RQES

Réseau québécois sur les
eaux souterraines

iah aih

CNC - SNC

Agricultural interactions with groundwater quality in southwestern Ontario

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Water Resources Engineering

G360 Institute for Groundwater Research

University of Guelph

UNIVERSITY of GUELPH

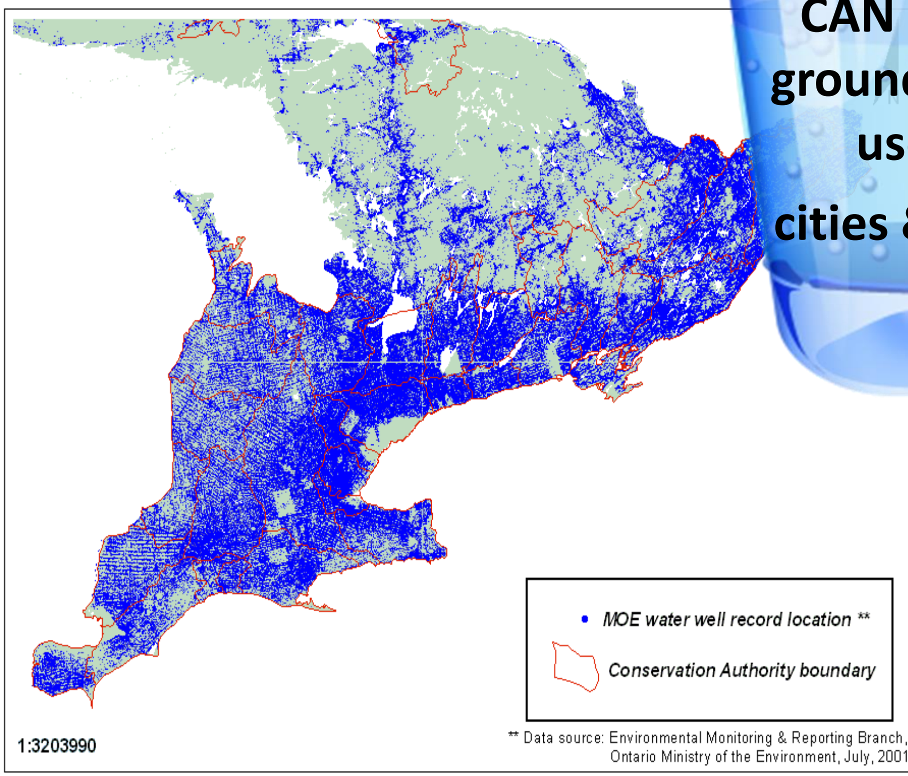
COLLEGE of ENGINEERING AND PHYSICAL SCIENCES

