can also infer that it will be good in other less vulnerable settings in the state.

Additional background for these and related topics can be accessed via links to our project web pages:

- Geology and ecological regions of NY
- Surficial geology
- Upper aquifers
- Federal ecological regions
- Where the pesticide user categories occur in upstate NY

2.1.1 Categorical sites

These sites (distributed as per Figure 2.1) were selected based on falling within one (or more) of the eight land use categories prioritized by NYS DEC for the current MOU, as shown in Table 2.1.

Table 2.1. Land use categories

Category	Typical pesticide uses
Golf courses	Insecticides, herbicides, fungicides, growth regulators
Sod farms	Insecticides, herbicides, fungicides
Other turfgrass	Insecticides, herbicides, fungicides
Greenhouses	Insecticides, fungicides
Outdoor nurseries	Insecticides, herbicides, fungicides
Fruit & vegetable farms	Insecticides, herbicides, fungicides
Vineyards	Insecticides, herbicides, fungicides
Utility/railroad rights of way	Herbicides

These categories have differing purposes and modes of use for pesticides. For example, vineyards, nurseries, greenhouses and fruit/vegetable farms have specialized insect, fungus, and disease control needs. Golf courses treat their greens and fairways to keep their specialty grasses uniform and free from pest and disease damage, while use on sod and other turfgrass is typically less intensive. Utility and road/railroad rights of way need to prevent the growth of weeds and trees, and thus, herbicides are a dominant focus. Several sites use Integrated Pest Management (IPM) and, accordingly, minimize their use of chemical pesticides when possible. As such, the potential pesticide residues from IPM sites should be less on average than from more conventional users.

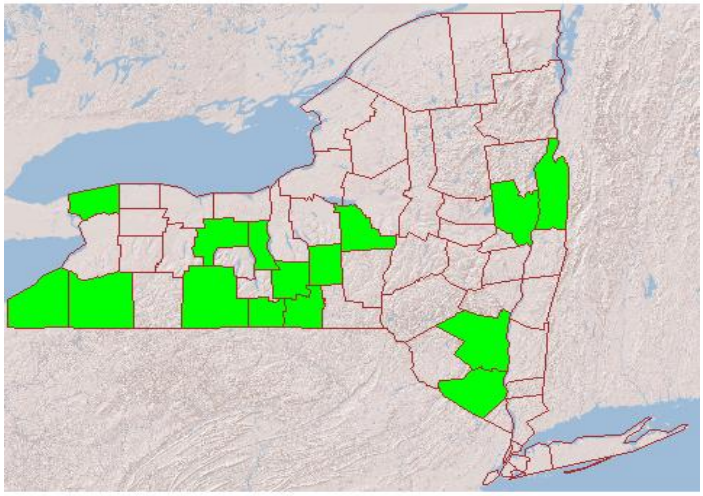

Figure 2.1. Upstate counties containing categorical sampling sites

Table 2.2 presents the roster of categorical sites, their general characteristics (aquifer type and presumed vulnerability), and sample counts through the end of 2023.

Table 2.2. Categorical sites inventory, characteristics, and samples collected through 2023.

Category	Site ID	Surficial Geology	Presumed leaching vulnerability	Samples
Golf courses	Golf-2	Glacial outwash	high	8
	Golf-7	Glacial outwash/alluvium	high	9
	Golf-9	Drained muck	low	8
Greenhouses	Green-16	Lake beach?	high	8
	Green-17	Alluvium?	high	6
	Green-18	Alluvium	high	9
Outdoor nurseries	Nur-2	Glacial outwash/alluvium	high	8
	Nur-3	Glacial drumlin	medium	15
	Nur-5	Alluvium	medium	15
Rights of way	ROW-1	Lake beach	high	5
	ROW-2	Glacial outwash/alluvium	high	14
	ROW-4-1	Glacial outwash	high	3
	ROW-4-2	Glacial outwash	high	3
Sod	Sod-2	Drained muck	low	8
	Sod-3	Drained muck	low	10
Turfgrass	Turf-1	Glacial outwash/alluvium	high	4
Vegetable & fruit farms	VegF-1	Lake/alluvium	high	23
	VegF-4	Drained muck	low	8
	VegF-6	Glacial outwash?	high	9
Vineyards	Vine-1	Filled-in valley	high	9
	Vine-3	Glacial till/outwash	medium	8
	Vine-4	Lake beach	high	14

Ecoregions represented in the sites in Table 2.2 include Allegheny, Ridge & Valley, Coastal, Great Lakes, and Northeast Highlands. Presumed vulnerabilities are based on the potential for leaching of pesticide residues to depths below one or two meters, as a function of soil and surficial geology type. This assignment is equivalent to most of NYS DEC's descriptive criteria for Principal Aquifers.

Given the twice-yearly sampling regimen, we strive to sample the sites in mid-to-late spring and again in mid-to-late fall each year. In view of upstate New York's generally uniform pattern of precipitation over the seasons and potential evaporation that is at its maximum during July andAugust , the potential for groundwater recharge (and thus

pesticide mobilization potential) is greater in the spring and fall than in the summer. The spring timeframe also coincides with start-of-season pesticide applications, while the fall represents the resumption of mobilization potential following the late spring and summer pesticide applications. This timing target was not possible for all sites in 2022 due to ongoing site recruitment and development, but the target schedule was fully realized in 2023 and beyond (Table 2.3).

Table 2.3. History summary of sampling categorical sites

When	Comments
Spring and summer 2022	Sites sampled as they joined and had wells installed: around half of site roster sampled for the first time.
Late fall 2022	Later sites enlisted (including some well installations) and sampled for first time. Second sampling for sites sampled earlier.
April-July 2023	All sites sampled for first round of 2023.
Sept-Nov 2023	All sites sampled for second round of 2023.
April-June 2024	All sites in process of sampling for first round of 2024.

Categorical sites are grouped into four zones to maximize the efficiency of travel for the multi-day sampling trips to the West (8 of 21 sites), Southeast (4 of 21 sites) and Northeast (5 of 21 sites). The remaining sites (termed the Central zone) can be reached by day trips from our base in Ithaca.

All 21 categorical sites were sampled three or four times in 2022 and 2023 (Table 2.3). The resulting sample count (Table 2.2) varied widely depending on how early they were recruited in 2022, how many wells are present at each site, whether wells had sufficient water present or needed redevelopment at any given sampling visit, and finally if anomalous results for on-campus tests suggested that a resample was needed.

2.1.2 Long-term sites

We initially hoped to fill the long-term site roster by re-recruiting participants in earlier projects (Figure 2.2). For various reasons (including many changes of ownership in the decade(s) since the initial sampling), the needed number of sites was not reached. Following NYS DEC's encouragement, we geographically diversified our site coverage of the state (including adding areas with no categorical sites present). In the summer of 2023, we also switched to primarily recruiting small businesses or other establishments (in place of typically non-responsive households), approaching sites ranging from arboretums to legal cannabis farms (where pesticide use can be heavy). We also went beyond the initial target of 24 sites, noting that some of the recruited sites may be provisional and not be continued past the first year or two. The roster as of the end of 2023 is shown in Table 2.4. Ecoregions

represented include all those for categorical sites with the addition of several sites in the Erie Drift ecoregion. The Site IDs in Table 2.4 were assigned in the order in which they became serious candidates.

In 2023, Cornell personnel, often with direct assistance from the cooperators, sampled 33 of the 34 agreed-to sites. Three of the sampled long-term sites had more than one sampling point that we deemed necessary to characterize the site, at least initially. In addition, site Long-40 was sampled twice (March and June, deeming the June sample more representative). The total 2023 sample tally from this roster was thus 37 samples.

Figure 2.2. Example of localized vulnerability used in selection of long-term monitoring site: wellhead at the base of upslope application area.

Table 2.4. Long-term site roster, general characteristics, and 2023 sample count.

County	Site ID	Surficial geology	Presumed area leaching vulnerability	Prior History	Samples
Broome	Long-50	Glacial kame/till	medium		1
Cayuga	Long-08	Glacial till	low	yes	1
Cayuga	Long-09	Lake silt/clay	low	yes	1
Cayuga	Long-24	Glacial till, lake silt/clay	low	yes	1
Chautauqua	Long-55	Alluvium	high		2
Chautauqua	Long-56	Alluvium/till	medium		1
Columbia	Long-62	Glacial outwash	high		1
Cortland	Long-03	Glacial outwash	high	yes	1
Cortland	Long-38	Glacial till	low		1
Cortland	Long-63	Glacial outwash gravel?	high	yes	1
Dutchess	Long-47	Alluvial fan	high		1
Genesee	Long-57	Glacial till	low	yes	1
Genesee	Long-58	Karst (dissolving limestone)	high	yes	2
Genesee	Long-59	Glacial till	low		1
Jefferson	Long-29	Lake sand	high		1
Jefferson	Long-30	Lake silt/clay	low		1
Jefferson	Long-32	Lake silt/clay	low		1
Jefferson	Long-33	Lake silt/clay	low		1
Jefferson	Long-34	Till/moraine	low		1
Jefferson	Long-35	Lake silt/clay	low		1
Jefferson	Long-44	Lake silt/clay	low		1
Jefferson	Long-45	Lake silt/clay	low		1
Onondaga	Long-40	Glacial till	low		2
Onondaga	Long-43	Glacial outwash	high		1
Onondaga	Long-52	Glacial till	low		1
Ontario	Long-53	Glacial till/perched water table	low		1
Orange	Long-41	Lake silt/clay	low	yes	1
Orange	Long-61	Glacial kame?	medium		1
Oswego	Long-49	Lake sand	high		0
Saratoga	Long-54	Bedrock	low		2
Schoharie	Long-51	Glacial till	low		1
St. Lawrence	Long-26	Alluvium	medium		1
Tompkins	Long-25	Glacial outwash	high		1
Wayne	Long-60	Glacial till, muck	low		2

2.1.3 Lake sites

The work plan originally specified sampling four lakes once per year at both inlet and outlet locations (yielding eight samples per year total). As the project progressed, we recognized the need to modify this based on conditions at the lakes chosen and on the perspectives of CSLAP volunteers at two lakes. A roster of four lakes and two samples per lake per year could not represent the hundreds of greatly varied lakes in upstate New York; thus, we tried for diversity in size (0.2 to 21 square miles) and location, spanning from near Lake Erie in the West to near the Connecticut border in the east. Sampling approaches varied from boats to bridges. The first two sampling years, 2022 and 2023, can be considered a developmental pilot effort. Sampling approaches for the lakes are summarized in Table 2.5.

Cornell personnel sampled Little York and Canadarago Lake, while CSLAP volunteers sampled Lake Waccabuc. CSLAP volunteers (with their own boats) sampled Chautauqua Lake in 2022 at two traditional CSLAP locations in the lake's northwestern and southeastern lobes and one more location they favored. Taking over sampling in 2023, Cornell project staff narrowed the sampling coverage to Chautauqua Lake's southern lobe, including its main inlet – the junction of the northern and southern lobes at Bemus Point – and the lake's outlet in Celeron and Jamestown. Samples were collected from the Bemus Point-Stow ferry and public docks. The total sample counts are enumerated in Table 2.6.

Table 2.5. Four contrasting lake sampling locations and approaches

Lake	Ecoregion	Sampling locations	When	Samplers
Upper Little York	Allegheny	2-3 samples taken near inlets, 1 at outlet, 1 in mid-lake	Once (spring or summer)	Cornell
Waccabuc	Coastal	1 mid-lake at CSLAP location, 1 near tributary input	Twice (late spring to early fall)	CSLAP volunteers
Chautauqua	Erie Drift	Varied between years; most recently on lake near inlet, and two areas near outlet	Once (spring or summer)	CSLAP (2022) Cornell (2023)
Canadarago	Allegheny	Samples taken at bridges over two major tributary streams and outlet stream	Once (summer or fall)	Cornell

Table 2.6. Samples collected from lakes by lake and type of sampling point, 2022-2023

Lake	Location	Location type	Samples 2022	Samples 2023
Canadarago	Mink Creek inlet	Lake - stream inlet	1	1
	Oaks Creek outlet	Lake - outlet	1	1
	Ocquionis Creek alt, inlet	Lake - inlet	0	1
	Ocquionis Creek inlet	Lake - stream inlet	1	1
Chautauqua	DeepCHQ	Lake	1	0
	NorthCSLAP	Lake - CSLAP	1	0
	ShallowCHQ	Lake	1	0
	SouthCSLAP	Lake - CSLAP	1	0
	Aboard Ferry	Lake - inlet	0	1
	Outlet (Lucy Park)	Lake - outlet	0	1
	McCrea Park	Lake - outlet	0	1
Waccabuc	CSLAP	Lake - CSLAP	2	2
	Tributaries	Lake - near inlet	2	2
Little York	Dam	Lake - outlet	1	1
	East inlet	Lake - near inlet	0	1
	Mid inlet	Lake - near inlet	1	1
	Middle	Lake	1	0
	North inlet	Lake - near inlet	1	1

2.2 Sample collection and analytical methods

Methods are presented here in brief. Fully detailed documentation about sample collection, processing, and storage is available at: https://soilandwaterlab.cornell.edu/wp-content/uploads/static/dec-web/qapp/QAPP-main.html.

2.2.1 Sample collection from existing landowner wells

Samples at some categorical sites and almost all long-term sites are taken using the owner's well pump. In almost all cases the selected sampling point is through a tap that draws water before any in-line treatment. Some sites are publicly-accessible flowing springs, from which containers can be filled directly.

2.2.2 Sample collection from installed shallow wells

The project's shallow monitor wells (all at categorical sites) are sampled using a peristaltic pump. These wells are pumped to waste until sufficiently purged. Purge water is monitored

for specific conductance and temperature using handheld pH/EC meters until both readings stabilize, indicating fresh groundwater inflow into the well. The sample is then collected in bottles as noted above. In some cases, a very slowly refilling well is purged by pumping on the first day then revisited the following day to collect the sample. The pumps and hoses are cleaned between each well. Well sounders are used to measure depth to water table in monitor wells (and when possible, landowner wells).

Site-specific notes: Site Nur-2 has one existing irrigation well that has no pump of its own. Thus, we use the peristaltic pump and hose there. Categorical site VegF-6 has an unused owner well in a good position to serve as an upgradient well, but it is so large that it cannot be effectively purged. We, therefore, need to settle for a sample without purging. Long-Term site Long-53, at an organic farm with pesticide-using neighbors, has an abandoned well that also can be an upgradient well and is treated the same as the well at VegF-6. Finally, site Vine-1 has a spring that emerges into an excavated, covered chamber from which we draw a sample using a peristaltic pump.

2.2.3 Sample collection from groundwater-fed ponds

In several cases, we draw samples from shallow groundwater-fed ponds. These ponds represent groundwater recharged on an adjacent property rather than the cooperator's land. The samples are drawn using a dipping cup on a rod or with a peristaltic pump with a hose attached to a longer segmented rod and having a float to keep the intake hose a few inches below the water surface. Bottle filling is as described above.

2.2.4 Sample collection from lakes, input tributaries, and outlets

Volunteers and Cornell SWL staff sample using Kemmerer devices (Figure 2.3) or peristaltic pumps from boats, bridges, or long docks. The standard depth of Kemmerer sampling is for the top of the cylinder to be 1.5 meters below the water surface. Sampling shallow lake inlet tributaries gets the intake hose below the water surface.

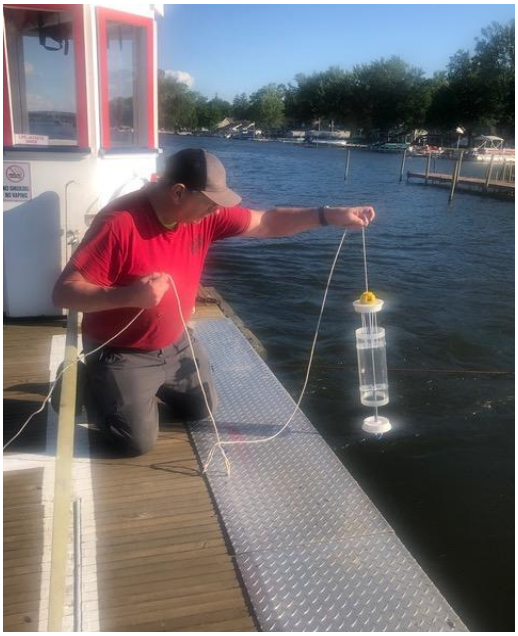

Figure 2.3. Kemmerer lake sampler.

CSLAP volunteers collected samples following CSLAP protocols from motorboats using a Kemmerer sampler. One of their 2022 Chautauqua Lake samples was taken at greater depth closer to the lake bottom, while the rest of the samples at both lakes were shallow samples (1.5 meters deep). In 2023, Cornell staff sampled from the Bemus Point - Stow ferry and from two docks near the lake's outlet using a Kemmerer sampler. Cornell personnel sampled Little York Lake with a Kemmerer sampler from a boat, and sampled the inlets and the outlet of Canadarago Lake from bridges using a Kemmerer sampler or a peristaltic pump.

2.2.5 Sample handling and analytical methods

Upon arrival at the Cornell campus, liquid samples are processed by agitation to mix, then pouring off multiple aliquots (subsamples) for different analyses. The remaining field sample volumes are frozen and the aliquots are refrigerated or frozen as specified.

Lake samples from CSLAP volunteers arrive at Cornell frozen and are thawed before making aliquots and re-freezing the remaining volumes.

Aliquots for DEC remain frozen until packing with additional ice in insulated boxes for express shipment to the NYS DEC laboratory, which keeps them frozen until thawing for their analyses.

We periodically check field pH and EC meters against standards of known pH or ionic strength, recalibrating when indicated.

Anions analysis (for nitrate, sulfate, orthophosphate and chloride) is carried out via ion chromatography at the USDA Robert Holley Laboratory on the Cornell Ithaca campus. Cation analysis (for calcium, sodium, etc.) is carried out at the same facility via multichannel inductively-coupled plasma (ICP) spectroscopy. Each procedure has built-in quality assurance tests.

NYSDEC measures pesticides and breakdown products (metabolites) in almost all cases using a liquid chromatograph with tandem mass spectrometer. Samples are not preprocessed; a direct injection method is used. Analytical detection limits are as low as 0.01 micrograms per liter.

Additional detail on analytical methods can be found at: https://soilandwaterlab.cornell.edu/wp-content/uploads/static/dec-web/methods-detail-analytical.html.

2.3 Analyte selection

PSUR data indicate hundreds of potential active ingredients (in addition to the degradation products of certain widely-used active ingredients (AIs)) that could be tested for, representing an analytical scope far in excess of project resources. As such, targeting of the most important compounds for analysis was a key task. Figure 2.4 is a flowchart indicating the key steps and factors used in this process. Note that both development and implementation of this approach was iterative as multiple steps needed to be revisited.

The categorical sites hold the primary place in the project, as reflected by the greatest allocation of total wells and samples. As such, we began looking for candidate analytes by first polling the categorical landowners for the products they used (since there would be little point in collecting and testing samples from a site when none of the active ingredients in use would be analyzed for). This polling began with the earliest cooperators but continues as cooperators feel more comfortable discussing their product use.