SCHOOL OF ENGINEERING

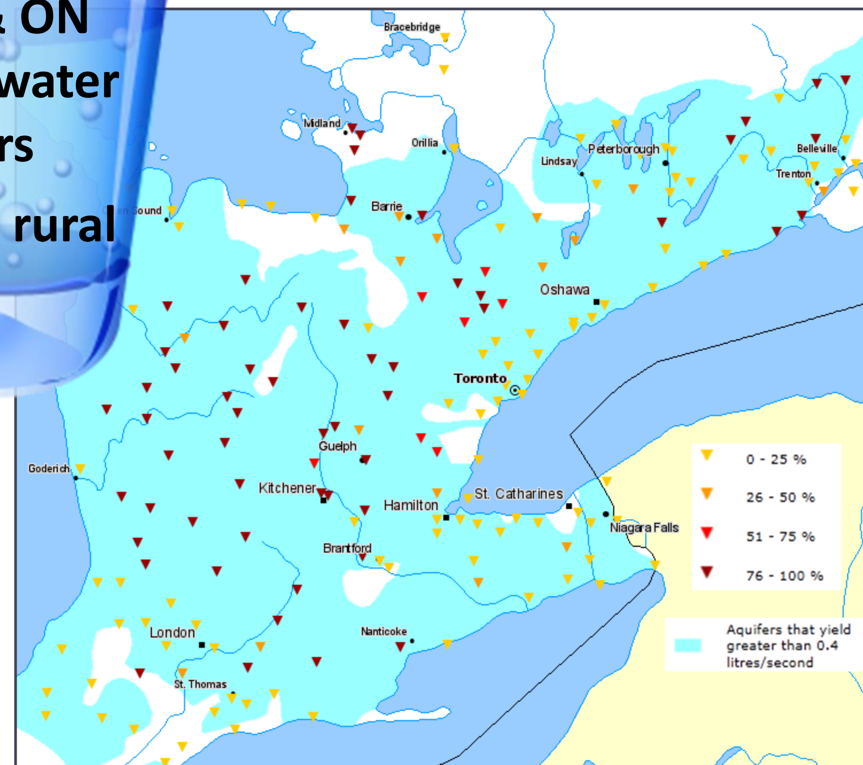
360

Motivation

~ 30%
CAN & ON
groundwater
users
cities & rural

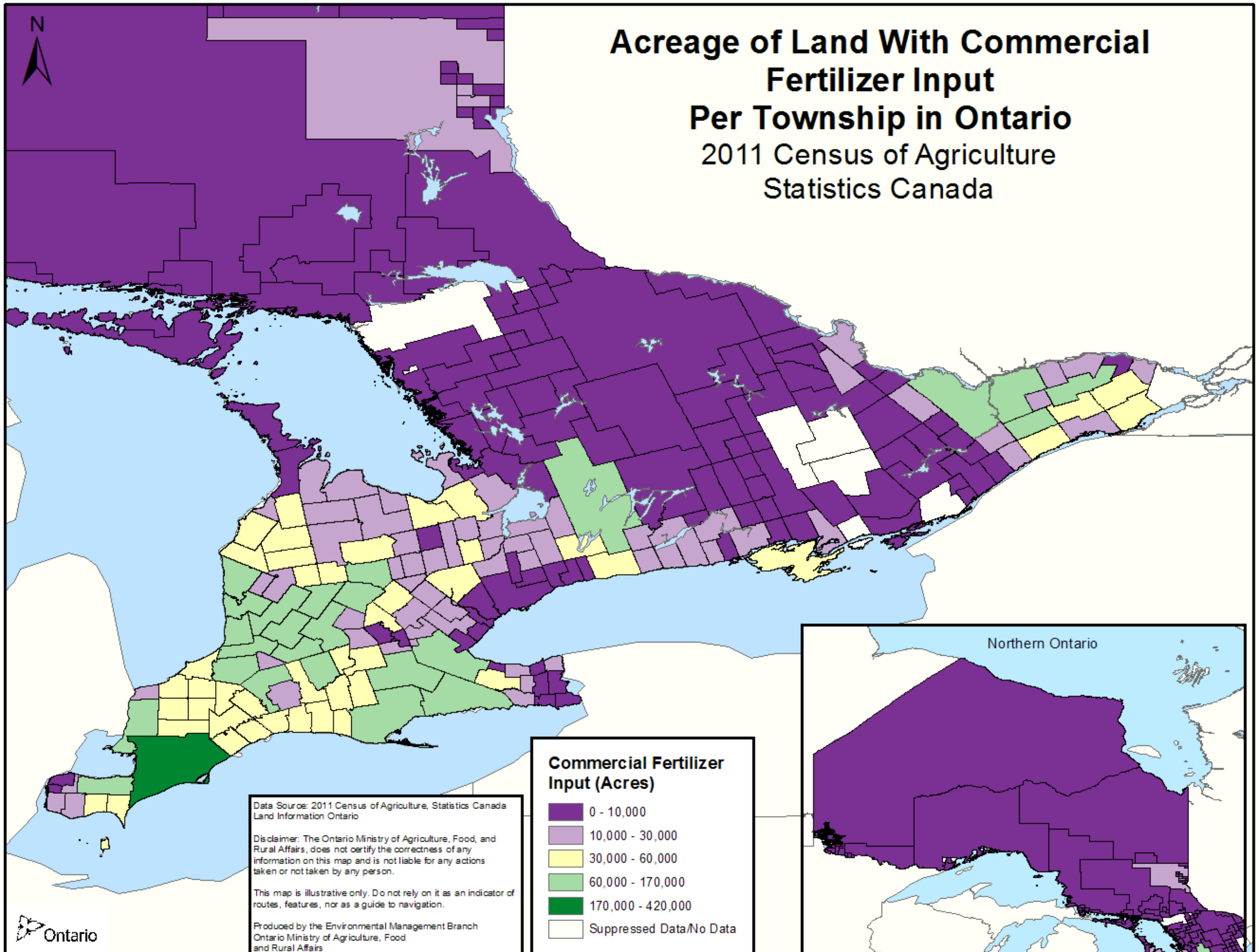


Distribution of MOECC water well records (Novakowski et al., 2006)