The union of these product lists from cooperators ("categorical use list" in Figure 2.4) was a key input for analyte choice for this project. This was combined with the analyte list from

our earlier DEC projects. This list had a strong focus on field crop AIs and had more recently been refined for use in lake sampling projects. The AI list from the Suffolk County Department of Health Services (SDCHS) was also merged. The broader coverage of the previous Cornell SWG and SDCHS is especially useful for the long-term sites, lake sites of the project, and upgradient sampling points at the categorical sites. We added the aquatic herbicide endothall as an analyte at the request of Chautauqua Lake volunteers. Otherwise the analytes are effectively aimed at groundwater concerns.

Finally, DEC nominated certain analytes, in particular neonicotinoid compounds which are the subject of interest due to effects on pollinating insects. These four sources became the unified candidate list (Figure 2.4) which then proceeded to prioritization.

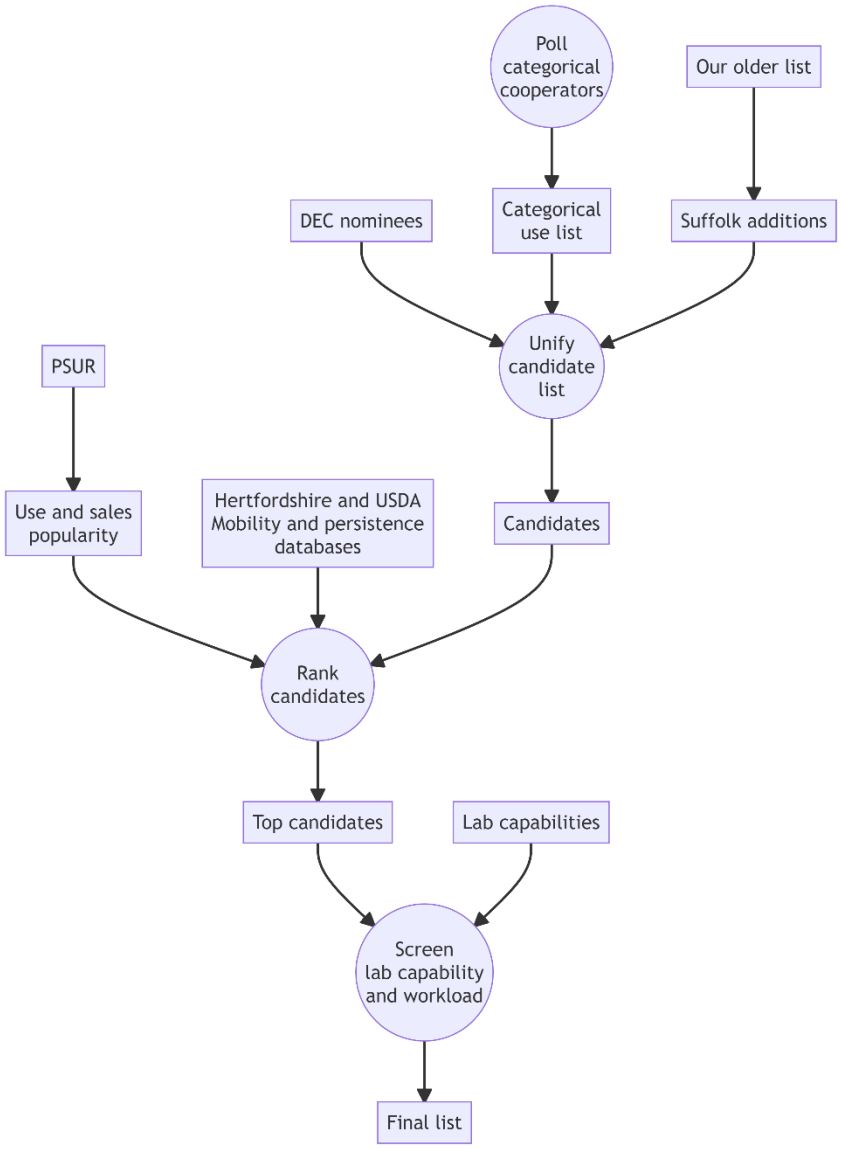

Figure 2.4. Factors and processes flowchart depicting choice of analytes

Several data sets were used to help prioritize the candidate list. PSUR data were used to index the *relative extent of use* (with greater use of a given AI increasing its priority). Two chemical properties databases were merged with the candidate list to help prioritize those AIs that were more mobile (lower sorptivity) and more persistent (slower degradation half-life).

Eighty-nine candidate analytes emerged from this screening process, of which circa 20 active ingredients came from the combined categorical sites usage list. Input on the NYS DEC laboratory's capabilities resulted in removal of dichlobenil as it required a completely different – and thereby uneconomical -- standalone analysis.

The full analyte list is summarized in Appendix Table A.1, which includes current detection limits, sorption parameters (Koc or Kfoc), the persistence as represented by the half-life (days), and the groundwater ubiquity score (GUS).

For the 2022 samples, in early 2023 the NYS DEC laboratory first tested only for the new analytes for categorical sites and new DEC-nominated AIs (28 analytes in total), and then tested for the rest of the full analyte list later in 2023. The laboratory then analyzed the full 2023 array between January and May 2024.

3 Results

Given the many thousands of analytical results — most being non-detections of pesticide analytes — the focus in this section is on those samples *with detection*s of one or more AIs or degradation products.

This section presents the results in a minimalist fashion without interpretation. The following section begins to look for patterns and potential causality by merging certain site characteristics.

3.1 Categorical sites results

Table 3.1 enumerates all of the NYS DEC pesticide lab's analytical detections at categorical sites, ordered by category, site, and relative sampling location (upgradient, downgradient, or within site application area) for 2022 and 2023. Land use categories or specific sites not appearing in these tables had no analytical detections of active ingredients nor degradation products during this time period.

The tables group all results for a given site by the sampling location: if there were multiple wells in a location (typically having the "within site" designation), the displayed result represents the total number of detections/non-detections from those multiple wells and the maximum concentration observed among them.

In addition to quantifiable detections, the tables list the number of non-quantifiable detections (NQD) where the analyte was clearly present but only at concentrations below the lower detection limit; thus our terminology is subtly wrong – the "detection" limit is actually a quantification limit. (In cases where NQDs were observed in the absence of any quantifiable detections, the maximum concentration displayed in the table is the lab's *estimate* of the highest NQD magnitude, which is lower than the lower detection limit (LDL). The minimum and maximum LDLs for a given analyte reflect instrument variation between analytical batches.

Table 3.1. Pesticide and metabolite (italicized) detections at categorical sites, 2022-2023. Single or grouped multiple wells by site LOCation (UPG- upgradient, DWG-downgradient, Within), Detections (number, number non-quantifiable (NQD), and maximum concentration (µg/L)), number of NonDetects (ND), and range of reported lower detection limits (LDL). Anonymous site identifiers are truncated to further protect cooperator privacy. Color bands group results from the same site.

Site	LOC	Analyte	Detections			# ND	LDL µg/L
			#	# NQD	Max µg/L		
Golf-	Within	Propiconazole	1	0	0.021	7	<0.01
		Metolachlor OA	0	1	0.033	7	<0.05-0.10
Green-	Within	Thiamethoxam	1	0	0.058	7	<0.025-0.100
Green-	DWG	Mefentrifluconazole	1	0	0.202	2	<0.025-0.050
		Myclobutanil	1	0	0.063	2	<0.025
		Paclobutrazol	1	0	0.051	2	<0.025
		S-Metolachlor	1	0	0.202	2	<0.025-0.050
Nur-	Within	Metolachlor OA	1	0	0.068	7	<0.05-0.10
Nur-	DWG	Carbaryl	0	1	0.042	6	<0.05
		Metolachlor OA	1	0	0.050	6	<0.05-0.10
	UPG	Atrazine	4	0	0.231	0	<0.01
		De Ethyl Atrazine	0	1	0.043	3	<0.05-0.25
		Hydroxy Atrazine	1	0	0.108	3	<0.05-0.25
		Metolachlor OA	0	1	0.033	3	<0.05-0.10
	within	*Metolachlor OA*	1	1	0.050	2	<0.05-0.10
Nur-	UPG	Atrazine	1	0	0.016	8	<0.01
		Glyphosate	1	0	5.140	4	<1.0
		Simazine	2	0	0.031	7	<0.01
		Acetochlor ESA	1	0	0.058	3	<0.05
		Metolachlor ESA	2	0	0.222	7	<0.05-0.15
	Within	*Acetochlor ESA*	0	1	0.048	3	<0.05
		Metolachlor ESA	1	0	0.218	5	<0.05-0.15
		Metolachlor OA	0	1	0.037	5	<0.05-0.10
ROW-	DWG	Simazine	1	0	0.012	7	<0.01
ROW-	DWG	*Metolachlor OA*	2	0	0.273	1	<0.05-0.10
ROW-	Within	*Metolachlor OA*	2	0	0.127	1	<0.05-0.10
Sod-	Within	Carbaryl	1	0	0.187	3	<0.05
		Metolachlor OA	1	1	0.053	2	<0.05-0.10
Sod-	Within	Imidacloprid	4	0	0.051	11	<0.025-0.050
		Hydroxy Atrazine	1	0	0.118	9	<0.05-0.25
		Metolachlor ESA	8	0	0.630	2	<0.05-0.15
		Metolachlor OA	8	0	0.799	2	<0.05-0.10

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Table 3.1. Pesticide and metabolite (italicized) detections at categorical sites, 2022-2023. Single or grouped multiple wells by site LOCation (UPG- upgradient, DWG-downgradient, Within), Detections (number, number non-quantifiable (NQD), and maximum concentration (µg/L)), number of NonDetects (ND), and range of reported lower detection limits (LDL). Anonymous site identifiers are truncated to further protect cooperator privacy. Color bands group results from the same site.

Site	LOC	Analyte	Detections			# ND	LDL µg/L
			#	# NQD	Max µg/L		
VegF	stream	*Metolachlor OA*	1	0	0.261	0	<0.05
		Metolachlor ESA	1	0	0.252	6	<0.05-0.15
	DWG	*Metolachlor OA*	4	0	0.105	3	<0.05-0.10
		Metolachlor OA	0	3	0.044	2	<0.05-0.10
	Within	*De Ethyl Atrazine*	2	0	0.098	4	<0.05-0.25
		Metolachlor ESA	2	0	0.755	4	<0.05-0.15
		Metolachlor OA	3	0	2.198	3	<0.05-0.10
VegF	Within	Bentazon	4	0	8.763	4	<0.5
		Propiconazole	1	0	0.043	7	<0.01
		Metolachlor ESA	7	0	0.832	1	<0.05-0.15
		Metolachlor OA	7	0	0.705	1	<0.05-0.10
VegF	Within	Carbaryl	1	0	0.279	5	<0.05
		Fluopyram	2	0	0.075	4	<0.025
		Simazine	4	0	0.050	2	<0.01
		Terbacil	0	1	0.379	5	<0.5
		Thiamethoxam	0	1	0.013	7	<0.025-0.100
		JSE76	1	0	0.070	5	<0.05
Vine	Within	Carbaryl	1	0	0.065	7	<0.05
		Imidacloprid	3	0	0.051	9	<0.025-0.050
		Oxadiazon	1	0	0.559	7	<0.025-0.100
Vine	Within	Carbaryl	1	0	0.253	7	<0.05
		Simazine	4	0	0.175	4	<0.01
Vine	UPG	*Metolachlor OA*	2	0	0.126	2	<0.05-0.10
	Within	Diuron	1	0	0.013	7	<0.01
		Metolachlor OA	0	1	0.024	7	<0.05-0.10

Table 3.2 presents summary lists of all analytes detected as a function of sample location (UPG vs. DWG and Within). More deeply itemized results are presented in the Appendix Table A2, consistent with preserving the anonymity of voluntary cooperators.

Although the subsequent discussion section will contain fuller analysis and synthesis of these results, several trends are evident:

- The active ingredients found at "within" and "downgradient" sampling points were much more diverse than those at "upgradient" sampling points. (This in part is due

to our site selection approach which favored sites that did not need an upgradient sampling point due to there being no upgradient pesticide use.) Also, our categorical sites are individually specialized in their pesticide selection and modes of use, compared to upstate New York's more widespread field crop producers for livestock who tend to emphasize a few herbicides like atrazine, metolachlor, and acetochlor and use fewer insecticides and fungicides.

- Metabolites of herbicides (metolachlor, atrazine and acetochlor) were by far the most common detections, appearing primarily in upgradient and a few within site locations. Some of the within site detections of these may actually originate from neighboring upgradient land uses.

Table 3.2. Summary of detected active ingredients and degradation products as a function of sampling location at categorical sites. JSE76 is a degradation product of chlorantraniliprole.

Active ingredients		**Degradation products**	
UPG	**Within and DWG**	**UPG**	**Within and DWG**
Atrazine	Bentazon	*Acetochlor ESA*	*De ethyl atrazine*
Glyphosate	Carbaryl	*De ethyl atrazine*	*Hydroxy atrazine*
Simazine	Diuron	*Hydroxy atrazine*	*JSE76 (from chlorantraniliprole)*
	Fluopyram	*Metolachlor ESA*	*Metolachlor ESA*
	Imidacloprid	*Metolachlor OA*	*Metolachlor OA*
	Mefentrifluconazole		
	Myclobutanil		
	Oxadiazon		
	Paclobutrazol		
	Propiconazole		
	Simazine		
	S-metolachlor		
	Terbacil		
	Thiamethoxam		

3.2 Long-term sites results

Table 3.3 reports the summarized detections, following the same general approach as was used for the categorical site tables above. However, given that the long-term sites are generally single-well sites, the Location column used in prior tables is not relevant. (One site — Long-58 — had two wells tested in 2023, hence two detections of several analytes are reported.)

There were no unusual pesticide detections in wells at long-term sites in 2023, our first year of long-term site sampling. Nearly all of the 20 detections in 11 different samples were

of popular herbicides atrazine, metolachlor (or isomer S-metolachlor), and simazine, with the highest detections on the order of 1 µg/L and 15 under 0.1 µg/L. Except for atrazine, whose drinking water standard is 3.0 µg/L, these chemicals fall under New York State's default drinking water standard of 50 µg/L. Our detections at circa 0.1 µg/L thus represent concentrations that are only 3% (atrazine) to 0.2% (all others) of the applicable drinking water standards. This mirrors the general findings of our 6 prior county-level monitoring projects in the 2000s and 2010s, in which no well yielded any active ingredient concentration of health concern.

Detections of degradation products were more widespread (34 detections in 16 samples of 6 degradation products) than the corresponding parent active ingredients (15 detections in 9 samples of 5 active ingredients). Detections of degradation products are similarly behaving consistently with findings in our earlier projects in which the most popular herbicides are being degraded in the environment but are clearly much more mobile than the parent compounds.

The results to date continue to show that the pesticide labels approved by NYS DEC are protective of groundwater vis-à-vis current grounwater standards. Detected metabolites indicate that the wells are tapping recharge water from areas where the parent active ingredients have been applied, and the soil is being effective in mitigation.

Table 3.3. Detections of active ingredients and metabolites (italicized) at long term sites, 2023. Number of Detections and NonQuantifiable Detections (NQD), maximum concentration (µg/L), and lower detection limits (LDL) during the analysis period.

County	Site	Analyte	Detections			LDL µg/L
			#	# NQD	Max µg/L	
Broome	**Long-50**	*Metolachlor OA*	1	0	0.795	<0.05
Cayuga	**Long-08**	*Metolachlor ESA*	0	1	0.037	<0.05
		Metolachlor OA	1	0	0.226	<0.05
	Long-09	Atrazine	1	0	0.034	<0.01
		De Ethyl Atrazine	1	0	0.105	<0.05
		Hydroxy Atrazine	1	0	0.104	<0.05
		Metolachlor OA	1	0	0.155	<0.05
Columbia	**Long-62**	Simazine	1	0	0.037	<0.01
		Acetochlor ESA	1	0	0.054	<0.05
Cortland	**Long-03**	Atrazine	1	0	0.035	<0.01
		Bromacil	0	1	0.026	<*0.05
		De Ethyl Atrazine	1	0	0.056	<0.05
		Metolachlor ESA	1	0	0.463	<0.05
		Metolachlor OA	1	0	2.825	<0.05
	Long-63	Atrazine	1	0	0.013	<0.01
		Acetochlor ESA	1	0	0.206	<0.05
		De Ethyl Atrazine	1	0	0.072	<0.05
		Metolachlor OA	1	0	0.256	<0.05
Dutchess	**Long-47**	Simazine	1	0	0.025	<0.01
		Metolachlor OA	1	0	0.075	<0.05
Genesee	**Long-57**	Atrazine	1	0	0.023	<0.01
		Acetochlor ESA	0	1	0.044	<0.05
		Acetochlor OA	0	1	0.038	<0.05
		De Ethyl Atrazine	1	0	0.058	<0.05
		Metolachlor ESA	1	0	0.147	<0.05
		Metolachlor OA	1	0	1.665	<0.05
	Long-58	Atrazine	2	0	0.067	<0.01
		Metolachlor	2	0	0.992	<0.025
		Propiconazole	1	0	0.063	<0.01
		S-Metolachlor	2	0	1.642	<0.05
		Metolachlor ESA	2	0	0.314	<0.05
		Metolachlor OA	2	0	1.681	<0.05
	Long-59	S-Metolachlor	1	0	0.068	<0.05

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County	Site	Analyte	Detections			LDL µg/L
			#	# NQD	Max µg/L	
Onondaga	**Long-40**	Atrazine	1	0	0.017	<0.01
		Fluxapyroxad	1	0	0.360	<0.25
		Metolachlor OA	1	0	0.071	<0.05
	Long-52	Atrazine	1	0	0.012	<0.01
		Metolachlor OA	0	1	0.036	<0.05
Ontario	**Long-53**	Atrazine	1	0	0.308	<0.01
		S-Metolachlor	1	0	0.107	<0.05
		De Ethyl Atrazine	1	0	0.063	<0.05
		Hydroxy Atrazine	0	1	0.035	<0.05
		Metolachlor ESA	0	1	0.036	<0.05
		Metolachlor OA	1	0	0.060	<0.05
Orange	**Long-61**	*Metolachlor OA*	0	1	0.042	<0.05
St. Lawrence	**Long-26**	*Metolachlor OA*	1	0	0.169	<0.05
Tompkins	**Long-25**	*Metolachlor OA*	1	0	0.302	<0.05
Wayne	**Long-60**	*Metolachlor ESA*	1	0	0.140	<0.05
		Metolachlor OA	1	0	0.537	<0.05

3.3 Lakes results

Table 3.4 enumerates all detected analytes in lake samples (Figure 3.1).

Lake Waccabuc has a largely forested watershed, with residential and golf course land uses near the lake. Only tiny traces of fungicides, perhaps used at the golf course, have shown up in samples from the current project and an earlier project.

In contrast, the other three lakes have watersheds containing considerable farmland thus the lake samples contain typical metabolites (metolachlor OA and ESA) and parent compounds (atrazine, S-metolachlor, 2,4-D) of popular upstate agricultural herbicides.

Figure 3.1. Lake outlet sampling in progress.

Table 3.4. Detections of active ingredients and metabolites (italicized) at lake sites, 2022-2023. Number of detections and nonquantifiable detections (NQD), maximum concentration (µg/L), number of non-detects (ND), and lower detection limits (LDL) during the analysis period.

Lake	Sampling location	Loctype	Analyte	Detections			# ND	LDL µg/L
				#	# NQD	Max µg/L		
Canadarago	Mink Creek inlet	stream inlet	*Metolachlor OA*	1	0	0.056	1	<0.05-0.10
	Oaks Creek outlet	outlet	Atrazine	1	0	0.019	1	<0.01
			Metolachlor OA	1	0	0.085	1	<0.05-0.10
	Ocquionis Creek alt inlet	inlet	Atrazine	1	0	0.112	0	<0.01
			Metolachlor OA	1	0	0.199	0	<0.05
	Ocquionis Creek inlet	stream inlet	Atrazine	1	0	0.241	1	<0.01
			S-Metolachlor	1	0	0.064	1	<0.025-0.050
			Metolachlor ESA	0	1	0.045	1	<0.05-0.15
			Metolachlor OA	1	0	0.523	1	<0.05-0.10
Chatutauqua	NorthCSLAP	lake	Atrazine	1	0	0.011	0	<0.01
	ShallowCHQ	lake	Atrazine	1	0	0.015	0	<0.01
			Imidacloprid	2	0	0.040	0	<0.025
	Ferry	inlet	Atrazine	1	0	0.013	0	<0.01
			Metolachlor OA	1	0	0.054	0	<0.05
	McCrea	outlet	Atrazine	0	1	0.009	0	<0.01
			Metolachlor OA	0	1	0.040	0	<0.05
	outlet	outlet	Atrazine	1	0	0.011	0	<0.01
			Metolachlor OA	0	1	0.042	0	<0.05
Waccabuc	Tribs	near inlet	Mefentriflu-conazole	1	0	0.026	3	<0.025-0.050
Little York	Dam	outlet	2,4-D	1	0	1.530	1	<0.2-0.5
			S-Metolachlor	1	0	0.031	1	<0.05
			Metolachlor ESA	1	0	0.278	1	<0.05-0.15
			Metolachlor OA	1	0	0.147	1	<0.05-0.10
	East inlet	near inlet	*Metolachlor OA*	1	0	0.171	0	<0.05
	Mid inlet	near inlet	2,4-D	1	0	1.610	1	<0.2-0.5
			Metolachlor ESA	1	0	0.306	1	<0.05-0.15
			Metolachlor OA	1	0	0.187	1	<0.05-0.10
	Middle	lake	2,4-D	1	0	1.720	0	<0.2
			Metolachlor ESA	1	0	0.279	0	<0.15
	North inlet	near inlet	2,4-D	1	0	1.330	1	<0.2
			Atrazine	1	0	0.013	1	<0.01
			Metolachlor ESA	1	0	0.321	1	<0.05-0.15
			Metolachlor OA	1	0	0.235	1	<0.05-0.10

4. Synthesis and Interpretation Approaches

This section relates our work to date in synthesizing the cumulative results database from 2022 and 2023, and in developing interpretive approaches to help understand the emerging patterns of detections in our sample array.

By way of a simple summary overview, several pie charts convey graphically the results of the groundwater sampling (both categorical and long-term sites) to date in their most basic form. Figure 4.1 represents the number of detections as a proportion of the 19,371 total analyses to date. "Total analyses" are defined as the number of samples × number of analyses per sample for active ingredients and degradation products. Total nondetects in this period were 19,205, while the greatest proportion of detections (84) fell in the lowest concentration range of 0.01-0.10 µg/L. There were 69 detections within the 0.1-1.0 µg/L range, and only 13 detections greater than 1 µg/L.

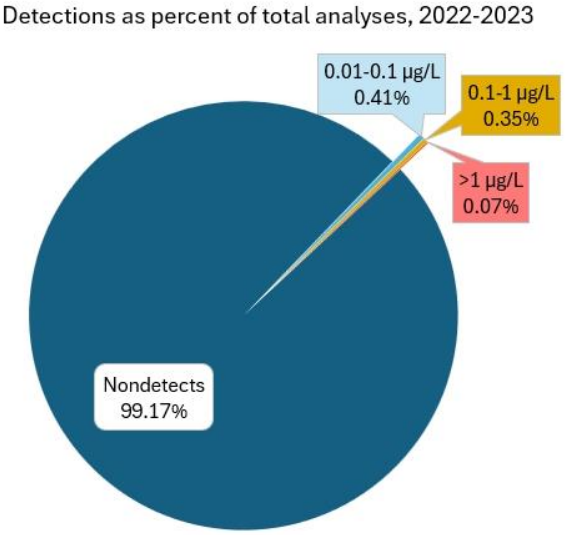

Figure 4.1. Proportions of detections and their concentration ranges, as percent of total groundwater analyses.

The detections in Figure 4.1 (which represented 0.8% of all tests) primarily consisted of herbicides and their degradation products, as shown in the breakdown of herbicides vs. all other detections in Figure 4.2.

Metolachlor degradation products (metolachlor ESA and especially metolachlor OA) alone accounted for nearly half of all detections. This level reached 54% of detections when the parent compounds (metolachlor and S-metolachlor) were included. Atrazine and its metabolites comprised 15% of detections, while simazine

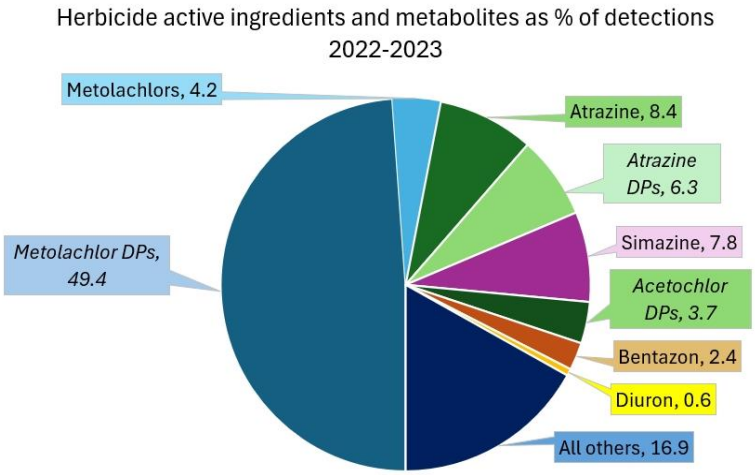

Figure 4.2. Herbicides dominate groundwater detections of active ingredients and metabolite/degradation products, as percent of total detections. "All others" (16.9%) includes all other types of pesticides.

represented 8%. Acetochlor DPs (no parent present) were 4%, while bentazon and diuron represented 3% of detections. All other detections (17%) comprised all other analytes. These "all others" detections are enumerated in Figure 4.3, in which all detections but one were of parent compounds. These detections were dominated by imidacloprid (4%), carbaryl (3%) and propiconazole (2%). All other detections shown in the figure were the result of either a single detection (0.6% of all detections), or two detections (1.2%). JSE76 was the sole degradation product (of chlorantraniliprole) in this group.

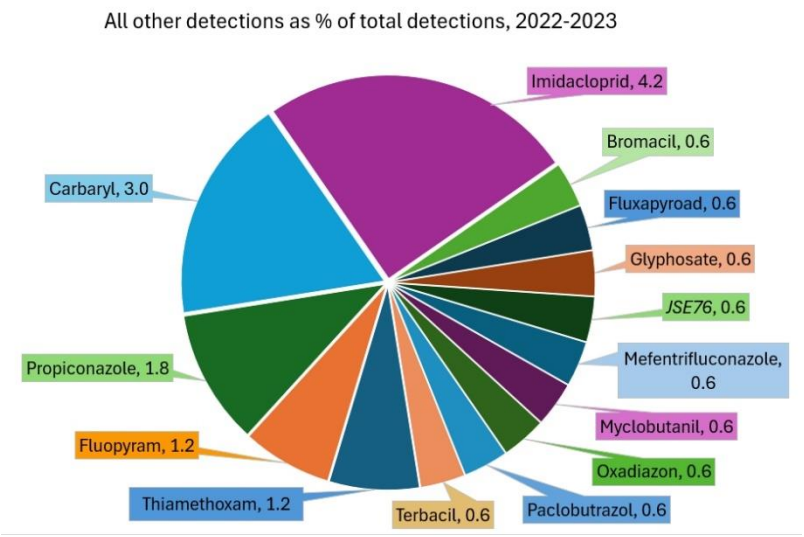

Figure 4.3. All other detections of active ingredients and metabolite/degradation products (DP's), as percent of total groundwater detections.

Given the relatively small sample array to date (30), a visual summary of detections in lakes samples is best represented as detection frequency (Figure 4.4). Herbicides (2,4-D, atrazine, S-metolachlor) and metolachlor metabolites again dominate the observed detections. Atrazine and metolachlor OA were present in 30% to 37% of lake samples. There were conversely few detections of other classes of analytes, representing detections in only one or two samples (mefentrifluconazole, imidacloprid).

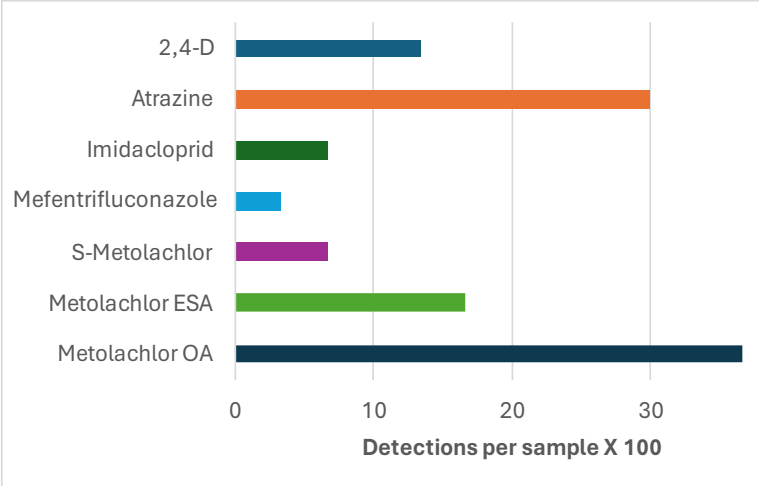

Figure 4.4. Lake sample analyte detection frequency

In the following sections, we will enumerate our three principal synthesis/interpretation approaches and the current status of each in view of both ongoing development as well as continuing data collection in Years 4 and 5. These approaches are:

Section 4.1 Using cross-tabulations to characterize detection patterns
Section 4.2 Development of the Theoretical Groundwater Ubiquity Score (TGUS)
Section 4.3 Development of Interactive Machine Learning Detection Assessment (IMLDA)

4.1 Using cross-tabulations to characterize detection patterns

This section relates a series of cross-tabulation analyses of groundwater detections to date, each based on *one primary analyte characteristic* (Koc, half-life) *or site characteristic* (land use, ecoregion, aquifer vulnerability), typically with secondary consideration of additional properties.

4.1.1. Analyte sorption strength Koc

The organic-carbon partition coefficient (Koc) and Freundlich coefficient (Kfoc) describe the sorption affinity of the analyte in question for the organic carbon in the soil. The cross-tabulations are summarized in Figures 4.5 and 4.6. Figure 4.5 presents the detection frequency as a function of adsorption strength. The analyte detection frequency on the y-axis is expressed on a permille (0/00) basis of total analytes (i.e., the number of analytes determined per sample summed over all samples). In Figure 4.6, the average number of detections is expressed in percent per sample. Some samples had several detections, so the number of samples with detections is less than indicated in Figure 4.6. Detections decrease as Koc increases (Figure 4.5), and the concentrations of those detections concurrently diminish, as reflected in proportionally fewer detections above 1 µg/L as Koc increases (Figure 4.6).

Despite the decreasing number of detections with increasing Koc values, the relatively large number of detections with a Koc value greater than 60 was unexpected based on the traditional advective dispersive theory generally used in predicting leaching risk. To demonstrate this, we calculated the average annual displacement of pesticides in soil using advection but omitting dispersion for simplicity for a typical Upstate NY climate with an annual recharge of 0.4 m/y and soil with 2% organic matter content, bulk density of 1.3 g/cm^3, and field capacity of 0.2 cm^3/cm^3. The resulting approximate average pesticide movement per year is shown in Table 4.1. Since dispersion was not considered, pesticides

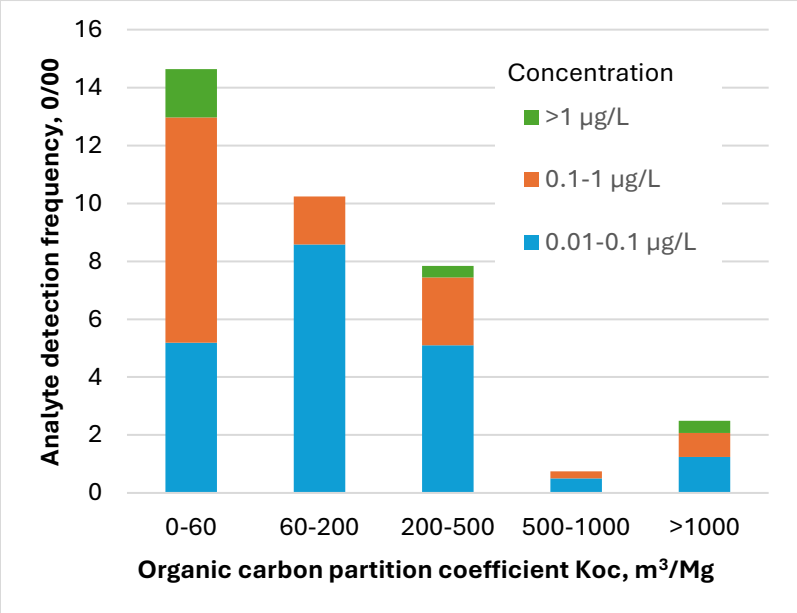

Figure 4.5. Detection frequency (detections per thousand analyses) of 2022-2023 groundwater samples and concentration ranges as a function of Koc class (or Kfoc where noted in Table 4.2.

with Koc values between 0 and 60 could likely be found in the groundwater, given a large half-life.

Table 4.1. Koc effect on leaching	
Koc, m^3/Mg	Displacement, m/y
0	2.00
60	0.41
200	0.14
500	0.06
1000	0.03

However, based on the traditional advective dispersive theory it is unlikely that pesticides with Koc values greater than 200 and average movement of less than 14 cm/year will reach groundwater at 2 m and beyond within the duration of this project.

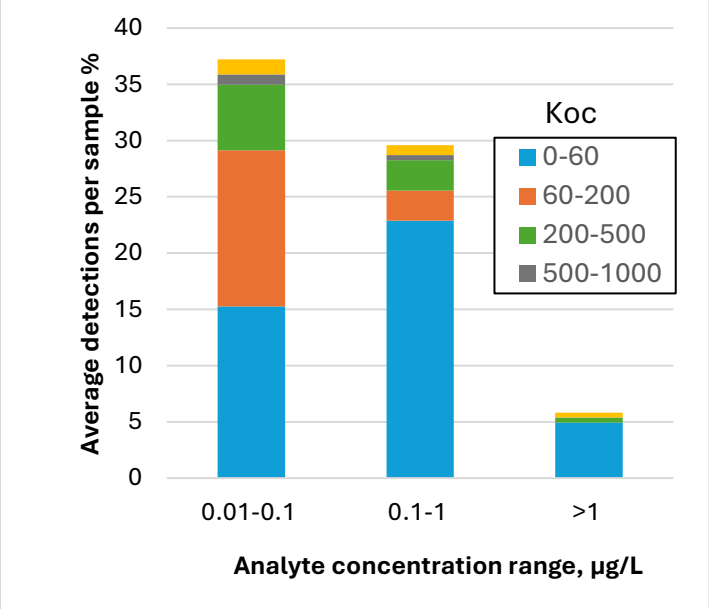

Figure 4.6. Average pesticide and metabolite detections per sample of the 223 groundwater samples collected in 2022 and 2023.

As detailed in Section 4.2, pesticides transported directly by preferential flow from the surface to groundwater with minimal adsorption during transport are consistent with the data presented in Figures 4.5 and 4.6. In addition, as seen in Figure 4.6, the proportion of pesticides with Koc values of less than 60 increases for increasing concentrations. This reflects the lower concentration of pesticides in the water phase at the surface with greater Koc values.

*Table 4.2. Detected pesticides and metabolites (italicized) groups by a range of organic sorption coefficients (Koc or *Kfoc).*	
Koc range m^3/Mg	Detected active ingredients and metabolites
>1000	Propiconazole*, glyphosate, oxadiazon,
500-1000	Diuron
200-500	Imidacloprid*, fluopyram, carbaryl, S-metolachlor*
60-200	*De ethyl atrazine*, simazine, metolachlor, atrazine
0-60	Dicamba*, bentazon, *metlachlor ESA, metolachlor OA*

4.1.2 Analyte half-life in soil

Persistence of pesticides and their degradation products in soil and aquifers is the second cardinal factor contributing to their presence and detection in groundwater. This is characterized by the in-soil half-life (days) representing the mean time for a given compound to degrade to half its initial mass, primarily via biodegradation. Given the range of soil conditions encountered, the half-life for a single compound can vary considerably, and data may be reported as "field" or "typical". Detected compounds summarized by half-life range classes in Table 4.3 are also segregated by the type of half-life data we were able to locate.

Table 4.3. Half-life ranges for detected active ingredients and metabolites (italicized), groups by data classified as "field" or "typical" half-life.

Half-life range	Detected active ingredients & metabolites	
	Field	Typical
>200 days	Diuron	*Metolachlor ESA*, *metolachlor OA*,
100-200	Fluopyram, imidacloprid, mefentrifluconazole, oxadiazon	*Hydroxy atrazine*, *JSE76*, terbacil,
50-100	Simazine	*Acetochlor ESA*, bromacil
25-50	Atrazine, myclobutanil, paclobutrazol, propiconazole, thiamethoxam	*De ethyl atrazine*
5-25	*Acetochlor OA*, bentazon, glyphosate, S-metolachlor	Carbaryl
All data from Hertfordshire PPDB		

The detection frequency (as detections per thousand analyses) in our groundwater samples is shown in Figure 4.7 as a function of half-life range classes. Unsurprisingly, the most persistent compounds (half-life >200 days) were the most frequently detected (representing 53% of all detections) and at greater concentration ranges. With 91 combined detections, the degradation products of metolachlor (metolachlor OA and ESA) figure most significantly in this class.

For the 100-200 day class, only imidacloprid (7 detects) and hydroxy atrazine (4 detects) had more than 1 detection. In the 50-100 day half-life class, the extensive use of herbicides led to multiple detections of atrazine (14), simazine (13), metolachlor (2), and acetochlor ESA as the principal detections, with fewer detections of propiconazole (3) and thiamethoxam (2). Detections in the next shorter 25-50 days category were dominated by the de ethyl atrazine metabolite (7 detections).

The only detections with half-lives less than 25 days were for carbaryl (5 detections) and bentazon (4 detections). These two provide an illustration of the interplay of half-lives and other analyte characteristics, here Koc. While both had similar half-lives, the Koc of

carbaryl was an order of magnitude greater than bentazon, which would, according to the advective dispersive theory, lead to longer travel times and fewer to no detections. However, as shown in section 4.1.1. sorption strength and travel time are decoupled for pesticides moving with preferential flow. There were no detections for the most ephemeral (< 5-day half-life) compounds, such as 2,4-D, acetamiprid, chlorothalonil, thiacloprid, etc., despite their representing 15% of all tests performed.