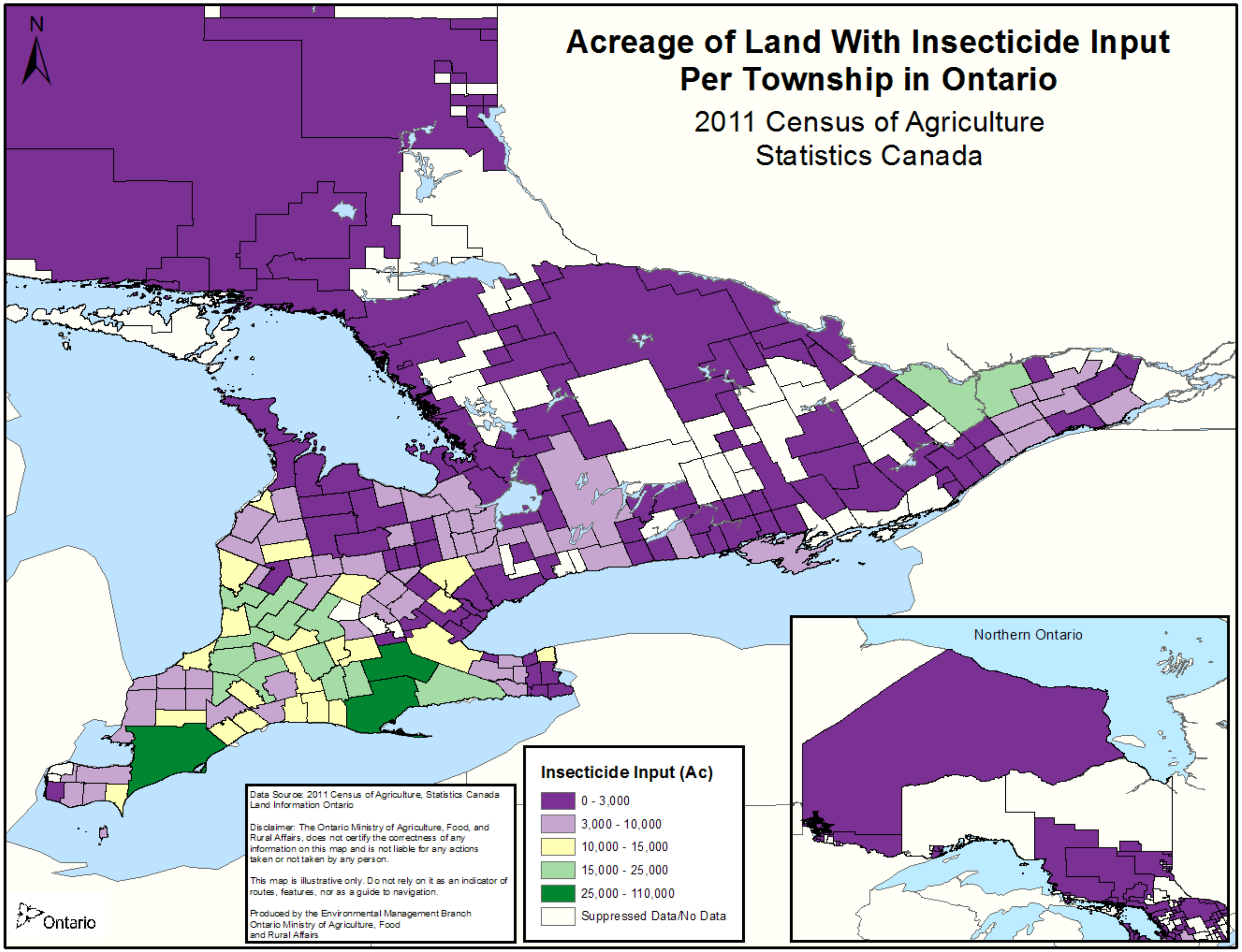
% using groundwater in municipalities (NRCan, 2011)