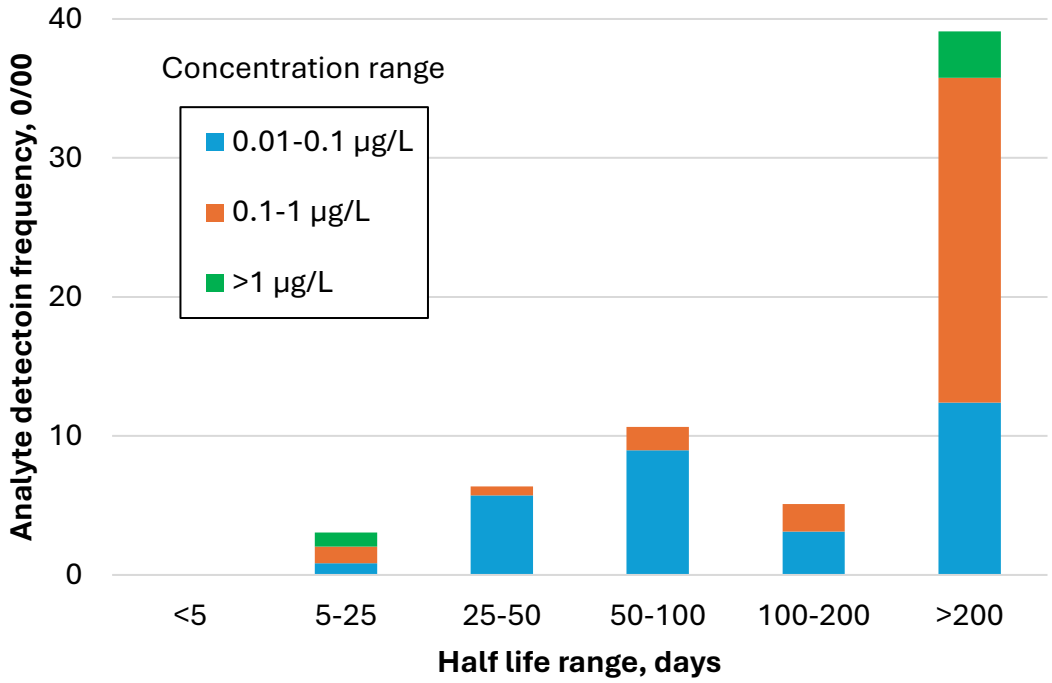

Figure 4.7. Detection frequency (detections per thousand analyses) of 2022-2023 groundwater samples) and detection concentration ranges, as a function of half-life class.

Table 4.4 shows an interesting contrast between the two most common herbicide detections of atrazine, metolachlor, and their metabolites. Both sets of parent compounds have comparable Koc and half-life values. The atrazine metabolites have similar Koc (where known) but, in the case of hydroxy atrazine, a longer half-life than all other atrazines. In contrast, the metolachlor metabolites have both reduced sorptivity (Koc<20) but hugely increased half-lives (325-400 days), both of which contribute to mobility and persistence, as reflected in their frequent detections in our samples.

Table 4.4. Comparison of primary herbicide-related compounds properties and 2022-2023 groundwater detections. (Half-life data are field-based unless noted as typical, t).

Compound	Koc, m^3/Mg	Soil half-life, days	Detection share, % of total detects
Atrazine	100	29	8.4
De ethyl atrazine	110	45	4.8
Hydroxy atrazine	n/a	164 (t)	2.4
Metolachlor	120	21	1.2
S-metolachlor	200 (Kfoc)	23	3.0
Metolachlor ESA	9	400 (t)	16.9
Metolachlor OA	17	325 (t)	31.9

4.1.3 Site land use type and sampling location

The targeting of categorical sites is, as described previously, intended to try to identify any detection patterns resulting from land use-specific practices (e.g. which active ingredients are used and when) and settings (soils or other site characteristics associated with a given land use). Table 4.5 shows the total sample counts and detections by location for each categorical land use. For the 204 samples collected for 2022-2023, there were 19 upgradient detections, 12 downgradient detections and 81 within-site detections, yielding a mean detection frequency of 0.55 detections per sample.

Table 4.5. Categorical sites summary: sample and detection counts, 2022-2023

Categories	Total samples	Detection counts		
		UPG	Within	DWG
Golf courses	25	0	2	0
Greenhouses	23	0	1	4
Outdr. nurseries	38	14	6	2
Right of way	16	0	0	1
Sod	18	0	24	0
Turfgrass	4	0	0	0
Veg & fruit farms	35	3	36	5
Vineyards	28	2	12	0
TOTALS	**187**	**19**	**81**	**12**

Figure 4.8 summarizes the results to date, with mean detection frequencies (detections per sample, as percent) broken out by the relative sampling location at the sites (upgradient, downgradient, or within the application area).

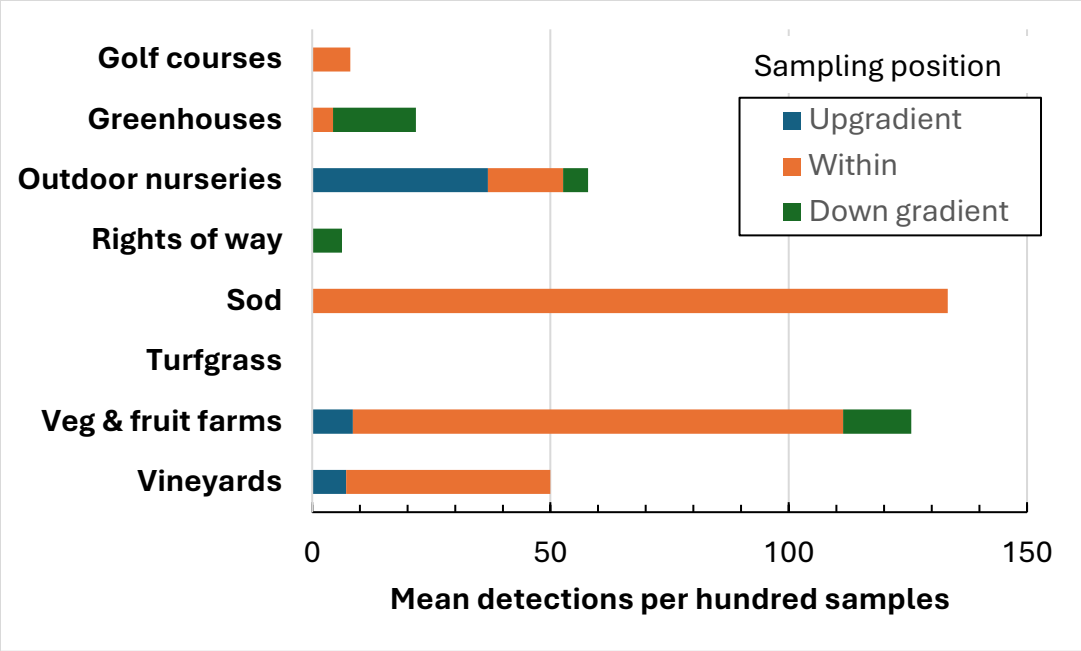

Figure 4.8. Detection frequency by land use category and sampling position, categorical groundwater sites, 2022-2023.

As is evident in Figure 4.8, there were marked disparities in detection frequencies among the categorical land uses, with no detections found at turfgrass (non-golf, non-sod farm) sites and very few at golf courses, greenhouses or under rights-of-way. Outdoor nurseries would have had a similarly low frequency if it was not for the substantial proportion of upgradient detections. Vineyards had a similar overall total but with less upgradient contribution. In contrast, the greatest detection rates were found at vegetable & fruit farms (~125% detection rate) and sod farms (~130% detection rate), primarily occurring at "within" wells.

Table 4.6 presents a more detailed data summary, which gives more insight into the detections occurring in these land use categories. Of particular note is the role of metolachlor degradation product detections. Combining the percentages of their detections at the nursery, sod farm and vegetable & fruit farms shows that these detections represent one-third of all groundwater detections. Table 4.6 also includes the contributions of the long-term sites to the overall groundwater detection patterns.

Table 4.7 allows more detailed comparisons of detections among the categorical site sampling locations. The "detection proportion" (D%) column indicates the proportion of samples in that land use category that had a positive detection, and the adjacent column indicates the maximum observed concentration.

There are a number of limitations and confounding factors that constrain our ability to make firm conclusions about categorical site land uses and detections at this point:

- Incomplete knowledge of what is being applied
- The possibility/likelihood that some of what is being applied is not represented on our analyte list.
- The recurring detection in “within” and “downgradient” samples of active ingredients and/or degradation products from formulations that are known not to be in use at those sites where we have good records.

Given that this work is ongoing, we will return to this question as more data is developed and as landowner information on pesticide uses is updated.

Table 4.6. Distribution of 2022-2023 detections by analyte (degradation products italicized) and site category, expressed as detection counts and as percent of all groundwater detections.

Analytes	Land Use Categories								Long-Term Sites	Total
	Golf	Green-house	Nurs-ery	ROW	Sod	Turf	Veg& Fruit	Vine-yard		
Acetochlor ESA			1						2	3.0
Acetochlor OA									1	0.6
Atrazine			3						5	8.4
De ethyl atrazine			1				1		3	4.8
Hydroxy atrazine			1		1				1	2.4
Bentazon							3			2.4
Bromacil									1	0.6
Carbaryl			1		1		1	1		3.1
*JSE76**							1			0.6
Diuron								1		0.6
Fluopyram							1			1.2
Fluxapyroxad									1	0.6
Glyphosate			1							0.6
Imidacloprid					2			2		4.2
Mefentrifluconazole		1								0.6
Metolachlor									1	1.2
S-Metolachlor		1							2	3.0
Metolachlor ESA			2		5		6		4	16.9
Metolachlor OA	1		4		6		10	2	10	31.9
Myclobutanil		1								0.6
Oxadiazon								1		0.6
Paclobutrazol		1								0.6
Propiconazole	1						1		1	1.8
Simazine			1	1			2	2	1	7.8
Terbacil							1			0.6
Thiamethoxam		1					1			1.2
Detections count:	2	5	22	1	24	0	44	14	54	166
% of detections:	1.3	3.1	13.8	0.6	15.0	0	27.5	8.8	28	
Samples count:	25	23	38	16	18	4	35	28	39	223
% of samples:	11	10	17	7	8	2	16	13	16	

*degradation product of cyantraniliprole

Table 4.7. Summary of all 2022-2023 water sample detections as delineated by site type: ***categorical sites*** *(further subdivided into downgradient (DWG), within site, and upgradient (UPG) sampling locations,* ***Long-term sites***, ***Lakes***, *and* ***All sites*** *combined data. Detection proportion (D%) entries represent the count of detections of the row analyte per 100 samples in each column (sample counts in bottom row); Max µg/L represents the maximum observed concentration of that analyte of that sample type.*

Analyte	Categorical sites sampling location						Long term sites		Lakes		All sites	
	DWG		Within		UPG							
	D %	Max µg/L	D %	Max µg/L	D %	Max µg/L	D %	Max µg/L	D %	Max µg/L	D %	Max µg/L
2,4-D									13	1.72	1.6	1.72
Acetochlor ESA			1	0.048	3	0.058	8	0.206			3.2	0.206
Acetochlor OA							3	0.038			0.8	0.038
Atrazine					16	0.231	25	0.308	30	0.241	12.6	0.308
De Ethyl Atrazine			2	0.098	3	0.043	14	0.105			5.1	0.104
Hydroxy Atrazine			1	0.118	3	0.108	6	0.104			2.4	0.118
Bentazon			3	8.763							1.6	8.763
Bromacil							3	0.026			0.8	0.026
Carbaryl	3	0.042	3	0.279							2.0	0.279
*JSE76**			1	0.07							0.4	0.07
Diuron			1	0.013							0.4	0.013
Fluopyram			2	0.075							0.8	0.075
Fluxapyroxad							3	0.360			0.8	0.360
Glyphosate					3	5.14					0.4	5.14
Imidacloprid			6	0.051					7	0.04	3.6	0.051
Mefentrifluconazole	2	0.202							3	0.026	0.8	0.202
Metolachlor							6	0.992			1.6	0.992
S-Metolachlor	3	0.202					11	1.642	7	0.064	4.3	1.642
Metolachlor ESA	3	0.252	15	0.832	6	0.222	19	0.463	17	0.321	15.8	0.832
Metolachlor OA	13	0.105	22	2.198	19	0.126	44	2.825	37	0.523	31.6	2.825
Myclobutanil	3	0.063									0.4	0.063
Oxadiazon			1	0.559							0.4	0.559
Paclobutrazol	3	0.051									0.4	0.051
Propiconazole			2	0.043			3	0.063			1.6	0.063
Simazine	3	0.012	7	0.175	6	0.031	6	0.037			5.9	0.175
Terbacil			1	0.379							0.4	0.379
Thiamethoxam			2	0.058							0.8	0.058
Samples per column	**38**		**117**		**32**		**37**		**30**		**253**	

*degradation product of cyantraniliprole

4.1.4 Site presumed vulnerability

This section evaluates the pattern of detections in comparison to the presumed site vulnerabilities, which are based on conventional assessments of aquifer and soil type. By way of review, we classified the presumed vulnerability of each site based on mapped soil/substratum composition:

- **High vulnerability:** alluvium, outwash, lake sands
- **Medium:** some glacial tills, mixed substrata
- **Low:** some glacial tills, lacustrine silt/clay deposits, organic/muck soils

These assessments are essentially *textural* (e.g., based on grain sizes and distribution and consequent hydraulic conductivities) except for organic/muck soils (histosols) whose elevated organic matter contents would be expected to provide a highly-chemosorptive matrix for pesticides and residues, thus preventing their downward migration.

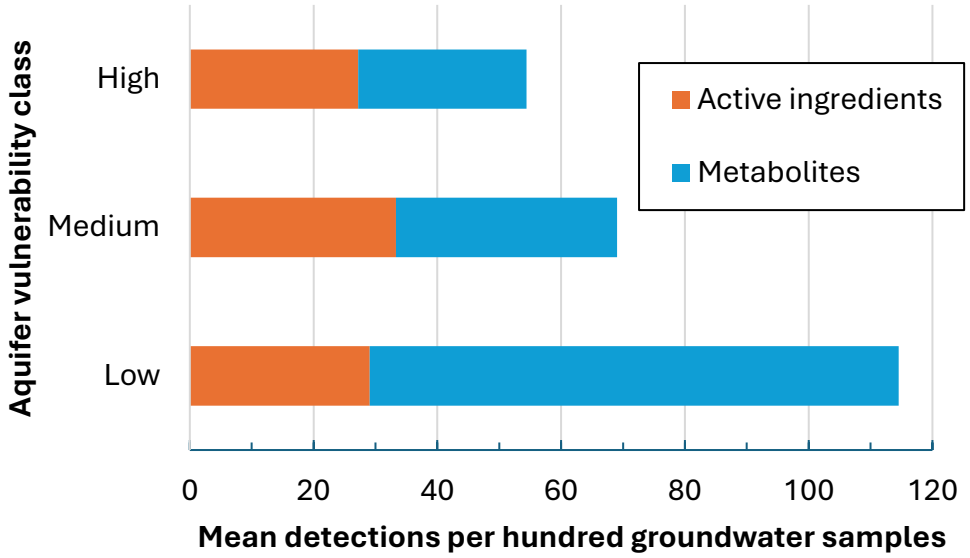

Figure 4.9. Mean detection frequencies by presumed site aquifer vulnerabilities and type of analyte, 2022-2023 groundwater samples.

However, it is clear in Figure 4.9 that these vulnerability assessments were not at all predictive of the observed detection patterns. Indeed, the detection frequencies of ~30% for active ingredients (i.e., 30 detections per hundred samples, red bars) were essentially consistent across all vulnerability classes. Further, the detections of metabolites were greater by far in the low vulnerability class, which had a combined mean detection frequency of over 110% (i.e., 1.1 detections per sample).

Most of the detections in the low vulnerability class were the metabolites of metolachlor in the organic/muck soils in the sod and vegetable & fruit farm categories (Table 4.7). Given the low Koc values of these metabolites, it becomes clear that leaching potential is not precluded by the elevated organic carbon content of these soils. That, coupled with the shallow water table of these soils, instead makes them highly vulnerable to transport risk. The occurrence of preferential flow (in this case via unstable wetting front fingers arising due to soil water repellency) has likely been underestimated as well. In view of this, the vulnerability classification of these sites needs to be revisited.

4.1.5 Site drainage class

This section compares the detection frequencies of the sites based on their mapped soil characteristic of drainage class, which range from excessively drained sands and gravels that are poor at retaining water to very poorly drained soils. It is critical to note that the mapped soil properties are based on the soil formation conditions (i.e., their pedogenesis) and do not reflect subsequent site modifications of the drainage status. This is particularly important for the organic/muck soils which formed in swamps but which were subsequently (in the case of our sites) drained to lower the water tables, at least during the growing season.

The 2022-2023 detection frequencies in Figure 4.10 are for samples collected from categorical sites which have more intensive definition of the site characteristics and thus can support this approach. The detection frequencies reflect the expected effects of the rapid permeability of the excessively drained sites, with detection frequencies of ~12 detections per thousand analytes, although all occurred in the lowest concentration range. The next four drainage classes had lower and generally comparable detection frequencies. It should be noted that "prime agricultural soils" would generally fall in the well-drained and moderately well-drained classes. The previously noted high levels of detections in the organic/muck soils appear here in the "very poorly drained" class and particularly predominate in the higher detection concentration ranges, with 12 detections per thousand analyses in the range of 0.1 to 1 µg/L, and one well at a muckland farm yielding concentrations of 2-10 µg/L of bentazon.

Contributors to this elevated level of detection for this drainage class include not only the factors discussed above (persistent metolachlor metabolites with low Koc values) but also the presence of preferential flow paths. While organic soils are not expected to have persistent structural cracks facilitating flow, they likely do support finger flow in which flow is channeled into fingers (the result of unstable wetting fronts) that support rapid downward flow. Fingering is most likely in hot summer months when the soil surface becomes dry and hydrophobic. Water at the surface thus accumulates until it develops – and rapidly flows down through – a finger that bypasses the bulk of the soil matrix. The percolating water in these soils then encounters drainage tiles, man-made macropores that further enables rapid transport from the field. Considering the site flow characteristics,

leaching to the typically shallow groundwater is thus highly possible. This and other considerations discussed above indicate the need to 1) continue and possibly increase the frequency of sampling at these sites to better define them, and 2) with sufficient data on hand, reclassify these farmed organic/muck soils to better reflect their characteristics with regard to potential transport.

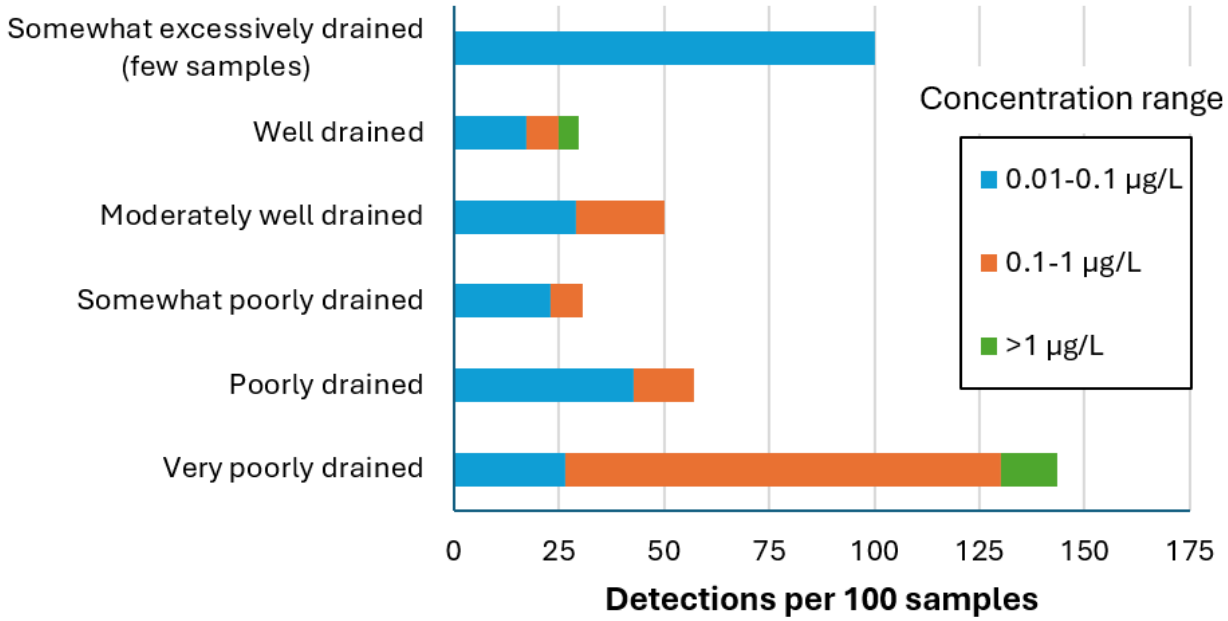

Figure 4.10. Detection frequency (detections per hundred samples) and concentration ranges for 2022-2023 samples from categorial sites grouped by soil drainage class.

4.2 Development of the Theoretical Groundwater Ubiquity Score TGUS: an improved pesticide leaching index for upstate NY

Introduction

In section 3, we showed that only a few of the 84 pesticides tested for were detected in groundwater at low concentrations that did not exceed any water quality standards. In this section, we investigate what combinations of soils, land uses, and pesticide properties might facilitate the occurrence of low but persistent concentrations in groundwater.

Soils in upstate New York vary greatly in their properties, from highly permeable sands to poorly drained clays and organic soils. This can mean that a pesticide classified as a leacher in one soil type might be classified as a non-leacher in another. The dataset we are collecting is ideal for testing the leachability of pesticides. While there are many transport models, no tool (model or index) in common use predicts the observed low pesticide concentrations in groundwater.

One index often used to indicate the relative leachability of pesticides is the Groundwater Ubiquity Score (GUS). GUS was derived by D.I. Gustafson (1989), who plotted the log of the adsorption partition coefficient K_{oc} (reflecting pesticide sorption to organic carbon) versus the log of their half-life, $t_{½}$. The 29 pesticides that Gustafson (1989) used were classified by Wilkerson and Kim (1986) and employed by the California Department of Food and Agriculture (CDFA) to differentiate known contaminants of groundwater (leachers), known non-contaminants (non-leachers), and transition pesticides for which inconsistent evidence was available of groundwater contamination. After plotting the log of these two pesticide properties, Gustafson (1989) devised a hyperbolic scoring equation expressing how both sorption and degradation affect pesticide occurrences in groundwater:

$$\mathrm{GUS} = \log(\mathrm{t}_{½})\,(4 - \log(\mathrm{K}_{\mathrm{OC}})) \qquad (1)$$

where $t_{½}$ is the half-life of the pesticide in the surface soil (day), and Koc is the organic carbon partition coefficient.

The drawback of GUS (Eq. 1) is that this empirical form does not have a theoretical basis. Therefore, its validity is limited to the pesticides and contexts Gustafson originally studied to draw conclusions about their leachability.

Consequently, we derived a GUS-like equation from first principles to evaluate and explain the data collected in upstate New York and to aid in the characterization of future pesticides. This equation is theoretically justified based on the following assumptions:

- That the sprayed pesticides adsorb and degrade in a thin distribution zone at the soil surface (Figure 4.11).

- A fraction of the applied pesticides are then transported rapidly to the groundwater via preferential flow paths during rainstorm events that raise the soil moisture content above field capacity.
- The water that moves through the soil matrix is slow-moving, affording sufficient opportunity for sorption and degradation to occur, and can be assumed to be pesticide-free when reaching the groundwater.
- The groundwater concentration is the mass-based average of the preferential flow and matrix flow contributions.

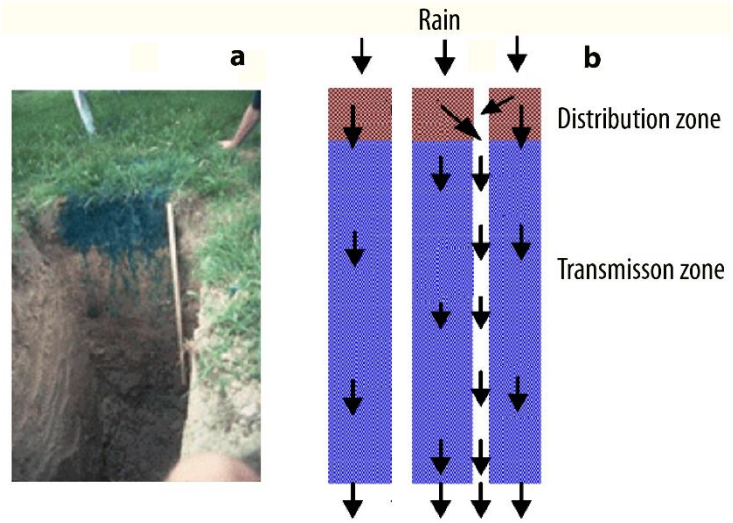

Figure 4.11. (a) Distribution of soluble blue dye in a soil profile following ponding at the surface (b) A schematic representation of the transport model includes an upper distribution zone and a lower transmission zone containing preferential flow paths (white) and the soil matrix (blue).

Our new index is termed the Theoretical Groundwater Ubiquity Score (TGUS), for which higher values indicate a higher potential for detectable leaching to ground water to occur (Steenhuis et al. 2024). The TGUS has the form

$$\mathrm{TGUS} = 0.025\left[t_{½}\log_{10}\left(\frac{\xi}{K_{OC}}\right) - 0.0003t\right] \qquad (2)$$

where t (days) is the elapsed time until the first significant leaching event after pesticide application, ξ (Mg/m^3) is a composite value that describes the soil leachability detection potential,

$$\xi = \frac{\lambda\Phi}{f_{OC}\rho} \qquad (3)$$

where λ is the is the fraction of recharge that reaches the aquifer by preferential flow (dimensionless), ρ is the soil's bulk density (Mg/m^3), f_{OC} is the organic carbon fraction in

the soil (dimensionless), and Φ is the ratio of the initial pesticide in the soil to the concentration at the detection limit:

$$\Phi = \frac{M_0^{app}}{C_{lim}^{w} d} \tag{4}$$

where M_0^{app} is the applied pesticide rate (g/m^2), C_{lim}^{w} is the detection limit concentration (g/m^3), and d is the thickness of the distribution layer (m). To determine the $t_{1/2}$ and K_{OC} for metabolites, we used the higher of two half-lives, that of the parent compound or the metabolite and the smaller K_{OC} value of the original two, thus calculating a conservatively worst-case scenario of pesticide leaching.

Thus, TGUS, similar to GUS, considers the degradation rate of pesticides and their adsorption to organic carbon. However, TGUS departs from the GUS approach to better provide a tool suited to comparing chemicals in usage and analytical contexts. TGUS does so by considering soil physical properties of organic matter content and matrix conductivity, the pesticide application rates, and the analytical detection limits. As such, the composite value of ξ is higher (increasing TGUS) when the preferential flow fraction and/or the ratio of application to analytical detection limit increase. Conversely, ξ is lower (decreasing TGUS) when soil organic carbon and/or soil bulk density are greater.

Leachability of pesticides: the leaching risk period

To define the relative detectable leachability of pesticides, GUS values below 1.8 are classified as non-leachers, and those above 2.8 are leachers, with GUS values between these two classed as transition pesticides.

Since the TGUS index is time-dependent, we defined a *Leaching Risk Period* (t_{LRP}) that defines the maximum period after application during which a significant rainfall event sufficient to bring the soil moisture content to at least field capacity can result in detectable concentrations of the pesticides in the groundwater. (While not explicit in the equations, climate data provides the timing of rainfall events that can leach pesticides into the groundwater.)

Rearranging the TGUS equation to find this time yields:

$$t_{LRP} = 3.333\, t_{½} \log_{10}\left(\frac{\xi}{K_{OC}}\right) \tag{5}$$

In parallel with data presented in Gustafson (1989), leachers are pesticides whose Leaching Risk Period index value is over 100 days, non-leachers are below 30 days, and transitional pesticides are between 30 and 100. For more detail, see Steenhuis et al.

Procedure to find GUS and TGUS values

Rewriting the t_{LRP} with all input parameters, and clarifying which input parameters are needed,

$$t_{LRP} = 3.333 t_{½} * \log_{10}\left(\frac{\lambda}{d}\frac{M_0^{app}}{f_{OC}\,\rho\,C_{lim}^{w}\,K_{OC}}\right) \qquad (6)$$

The half-life $t_{½}$ and the organic carbon adsorption partition coefficient Koc parameters are compiled in the University of Hertfordshire's PPDB: Pesticide Properties DataBase (more background https://sitem.herts.ac.uk/aeru/ppdb/en/docs/Questions_and_Answers.pdf). Note that half-lives can vary greatly in the literature. Currently, pesticide labels state allowable application rates up to a maximum value, M_0^{app}, although in practice operators may elect a lower actual application rate. The fraction of organic carbon, f_{OC}, can be found by multiplying the soil organic matter content by 0.6 (USDA NRCS, 2009). Soil organic matter can easily be measured for each site, or NRCS soil survey data may be used. In the soils in pesticide-treated areas near where we sample groundwater, the organic matter content varies from 1% for a mineral soil to 87% for a muck soil. Bulk densities, ρ, fall within a relatively narrow range for mineral agricultural soils and can be easily measured. Bulk densities for highly organic soils at our sites range from 0.16 to 0.6 g/cm^3. Analytical detection limits are provided in our case as part of the analytical results from the NYS DEC laboratory, ranging from 1.0 down to 0.01 µg/L.

The two parameters in the TGUS equation (Eq. 6) that are difficult to estimate are the preferential flow and recharge fraction, λ, and the distribution layer depth, d. Routine soil physical methods do not exist to measure these two variables. Based on our analysis, the fraction of preferential flow and total recharge is the most significant parameter for determining the leaching of pesticides and other adsorbed chemicals to groundwater. The data for the distribution layer are based on curve fitting of the pesticide concentration in the runoff and the pesticide concentrations assuming equilibrium adsorption. Steenhuis and Walter (1980) and Baker et al. (1978) found that the distribution layer depth was around 1 cm. Studies cited in Ahuja, L.R. (1986) found distribution layer depth between 1-10 mm.

Similarly, very little is known about how much preferential flow contributes to the total flow. Jarvis (2007) reported that the flux through preferential flow paths represents only a fraction of the total recharge, as groundwater recharge mainly occurs through the soil matrix; preferential paths flow only when the upper soil is saturated. However, the preferential paths are responsible for pesticide transport to groundwater, while the matrix flow only dilutes these concentrations.

Preferential flow can be initiated through biopores, old root holes, and structural fissures when the soil matrix cannot conduct the water. Pores greater than 0.2-0.3 mm are usually classified as macropores as they allow large enough velocities such that the adsorption of chemicals is minor (Scotter. 1978; Jarvis. 2007). Additionally, in sands and water-repellent soils, unstable fingers form that will move water preferentially through the soil, with smaller fingers and higher flow velocities occurring in coarser-textured soils.

To find λ and d we combine Eqs. 2 and 4 in Steenhuis et al. (2024) and find that the concentration in the preferential flow is

$$C^w_{prfl} = C^w_0 \exp\left(-\left(\frac{q}{W_{dist}} + a\right)t\right) \quad (7)$$

where C^w_{prfl} [M L^{-3}] is the dissolved pesticide concentration in the preferential flow path, q [L^3 L^{-2} T^{-1}] is the imposed flux or rain, t [T] is the time since the water was applied, and Wdist [L^3 L^{-2}] is the apparent water content of the pesticide distribution zone. Due to adsorption increasing the apparent water content of the distribution zone (Eq. 3a of Steenhuis et al.), the loss of pesticides in the distribution zone is small compared to the loss due to degradation (i.e., $a \gg q/W_{dist}$),

$$C^w_{prfl} = C^w_0 \exp(-a\,t) \quad (8)$$

To calculate the resulting concentration in the groundwater C^w_{gr} [M L^{-3}], the flux through the preferential flow paths is considered only as a small portion of the total recharge since most groundwater recharge is via the matrix (Jarvis, 2007)

$$C^w_{gr} = \lambda C^w_{prfl} \quad (9)$$

where λ [dimensionless] is the fraction of recharge that reaches the aquifer by preferential flow; C^w_0 is the initial pesticide concentration in the water in the distribution zone. It is found by assuming that the applied pesticide is uniformly mixed in the distribution zone and that the moisture content is smaller than the adsorption partition coefficient.

$$C^w_0 = \frac{M^{app}_0}{d\,\rho\,f_{oc}K_{oc}} \quad (10)$$

$$\frac{\lambda}{d} = \frac{C^w_{gr}}{M^{app}_0}\,\rho\,f_{oc}K_{oc}\exp\left(\frac{0.69t}{t_{½}}\right) \quad (11)$$

The parameter values of the right-hand side of Eq. 11 can be estimated or measured for the categorial sites and the active pesticide ingredients they use. To determine the ratio of $\frac{\lambda}{d}$ we used the metolachlor OA concentrations found at several of these categorial sites. The data are available in the appendix, and the resulting λ values are plotted below in Figure 4.12, assuming that d = 1 cm similar to Steenhuis et al.

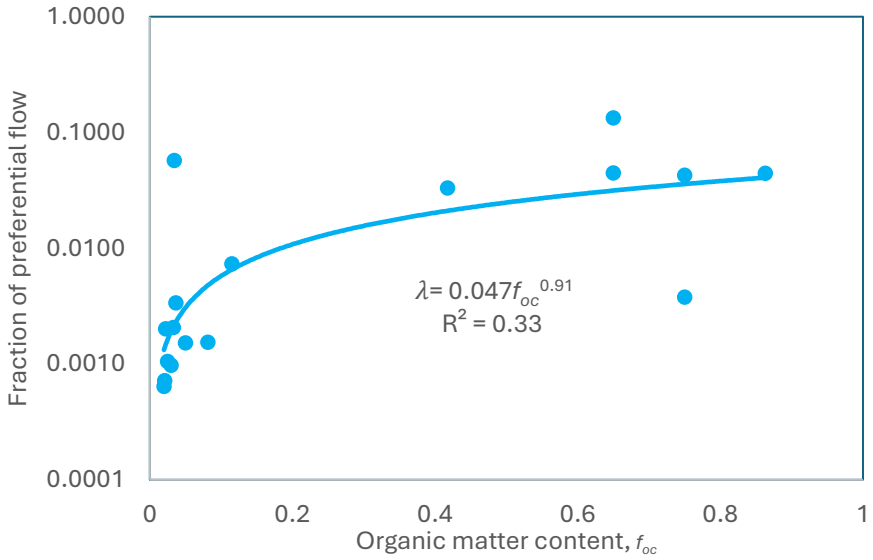

Figure 4.12. The distribution of the fraction of recharge that reaches groundwater through preferential flow λ as a function of the organic matter fraction in the categorical sites.

The soils in our study with high organic matter (greater than 20%) are classified as drained muck soils. For mineral soils, with one exception, Eq. 11 resulted in $\lambda = 0.004$ as the upper limit, and thus, we used that value for the sensitivity analysis. Using Eq. 11 to determine λ for the high organic matter (muck) soils resulted in much larger λ values than the mineral soils, ranging from 0.04 to 0.13. Greater values of λ indicate that more analyte molecules have preferentially traveled to groundwater. These results are consistent with the findings in literature (Rahbeh, 2019; Stumpp and Maloszewski, 2010; Ahuja et al., 1995). As opposed to the persistent macropore structure in mineral soils, water repellency in the muck and peat soil (Lachacz et al. 2009) leading to fingered flow is likely responsible for the preferential transport in these soils (Bauters et al., 2000). As a result, quantifying λ for these samples is not as straightforward; therefore, we decided, for the purpose of the TGUS model for the soils of upstate NY, to use the average λ value we calculated from only the sites with mineral soils, and $\lambda = 0.004$ was used.

Comparing GUS and TGUS for upstate New York data

GUS values and TGUS leaching detection risk periods (t_{LRP}) were plotted for all pesticides observed in groundwater in our study to check the utility of those indices for identifying pesticides that may leach into groundwater (Figures 4.13 and 4.14). Reviewing the classifications of Gustafson (1989), pesticides with GUS < 1.8 will not contaminate groundwater (non-leachers); pesticides with GUS > 2.8 will leach to groundwater (leachers), and transition pesticides sometimes found in groundwater have GUS values between 1.8 and 2.8. Analytical detection limits, pesticide application rates, and usage site

characteristics are all implicit in the GUS scores and thus are implicit in these definitions. By using the California database used by Gustafson (1989), we determined that pesticides with a TGUS $t_{LRP} < 30$ days are the non-leachers, leachers have a $t_{LRP} > 100$, and transition pesticides have scores between 30 and 100.

In Figures 4.13 and 4.14, the GUS (Eq. 1) and t_{LRP} (Eq. 5) values were plotted respectively in contour maps as a function of ξ / K_{OC} (x-axis) and half-life (y-axis). The data points' marker size indicates the number of times a particular pesticide was detected in our 2022-2023 data: the largest markers were for pesticides detected more than 20 times, while the smallest markers were for those with less than three detections. The value of ξ depends on whether GUS or TGUS is used. In plotting the GUS values in Figure 4.13, $\xi = 2240$ is used. Steenhuis et al. (2024) showed that when $\xi = 2240$ was used, TGUS gave nearly identical results to GUS for the original California data set employed by Gustafson (1989). Gustafson (1989) used the Koc on the x-axis. That was changed here to ξ / K_{OC} to make the GUS and TGUS plots more similar in appearance, but using this ratio instead of K_{OC} does not change the results (Steenhuis et al., 2024). For TGUS, the ξ value is not constant and changes for the different pesticides that, for example, have different application rates for soils with differing organic matter contents, bulk densities, propensity of preferential flow paths, and irrigation methods.

The t_{LRP} in Figure 4.14 was calculated using Eq 3-5 with average site characteristics of organic matter content (0.03 g/g soil, $f_{oc} = 0.18$) bulk density (ρ =1.3 Mg/m), the depth of the distribution zone ($d = 0.01$m), and the fraction of water that reaches the aquifer as preferential flow (λ=0.004). The pesticide-related specific properties were the maximum label-allowed application amount, the half-life, and adsorption partition coefficient. A laboratory-related parameter is the analytical detection limit of each pesticide.