Motivation



OMAFRA

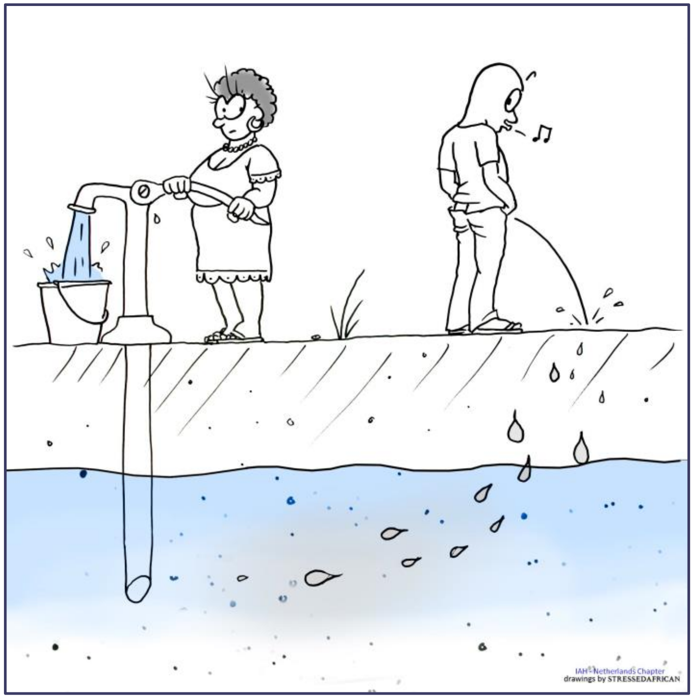
Motivation



OMAFRA

Why is groundwater vulnerable?

"There is widespread lack of understanding of groundwater linkages and dependencies (especially the vulnerability to land-use practices) and too many regard groundwater as an unlimited and uncoupled resource" (IAH, 2006)



IAH Netherlands (2011)

Two recent studies

Developing novel techniques for measuring in situ groundwater nitrate concentrations, vertical geochemical profiling, and real-time remote groundwater quality monitoring

MacDonald (2015)

Neonicotinoids in groundwater: presence and fate in two distinct hydrogeologic settings in Ontario, Canada

Browne (2017)

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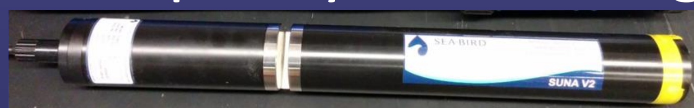
Developing novel techniques for measuring in situ groundwater nitrate concentrations, vertical geochemical profiling, and real-time remote groundwater quality monitoring



MacDonald (2015)

Neonicotinoids in groundwater: presence and fate in two distinct hydrogeologic settings in Ontario, Canada

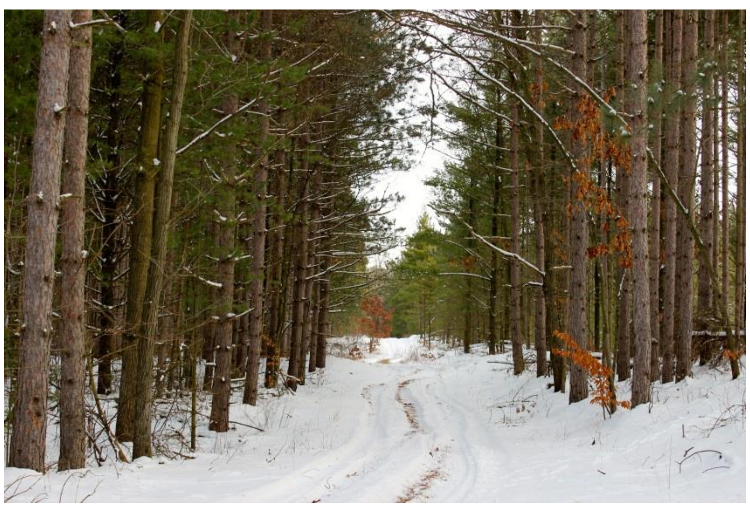
Browne (2017)

Problem statement

- Nitrate transport and fate is complex and obtaining accurate field measurements can be challenging
- Groundwater nitrate data is often captured at low temporal resolution and requires laboratory analyses

- **Can we develop new sampling methods to obtain new insights?**

Objectives



(Ryan Osman, 2015)