Figure 4.13 shows that the GUS index only identified as leachers 14 of the 24 pesticides we have detected in NYS groundwater in our current study. The leachers predicted correctly included pesticides and metabolites that were detected over ten times (metolachlor OA and ESA, atrazine, and simazine). Imidacloprid, fluopyram, terbacil, JSE76, bromacil, and thiamethoxam were each detected less than ten times.

In contrast, four analytes (propiconazole, mefentriflucinazole, oxadiazon, and glyphosate) characterized as non-leachers were found in the groundwater. It should be noted that the metabolites could have been leached as their parent pesticide to the groundwater, then converted after arrival. Glyphosate, classified as non-leacher, was found in a sample taken from a groundwater-fed pond after it had been applied near the rim of the pond, and some spray drift or overland flow might have caused the contamination; thus, the classification as a non-leacher was correct. Six pesticides (carbaryl, bentazone diuron, paclobutrazol, myclobutanil and metolachlor) were classified incorrectly as transition pesticides, given their detection in groundwater in our study and/or their TGUS classification. Overall, 9 out of 24 pesticides were misclassified by the GUS index, representing roughly one-third of the pesticides detected in groundwater.

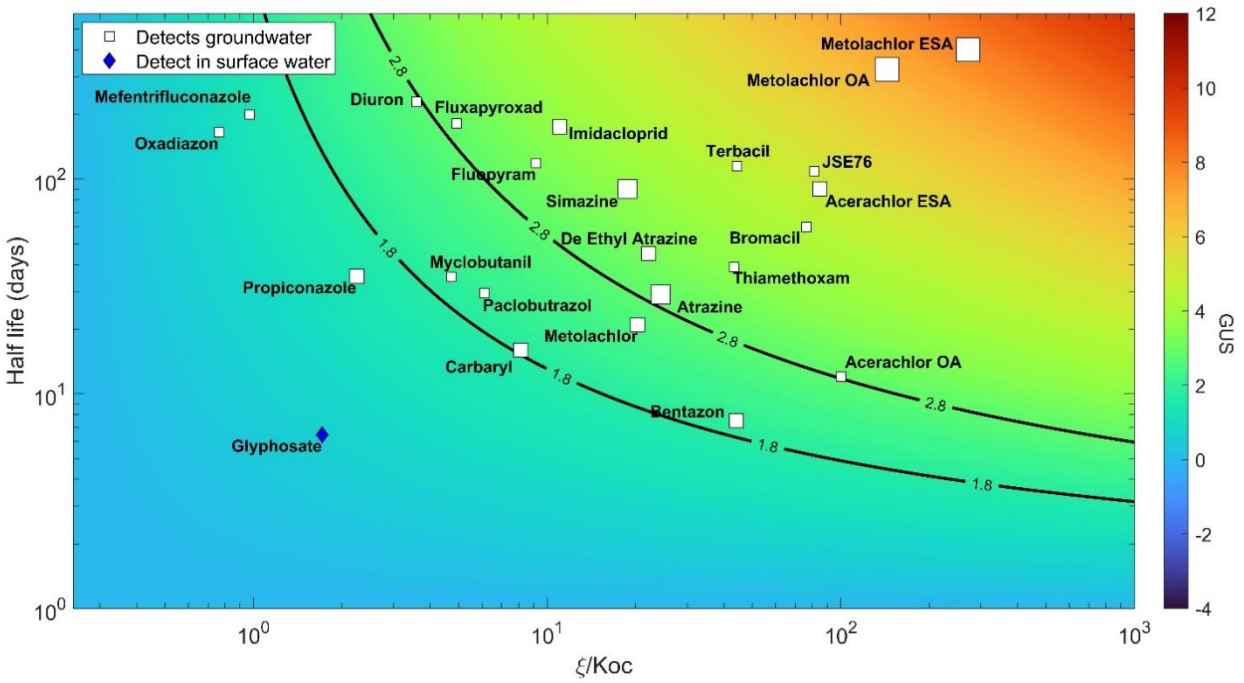

Figure 4.13. A contour plot of the Groundwater Ubiquity Score (GUS) index for the pesticide detected during the 2022-2023 sampling campaigns in Upstate NY. White squares represent the different groundwater pesticide detections. The four marker sizes indicate the number of times each pesticide was detected. From smallest to largest, they have less than three detects, 3-10 detects, 11-20 detects, and over 20 detects. The blue diamond marker indicates the single glyphosate detection probably transported by short overland flow to the sampled groundwater-fed pond. The mobility-detectability parameter ξ was 2240, based on Steenhuis et al. (2024)

Using the same approach, the TGUS Leaching Risk Period, t_{LRP}, is plotted in Figure 4.14. The t_{LRP} for all detected pesticides were greater than 100 days except for glyphosate, whose sole detection was probably due to surface runoff. The analytes with leaching detection risk periods of circa three years or greater (i.e., Metalochlor OA and ESA) were detected more than 20 times. Any analyte with this magnitude of a detectable leaching period and used in consecutive years, is likely to be consistently detected in shallow groundwater both onsite and downgradient offsite.

These results indicate that factors besides the half-life and the K_{oc} sorption, notably the maximum label-allowed application rate and analytical detection limit, significantly improve TGUS beyond the much simpler GUS.

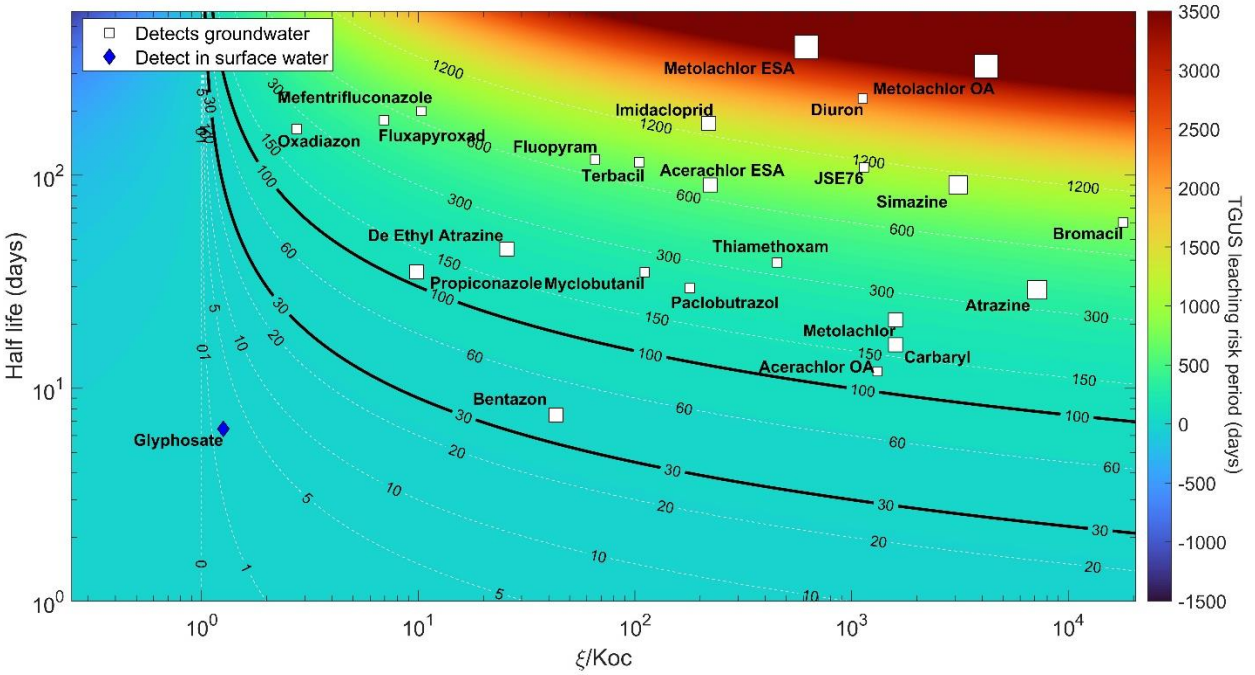

Figure 4.14: A contour plot of the Theoretical Groundwater Ubiquity Score (TGUS) leaching detection risk period index for the analytes detected during the 2022-2023 groundwater sampling in Upstate NY. White squares represent the different groundwater pesticide detections. The four marker sizes indicate the number of times each pesticide was detected. They are, from smallest to largest, less than 3 detects, 3-10 detects, 11-20 detects, and over 20 detects. The blue diamond marker indicates that the single glyphosate detection was likely transported by overland flow to a sampled pond. The mobility-detectability parameter ξ was calculated using the maximum pesticide usage specified by the label, laboratory detection limit, and average mineral soil characteristics.

The effect of soil parameters on the TGUS model

In the previous section, we investigated the pesticides detected in groundwater. We evaluated whether the model could predict if a pesticide would leach using pesticide half-life and Organic C partition coefficient to compute GUS scores. In addition, for TGUS we also used average site conditions and specific pesticide properties.

However, we did not examine cases where the pesticides were known to be applied and did not leach to groundwater at detectable levels. For example, one categorical vegetable & fruit farm used atrazine, ethofumesate, linuron, metolachlor, and metribuzin, but none were detected in the groundwater samples. The three metabolites (de ethyl atrazine, metolachlor ESA, and metolachlor OA) were the only detects. All the detects were in the low concentration range, beneath the health or environmental risk thresholds. There could be several possible explanations for this, such as the application location being on a different part of the farm than the location of the well, the amount applied to be less than the maximum label-allowed rate, and the site characteristics diverged from the assumed

mean values. For example, the data in Figure 4.15 shows that when plotted as a function of drainage class, pesticides were most detected in mucklands (as noted above) and less-common (in our project) "somewhat excessively drained" soils.

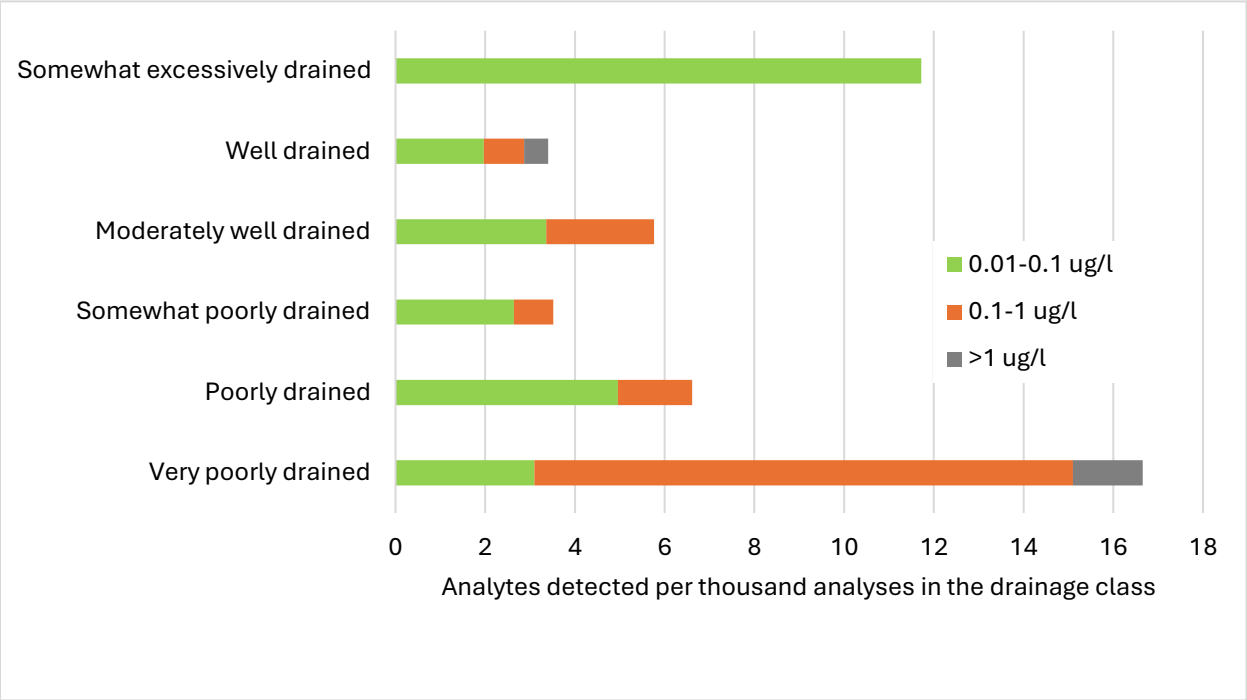

Figure 4.15. Distribution of detections in groundwater by nearby soil drainage class. Colors indicate magnitude ranges of detected concentrations.

To illustrate this effect and the possible resulting changes to the TGUS t_{LRP}, we consider eight pesticides with a wide range of half-lives and organic carbon partition coefficients. These pesticides were acetamiprid, glyphosate, bentazon, atrazine, metolachlor, malathion, fluazinam, and oxadiazon. Some of the pesticides leached to groundwater, while others were not detected. As input parameters, we used the same pesticide parameter values to calculate the t_{LRP} as used in Figure 4.14. In addition to the pesticide-specific half-life and organic carbon partition coefficient, the maximum label-allowed active ingredient application rate and the detection limit were also used. Site characteristics that were varied consisted of λ, f_{OC}, and ρ, varied as per the ranges shown in Table 4.8. These variables were kept within realistic ranges for the soil and site characteristics common in upstate NY mineral soils. For these pesticides, t_{LRP} was calculated using Eq. 5.

Table 4.8. Soil parameters value ranges for calculating the soil leachability/detectability parameter ξ.

Parameter	Unit	Min	Max
ρ	g/cm^3	1.05	1.4
f_{oc}	-	0.01	0.06
λ	-	0.004	0.1

Figure 4.16 shows the span of predicted pesticide leaching risk periods when varying λ across the full range noted in Table 4.8 while keeping bulk density and organic carbon content constant. A white horizontal bar marks the predicted range of each pesticide's potential leaching risk period, with the width dependent of the magnitude of imposed variation in the λ parameter (which in turn affects the composite ξ/Koc parameter). The vertical black bar emphasizes the threshold ξ/Koc values of 10^0: anything to the left of the line will be a non-leacher no matter its half-life value. Conversely, any pesticide to the right of the line will have its TGUS value affected by both the half-life and ξ/Koc values.

As with Figure 4.14, pesticides shown in this figure with leaching risk periods under 30 days are considered non-leachers, while those above 100 days are leachers. The widths of the bars indicate that the leaching detection risk period can change significantly due to changes in λ. Under this parameter range, many pesticides that would be considered non-leachers (like glyphosate, fluazinam, and oxadiazon) can, when λ is high, behave as leachers according to their t_{LRP}. Furthermore, incorporating organic muck soil parameters into the TGUS model may not greatly reduce the predicted leachability of the pesticides (compared to mineral soils) since the soil sorptivity due to the elevated organic matter content may be offset by a greater occurrence of preferential flow (increasing λ) in the t_{LRP} equation.

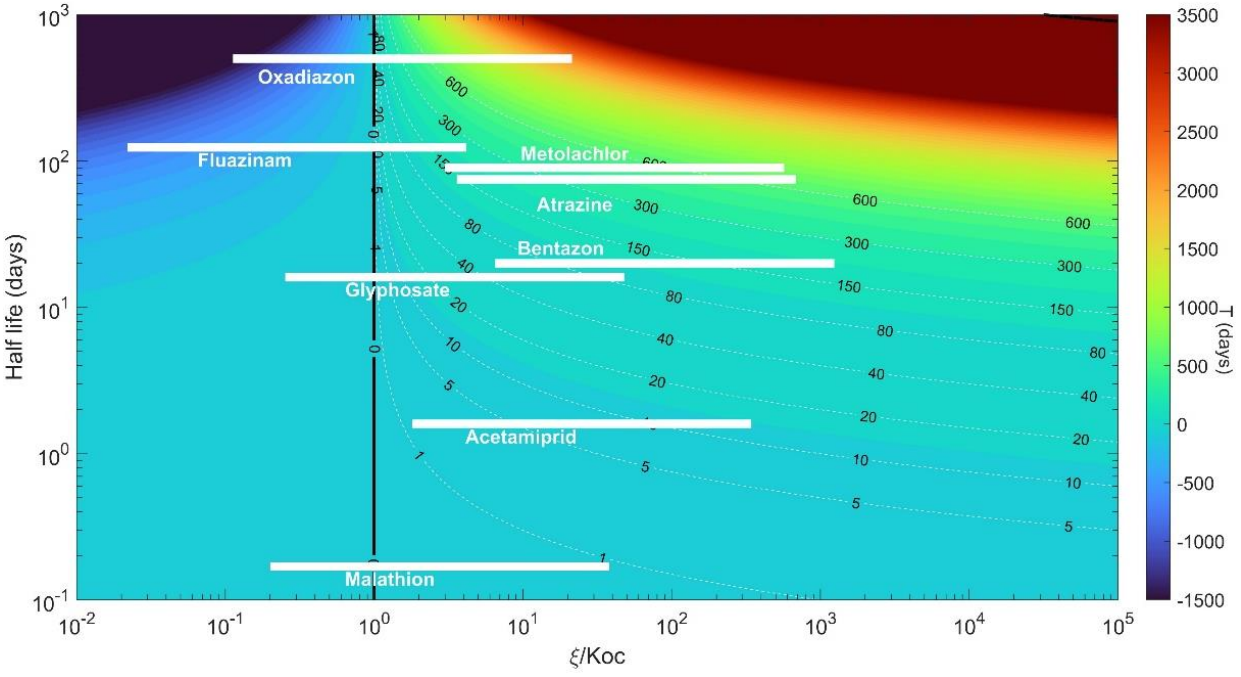

Figure 4.16. Sensitivity analysis plot of the Theoretical Groundwater Ubiquity Score (TGUS) t_{LRP} ranges for eight pesticides. White horizontal bars represent the effect of varying λ (range 0.0006 < λ < 0.1) for each pesticide. The half-life, organic carbon partition coefficient, application rate, and detectable concentration were specific to each pesticide, while the other parameters are site-dependent or are those listed in Table 4.8 (ρ = 1.3 g/cm³, and f_{OC} = 0.01).

Similarly, varying the soil organic carbon content (f_{oc}) also affects the predicted leaching risk periods. However, the range of possible organic carbon contents is far smaller than the range of λ, which in turn makes the resulting ranges of predicted t_{LRP} markedly narrower, as seen in Figure 4.17, which has constant λ and soil bulk density values.

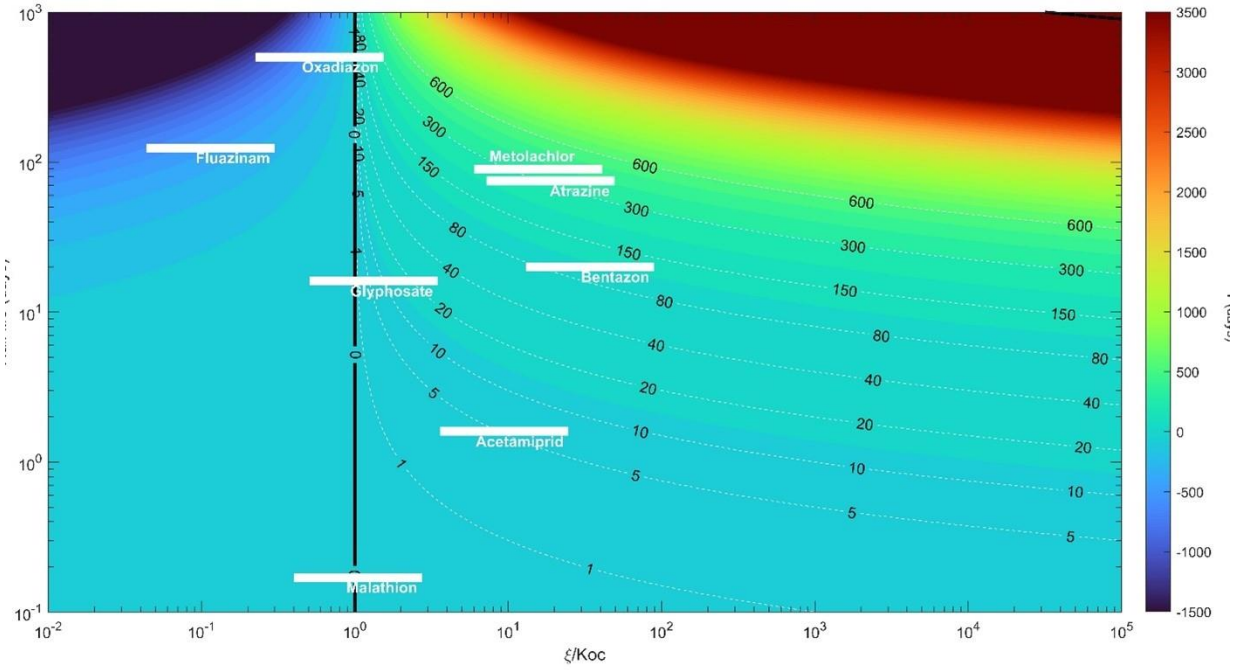

Figure 4.17. Sensitivity plot of the Theoretical Groundwater Ubiquity Score (TGUS) t_{LRP} ranges for eight pesticides. White horizontal bars represent the different ranges of each pesticide as affected by varying soil organic carbon content (foc). The half-life, λ, application rate, and detection concentration were specific to each pesticide, while the other inputs were site-dependent or as listed in Table 4.8 (λ = 0.004. ρ = 1.3 g/cm³).

This narrowed range of predicted leaching risk period is even more pronounced in Figure 4.18, where the narrow range of possible bulk density values results in the spans of predicted t_{LRP} being even smaller.

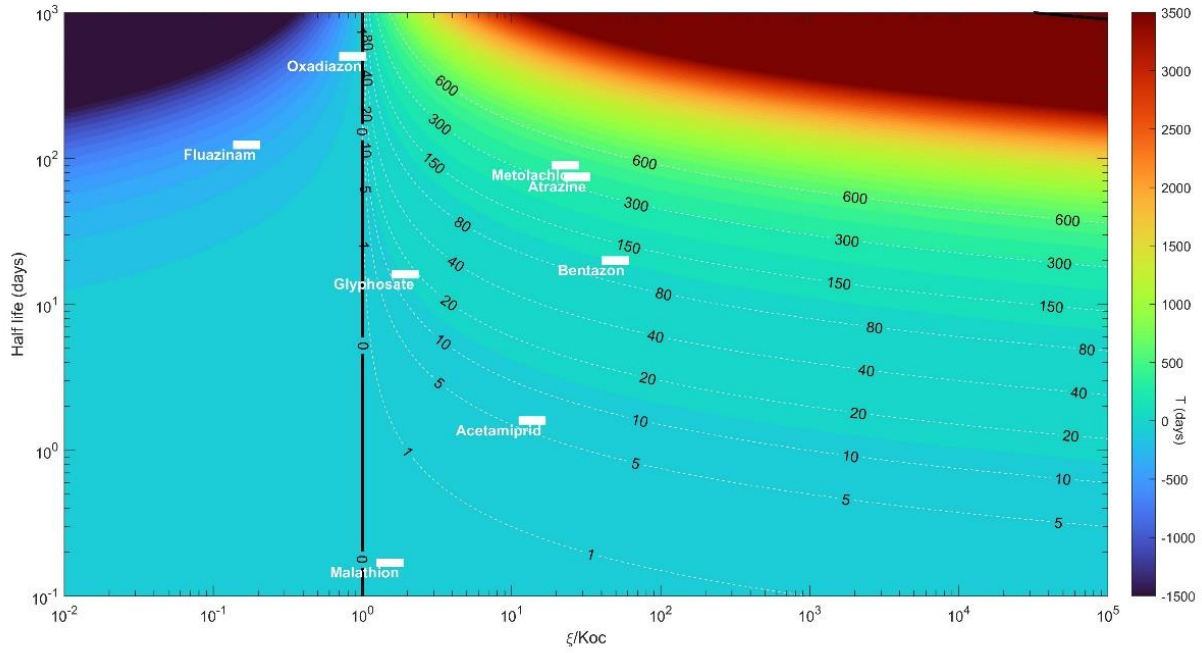

Figure 4.18. Sensitivity plot of the Theoretical Groundwater Ubiquity (TGUS) t_{LRP} ranges for eight pesticides. White horizontal bars represent the different ranges of each pesticide as affected by varying soil bulk density. The half-life, λ, application rate, and detection concentration were specific to each pesticide, while the other parameters are site-dependent or as listed in Table 4.8 (λ = 0.004. and foc = 0.018).

The result of varying all three parameters (λ, organic matter content, and bulk density) and plotting the resulting ranges of t_{LRP} for the complete range of parameters is seen in Figure 4.19. This figure shows the combined effects of low λ, high organic carbon and high bulk density (which together would maximize predicted retention of pesticides) vs. the effects of high λ, low bulk density, and low organic carbon (which minimize predicted retention of pesticides and thus promote leaching). Unsurprisingly, in view of the above discussion of the impacts of varying individual inputs, the resulting spans are only slightly wider than the spans generated by varying λ.

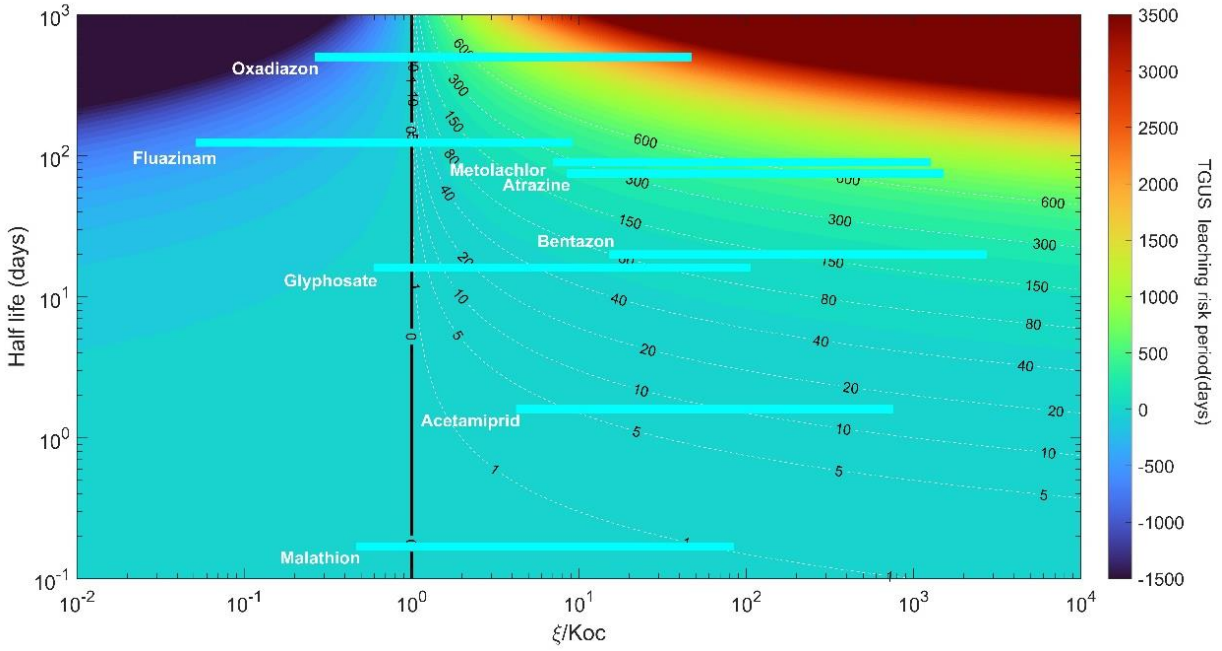

Figure 4.19. A contour plot of the Theoretical Groundwater Ubiquity (TGUS) LRP ranges for eight pesticides. Cyan horizontal bars represent the resulting different ranges for each pesticide under simultaneously varied λ, soil organic matter content, and soil bulk density. The half-life, organic carbon partition coefficient, application rate, and detectable concentration were specific to each pesticide, while the other parameters are site-dependent.

Further work is needed to model offsite transport in groundwater. In the future, we will be analyzing TGUS results from selected long-term sites where well characteristics, pesticide use, groundwater flow and soil/aquifer characteristics are reasonably well-defined. This will enable us to evaluate whether the site-specific parameters (acting as inputs to TGUS) can help explain the non-detection of known-use pesticides and predict which pesticides are more likely to leach into groundwater.

4.3 Development of Interactive Machine Learning Detection Assessment

Machine learning has gained attention as a potential tool for managing surface and groundwater quality. We are interested in testing the utility of machine learning to predict the likelihood of detectable leaching events in upstate NY (hence the title Interactive Machine Learning Detection Assessment, IMLDA) and identify the important contributing factors. Our specific aim is to determine if machine learning can effectively rank the importance of these factors and assess the performance of GUS and TGUS indices to predict the detection of pesticides in groundwater. We also aim to identify potential additional factors that could enhance the performance of the TGUS index.

Model selection

For model selection, we developed a binary classification setup to predict whether a specific pesticide would be detected at a particular sampling point based on nearby soil characteristics and pesticide properties. Several algorithms are available to find patterns in the data, such as Gradient Boosting Classification (GBC), Perceptron Classification and Support Vector Classification (IBM, 2024; Masui, 2024). In our initial testing, the GBC performed best and was the only model that inherently identified the most important environmental factors and pesticide characteristics for prediction. The GBC was, therefore, selected for this project. More information about its use can be found here: https://scikit-learn.org/stable/modules/generated/sklearn.ensemble.GradientBoostingClassifier.html

GBC is a supervised machine learning model that builds an ensemble of weak learner Decision Trees. The gradient descent method is applied to each tree sequentially to improve its predictive power. This optimization process makes GBC more powerful than other ensemble models, such as Random Forest Classification.

The GBC machine learning algorithm uses input data from our analytical measurements and site characterizations to identify which pesticides and metabolites will leach into groundwater without being hard-coded beforehand to produce a particular outcome. The process begins with a training phase, where the algorithm is provided a portion of the dataset containing pesticide/site characteristics and whether the pesticide was detected. It then learns how to best predict pesticide leaching events for this input. Once trained, the algorithm can predict whether a pesticide will be detected for different datasets, as well as the probability of detection. Its performance can be tested on the remaining data portion that was not used during training.

Dataset

The analytical test data from the 21 categorical sites was filtered by three groups for the machine learning analysis:

- Pesticide applied, and parent compound or metabolite NOT detected in groundwater

- Pesticide applied, and parent compound or metabolite detected in groundwater
- Pesticide NOT applied or application status UNKNOWN and parent compound or metabolite detected in groundwater

This filtering left 348 analytical results (coded as either detected or undetected) with matching *feature* (independent variable) data. It included 46 pesticide detections for 11 different pesticides and 302 non-detections for 22 different pesticides. Features collected for each sampling point were: soil organic matter, bulk density, saturated hydraulic conductivity, drainage class, presumed aquifer vulnerability, and sampling point position (upgradient, within, and downgradient) relative to the pesticide use areas on the property. Features of the analyzed pesticides and metabolites included the organic carbon partition coefficient, degradation half-life, and analytical detection limit. From the soil and pesticide characteristics, the GUS index and leaching risk periods (t_{LRP}; for simplicity here LRP) were calculated, and a "leacher" or "non-leacher" label was given to each analytical result based on the respective index boundaries. We used a boundary of 2.8 for GUS and 100 days for the TGUS LRP, with the transition region ignored for simplicity.

There is uncertainty regarding pesticide use as this information is informally obtained from growers. Group 3 reflects this, as pesticides are found in groundwater only when applied. However, there were 18 detections for pesticides that growers reported as definitively not applied, and 22 detections with unknown application status. This uncertainty is also reflected in Group 1, as the pesticide application location is unknown, and they could be sprayed on a part of the farm outside the sampling point's catchment area. Only 6 of the 46 detections came from Group 2 with known application. Table 4.9 provides an overview of the groups separated by location. We will improve on this dataset in the future with successive years of data and improved site characterizations.

Table 4.9. Counts of analytical tests in each filtering group, separated by location.

Group	Location			
	Upgradient [count]	Within [count]	Downgradient [count]	**Total**
1. Applied, not detected	41	211	50	**302**
2. Applied, detected	0	5	1	**6**
3. Unknown or no application, detected	8 (8 unknown, 0 definitive)	29 (11 unknown, 18 definitive)	3 (3 unknown, 0 definitive)	**40**
Total counts	**49**	**245**	**54**	**348**

Model application

The dataset was further partitioned into the following four scenarios to demonstrate the capability of machine learning and identify the importance of the features. Each scenario included the following features:

1. **LRP > 100 + Select Raw:** LRP > 100 label, Koc, soil half-life, detection limit, location
2. **GUS > 2.8 + Select Raw:** GUS > 2.8 label, Koc, soil half-life, detection limit, location
3. **Select Raw:** Koc, soil half-life, detection limit, location
4. **All Raw:** Koc, soil half-life, detection limit, location, applied amount, hydraulic conductivity, organic matter, bulk density, presumed aquifer vulnerability, drainage class

Table 4.10 summarizes the model scenarios and the features used in each. The All Raw Scenario used all available site and pesticide characteristics (consisting of TGUS parameters, hydraulic conductivity, presumed aquifer vulnerability, drainage class, and location). Thus, since the All Raw Scenario contains the same pesticide and site characteristics, the machine learning results can be used to determine whether any other parameters should be added to TGUS to improve its performance, or if there is a better way to write the equation with the existing variables. The Select Raw Scenario was intended to identify if the subset of the features (Koc, half-life, location, and detection limit) would perform the same as Scenarios with more features. The first two scenarios in Table 4.10, LRP > 100, and GUS > 2.8, together with the Select Raw features, were designed to determine whether the function used for these indices could be improved. These Scenarios give the GBC algorithm the option of learning from the raw values (Koc, soil half-life, detection limit, and location) or the leacher/non-leacher label of the theoretical index. If the index is highly accurate at predicting leaching, the algorithm will often choose the labels and not use the raw values.

Table 4.10. Machine learning model scenarios and the features that were used in each.

Scenarios	Features											
	Soil Half-life	K_{OC}	GUS > 2.8 Label	LRP > 100 Label	Presumed Aquifer Vulnerability	Drainage Class	Location	Amount Applied	Hydraulic Conductivity	Bulk Density	Detection Limit	Organic Matter
1. LPR >100 etc	x	x		x			x				x	
2. GUS >2.8 etc	x	x	x				x				x	
3. Select Raw	x	x					x				x	
4. All Raw	x	x			x	x	x	x	x	x	x	x

Evaluation criteria

Binary classification in machine learning uses an error matrix (also called confusion matrix) that identifies whether the model correctly identified the detection or non-detection of pesticides in groundwater. There are four possible outcomes (Figure 4.20):

- True negative (TN): the analyte (pesticide or metabolite) was not detected in the groundwater sample, and the machine learning model identified it correctly as not detected.
- True positive (TP): the analyte was detected in the groundwater sample, and the machine learning model identified it correctly as detected.
- False positive (FP): the analyte was not detected in the groundwater sample, but the machine learning model identified it incorrectly as detected.
- False negative (FN): the analyte was detected in the groundwater sample, but the machine learning model identified it incorrectly as not detected

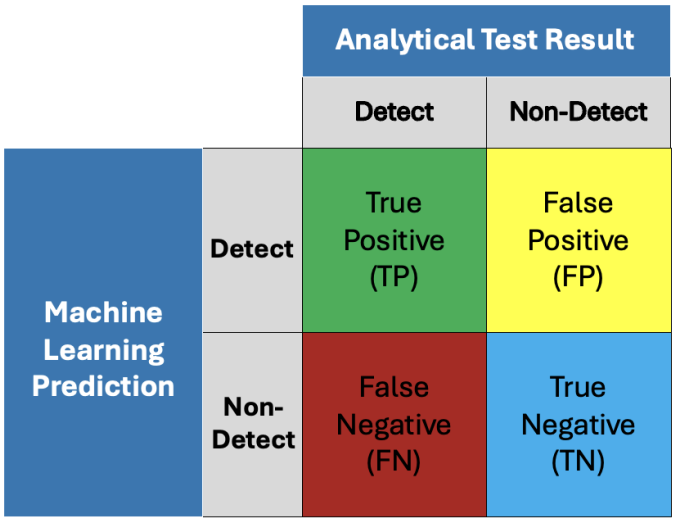

Figure 4.20. Confusion matrix for the binary classification

The following criteria make use of the above outcomes to evaluate the performance of the machine learning model.

Prediction Accuracy

Accuracy tells us the fraction of correctly identified outcomes out of all the predictions.

$$\text{Accuracy} = \frac{\text{TP} + \text{TN}}{\text{TP} + \text{FP} + \text{TN} + \text{FN}} \quad (1)$$

Accuracy can be misleading for unbalanced datasets such as ours, with an approximate 1:8 ratio of detects to non-detects. Labeling everything as a non-detect means the machine learning algorithm can achieve 88% accuracy, which appears high but is not a good model. While we did keep track of accuracy, we coded the machine learning model to focus on the following criteria instead.

Recall

Recall tells us the fraction of correctly identified detections out of the total number of observed detections.

$$\text{Recall} = \frac{\text{TP}}{\text{TP} + \text{FN}} \tag{2}$$

The recall value slants toward groundwater protection because a high recall value indicates that many of the pesticides that can potentially leach into the groundwater were identified. However, it does discount for overpredicting false positive detections. As noted before, this is the most protective measure for keeping groundwater free of pesticides.

Precision

Precision is the fraction of correctly identified detections out of the total number of predicted detections.

$$\text{Precision} = \frac{\text{TP}}{\text{TP} + \text{FP}} \tag{3}$$

Higher precision means the model can detect pesticides accurately without overpredicting false positives.

F-beta

This is a combination of both recall and precision called F-beta, F_β.

$$F_\beta = \frac{(1 + \beta^2) * \text{ Precision} * \text{Recall}}{\beta^2 * \text{Precision} + \text{Recall}} \tag{4}$$

in which β^2 is a positive weighing factor indicating that recall is β times as important than precision. $\beta = 0.5$ means recall is half as important as precision and $\beta = 2.0$ indicates that recall is twice as important as precision. The highest possible value of F_β is 1.0, indicating perfect precision and recall, and the lowest possible value is 0 if precision and/or recall are zero.

To prevent groundwater contamination, the model must accurately identify the types of chemicals and conditions under which a pesticide could leach into groundwater. Thus, false negatives (FN), where a pesticide is detected in the groundwater but not identified by the

machine learning model, can be environmentally damaging. In contrast, false positives (FP), where the model incorrectly predicts the pesticide is in groundwater, will not affect the environment. Still, too many false positives undermine the utility of the model.

Optimizer function and decision threshold

We used the F_β function as the optimizer for training the machine learning model. The recall is weighted over precision, with $\beta = 2$, indicating that recall is twice as important as precision.

By default, the model will predict that a pesticide will be detected if there is greater than 0.5 probability of detection. However, since our dataset is imbalanced, the model is biased toward predicting lower detection probabilities. We decreased the detection threshold to 0.3 to address this issue.

Methods

For each dataset, the following steps in the machine learning model were followed:

1. Randomly assigning 80% of the data to be used as a training set.

2. Train the GBC algorithm to make a model that predicts pesticide detection outcomes for an optimal F_β score.

3. Test and record the final model's performance on the remaining 20% of data.

4. Repeat the previous steps 100 times using a different random selection for the 80%-20% training-testing combinations and record all performance metrics. Repetition is necessary because random splits of the data can sometimes create poor training sets due to the imbalance of detects and non-detects.

Results

The average validation results on how well the trained machine learning model performs on 20% of the 348 entries (consisting of 70 tests) in the dataset are shown in Table 4.11. According to a two-sided, independent T-test, the All Raw Scenario had a statistically higher precision than every other scenario. Other than this, no statistical differences between the different scenarios were found for the precision, recall and F_β.

As part of the process of finding the optimum F_β, the feature importances are ranked. In GBC machine learning models, relative feature importance measures the effect of each feature in the decision tree (relative to all other features) on the determination of the final classification. In this case, it represents the relative effect of each parameter on the final

distribution of detect/non-detects that achieves the highest F_β. Since $\beta = 2$ most of the emphasis is on reducing the number of false negatives. The ranking of the importance of all or part of 12 features during training on 80% (consisting of 278 entries) of the datasets from the 100 iterations is shown in Figure 4.21.

Table 4.11. Performance metric averages from 100 iterations on the testing data portion (20% of total, 70 tests).

Scenario	Performance Metric Averages							
	Accuracy [%]	True Positive [count]	True Negative [count]	False Positive [count]	False Negative [count]	Precision [%]	Recall [%]	F_β [%]
LRP > 100 + Select Raw	94.2	7.6	58.3	2.4	1.8	77.7	82.0	80.2
GUS > 2.8 + Select Raw	94.7	7.7	58.6	2.1	1.7	80	81.9	80.8
Select Raw	94.4	7.3	58.8	2.2	1.74	77.8	80.4	79.1
All Raw	95.5	7.4	59.4	1.3	1.9	85.8	79.7	80.3

In the ranking, the Koc was the most significant parameter in all scenarios, followed by half-life, detection limit, and, to a lesser degree, in the All-Raw Scenario by application rate, bulk density, hydraulic conductivity, and organic matter. Aquifer vulnerability, drainage class, and location with respect to the fields were insignificant features. Surprisingly, in Scenarios (a) and (b) in Figure 4.21, very low significance was assigned to the LRP leacher label and the GUS leacher label, suggesting that better relationships in the data exist. Also, the location with respect to the application was insignificant, contrary to expectations that near application and downgradient wells would show correlations with pesticide detections while upgradient wells would not.

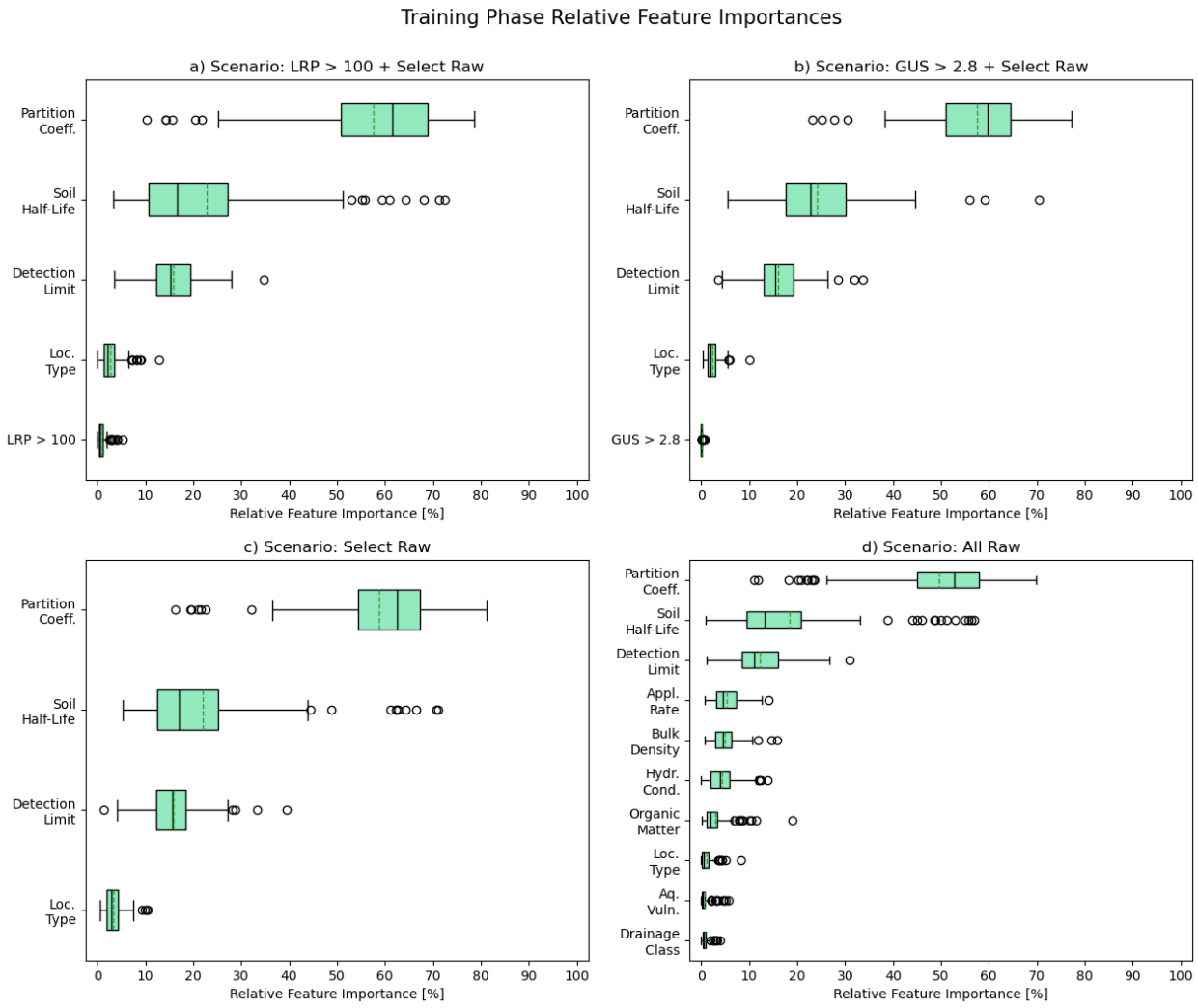

Figure 4.21. (a) Relative feature importances for LRP > 100 + Select Raw Scenario. (b) Relative feature importances for GUS > 2.8 + Select Raw Scenario. (c) Relative feature importances for Select Raw Scenario. (d) Relative feature importances for All Raw Scenario. Dashed lines represent mean values, while solid lines represent medians. Open circles represent outliers beyond 1.5 times the interquartile range (IQR).

Discussion

The current analysis using the machine learning model faces several limitations. A key issue is the small number of detections, which may limit the model's accuracy and cause important features to be underrepresented. Additionally, the more distinct values a feature has, the more precisely the algorithm can learn from that feature. This could explain why the LRP > 100 label, which has only two distinct values ("leacher" and "non-leacher"), has lower feature importance than Koc, which has 27 distinct values (Table 4.12). Its

importance could increase if its number of possible values was increased to 3 (by including the intermediate “transitional” value). One other result could be that the relative importance of Koc might decrease (but only slightly, since with 27 values it would still outnumber a feature that increases from 2 to 3 values). Overall, this modification may improve the predictions.

Moreover, if a feature correlates with another feature, such as soil hydraulic conductivity and aquifer vulnerability, the importances for both will decrease. Another consideration is that the feature importances are calculated during the training phase, so if the model is overfitted to the training data, this could increase or decrease a feature's importance.

Table 4.12. Unique values of model features.

Feature	Unique Values
Koc	27
Soil Half-Life	27
Application Rate	23
Organic Matter	17
Bulk Density	15
Detection Limit	9
Hydraulic Conductivity	8
Drainage Class	5
Aquifer Vulnerability	3
Location Type	3
LRP > 100 Label	2
GUS > 2.8 Label	2

It is important to remember the results in Table 4.11 are averaged for the 100 model iterations, and the values of recall, precision, and F_β vary between runs. Looking deeper, for example, at the All-Raw scenario’s ability to capture all detections, the model achieved perfect recall in the testing phase in 11 out of the 100 iterations. These occurred when the random selection of training data included at least 10 or all 11 of the detected pesticides. Table 4.13 summarizes these 11 iterations. The number of unique pesticides in the testing set is included, as well, to verify that these instances of perfect recall occurred at times when multiple unique pesticide detections were being tested for. This suggests that the GBC algorithm can best learn when many unique pesticides are represented during training. Many random splits of the data include fewer unique pesticides detected and result in lower recall. This is verified by Figure 4.22, which shows the moderate correlation between recall and the number of unique pesticide detections included in the training set.

Table 4.13. Results breakdown for the 11 iterations of the All Raw Scenario that achieved perfect recall score.

Results from Instances of Perfect Recall								
Accuracy [%]	True Positive [count]	True Negative [count]	False Positive [count]	False Negative [count]	Precision [%]	F_β [%]	Unique Pesticide Detections in Testing Phase [count]	Unique Pesticides Detections in Training Phase [count]
100	9	61	0	0	100	100	3	11
100	13	57	0	0	100	100	5	10
100	9	61	0	0	100	100	6	10
98.6	12	57	1	0	92.3	98.4	5	11
98.6	9	60	1	0	90.0	97.8	3	11
98.6	8	61	1	0	88.9	97.6	4	11
97.1	7	61	2	0	77.8	94.6	3	11
97.1	7	61	2	0	77.8	94.6	4	11
95.7	7	60	3	0	70.0	92.1	3	11
92.9	10	55	5	0	66.7	90.9	3	11
92.9	8	57	5	0	61.5	88.9	4	11

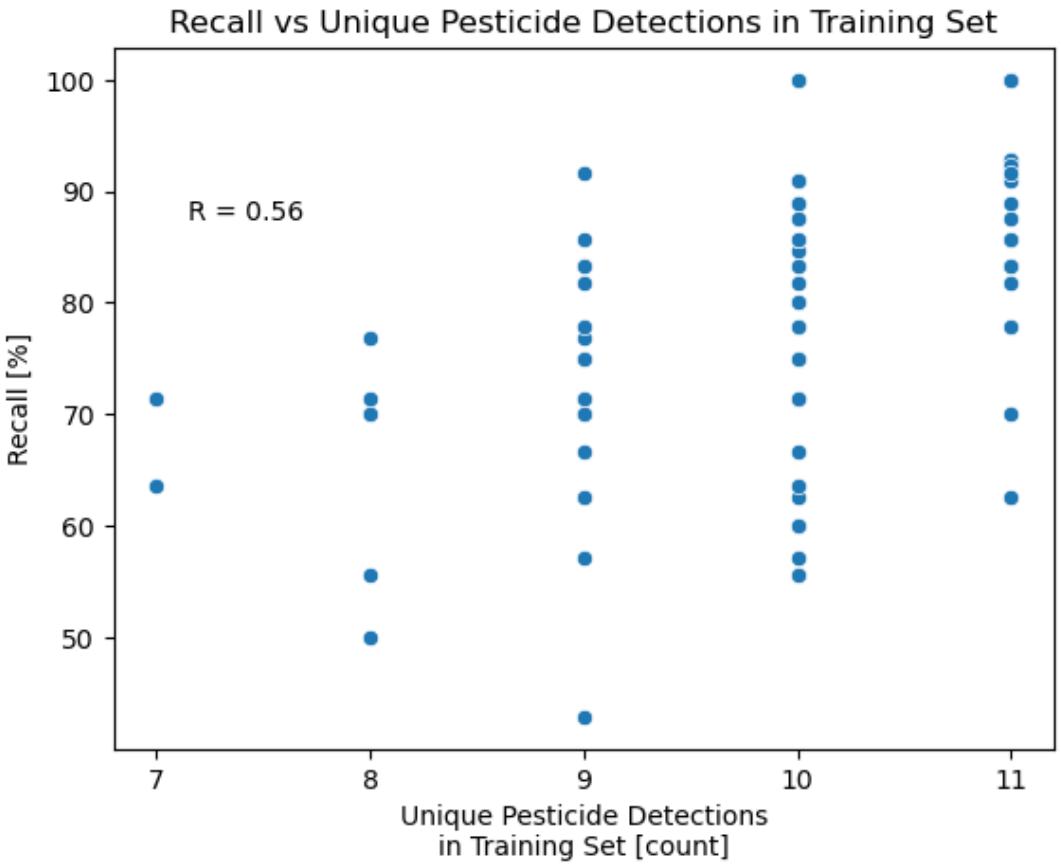

Figure 4.22. Number of unique pesticide detections in the training set vs. Recall value

More analysis is needed to determine if one of these iterations may represent the best possible model to be built from the data. They suggest a better relationship than the LRP or GUS equations may exist. The predictive outcomes of using just the LRP leacher boundary of 100 days and a GUS leacher boundary of 2.8 on the same 348 analytical tests as the machine learning model are shown in Table 4.14. While the LRP classification can achieve a perfect recall score, it has a lower precision score than any of the 11 instances from the machine learning model. The GUS classification has low recall and precision values. It is important to note that 55 of the false positives identified by LRP are for seven different pesticides detected elsewhere and that eight of the false positives identified by GUS are for one pesticide detected elsewhere.

Table 4.14. Performance Metrics for Leaching Risk Period and GUS alone.

Index Label	Performance Metrics							
	Accuracy [%]	True Positive [count]	True Negative [count]	False Positive [count]	False Negative [count]	Precision [%]	Recall [%]	F_β [%]
LRP > 100	57.5	46	154	148	0	23.7	100	60.8
GUS > 2.8	79.6	29	248	54	17	34.9	63	54.3

Further development of the machine learning model could yield a highly powerful leaching predictor that can serve as a tool by itself as well as assist with the refinement of the TGUS equation. The results so far confirm that the GUS and TGUS indices are thus based on two of the most significant parameters (i.e., Koc and half-life). Including the analytical detection limit and other variables in TGUS will refine the separation of detects and non-detects, consistent with the results in section 4.2. We plan to analyze the best instances and feature importances further. The model will improve as more data is gathered, and we can verify its performance on other pesticide datasets from different locations around the U.S. Like TGUS, the IMLDA is not empirical but rather a theory-based model. As such, these models should be broadly applicable as long as input parameters that are realistic for the intended context(s) are used.

Section 5. Ongoing work and considerations

This report has been compiled concurrently with our Year 4 sample collection, which will, once submitted and analyzed, nearly double the size of the results database being reported here. The Year 5 sampling will add that much again, leading to a cumulative database nearly triple in size compared to that which is being reported here.

As such, it is hoped that our substantial investment in data analysis and synthesis approaches (as presented in Section 4) will help facilitate the approaching omnibus assessment and synthesis of that database. Iterative manual cross-tabulation analysis will continue to play a critical role, but the innovations of the TGUS detectable-mobilization index and the IMLDA computer-assisted factor assessment will be necessary for this analysis as well.

In the face of such a large and growing database, it is important to recognize the inherent limitations present in both the quantitative and qualitative data components of the data:

Pesticide detection limits result in a *trimodal* reporting format for the laboratory analysis results:

1. A measurement of a sample's pesticide concentration which is *greater than the relevant detection limit* (technically, the reporting limit, or limit of quantification, LOQ) is reported as the measured numerical concentration.
2. Conversely, a *non-detect* result means that the laboratory could not distinguish an analyte's concentration from zero. The result is thus reported as "not detected" (ND) or "below detection limit" (BDL).
3. Between these two outcomes is a thin (and conceptually fuzzier) margin where an analyte is clearly "seen" by the instrument but at levels below the reporting (LOQ) limit. These trace detections are reported as *non-quantifiable detections* (NQD)

Detection/quantification limits change over time as equipment/protocols improve but also can be affected by sample matrices. As such, detection limits for a given analyte can vary between batches of sample analyses. We have high confidence in the laboratory's reported quantification limits (typically determined by repeated analysis of blank samples and calculated by the mean result plus a determined number of standard deviations about that mean). Nevertheless, we must recognize that variation in detection limits over time means that the same true low concentration from a sampling point could be reported as a numerical detection at one time, and as a "not-detect" or a NQD at another time.

Mapped soil/aquifer data used in our Section 4 assessments include several soil characteristics associated with mapped soil units from NRCS soil surveys. These include "category" drainage class, textural class, and numerical range estimates of organic matter content and bulk density. However, as NRCS points out, soils are mapped based on an

extensive (and not intensive basis), in which soil series are mapped based on topographic similarity to a subset of locations where shallow soil corings are made and examined. As such, NRCS warns about uncritically using their map units and related tables at a small scale. As such, nontrivial uncertainty is present in these assessments. Project staff do evaluate the soil map units shown on maps as we walk around the site with the owner and we overlay several other kinds of maps. We are also collecting localized soil samples for bulk density and organic matter analysis.

Pesticide degradation and sorption parameters such as Koc and degradation half-life are taken from international compilations that draw from literature reviews and individual publications. For simplicity, a single value is used, though some of the pesticide entries cite ranges of values. These parameters are determined in laboratory, essentially using a handful of soil, or in a field site with specific local conditions (climate, seasonal variation, soil/aquifer mineralogy, etc.). As with mapped soil data, the inherent limitations of scale are obvious, yet these remain critical parameters for understanding potential transport and fate, so we apply our best judgement for using available data.

Overall, the imprecision and possible inaccuracy of the "characteristics data" (of both pesticides and soil/aquifer setting) make robust machine learning (IMLDA) and empirical index (TGUS) methods an important alternative to using multivariate statistical methods that can be used when data are precisely measured in a research context. For example, the machine learning tree methods do not assume anything about the shapes of statistical probability distribution but are simply using the input data as provided.

An essential aspect of any modeling approach (whether TGUS analytical or IMLDA exploratory) is the use of sensitivity analyses wherein we assess the potential effects of the presence of incorrect and/or imprecise data on model predictions. This helps us focus on which factors may carry the greatest weight and thus warrant the most attention for further refinement.

The project team continues to compile supporting data (including ongoing reporting from landowners on site characteristics and use patterns). We will also explore potential correlations with other analytical results (anions, cations, etc.) which we have collected but not yet assessed in depth.

Finally, the project team greatly appreciates the active ongoing engagement with NYS DEC – ranging from project design guidance to sample analysis to ongoing collaborative review of results and future directions.

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