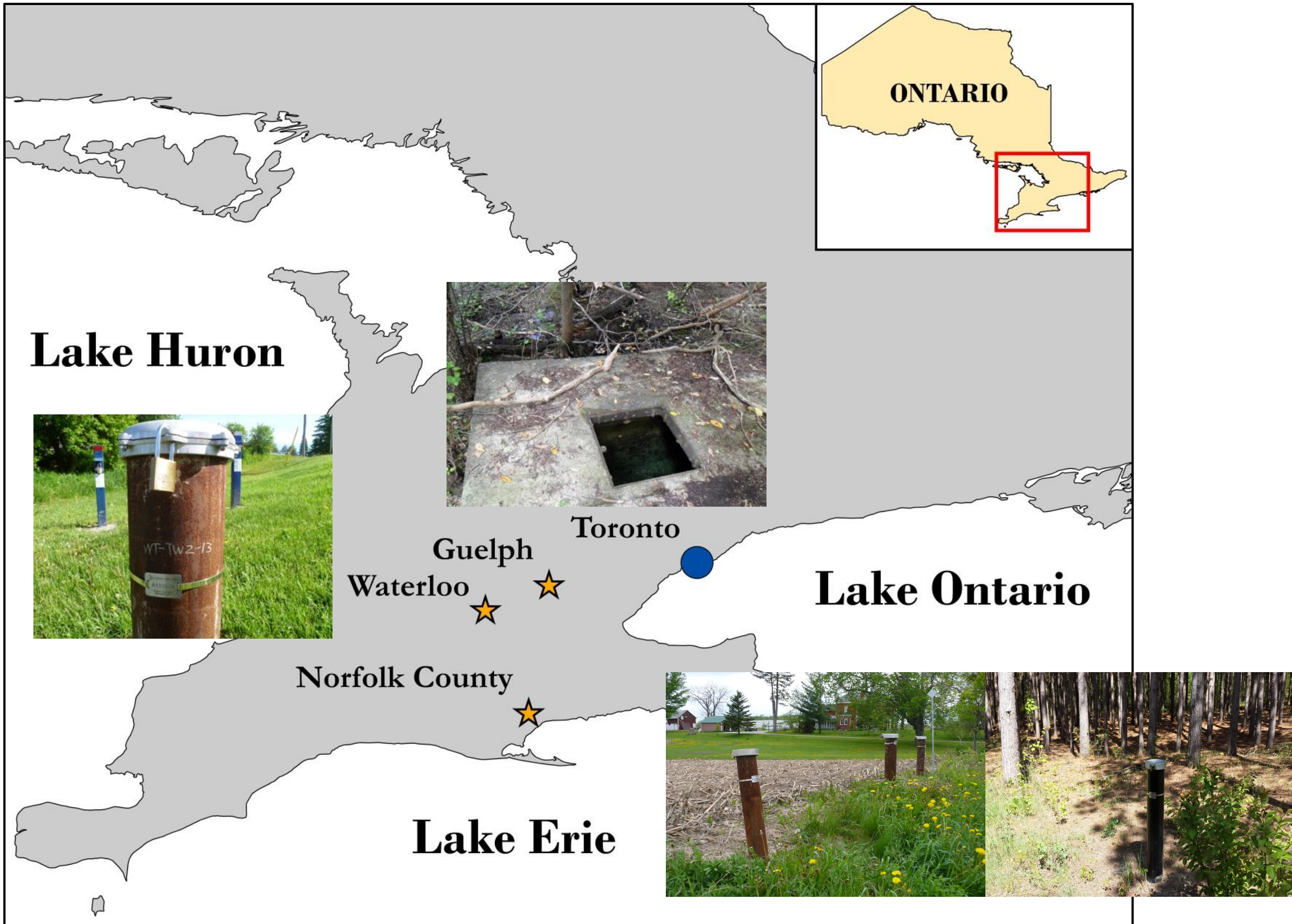
- Test and evaluate innovative sensor equipment in groundwater environments

- Develop novel monitoring methods that can be used to:

1. Obtain precise nitrate measurements in the field
2. Measure down-hole vertical profiles of groundwater chemistry
3. Monitor groundwater quality parameters at a high temporal resolution

MacDonald et al. (2017)
Groundwater Monitoring & Remediation

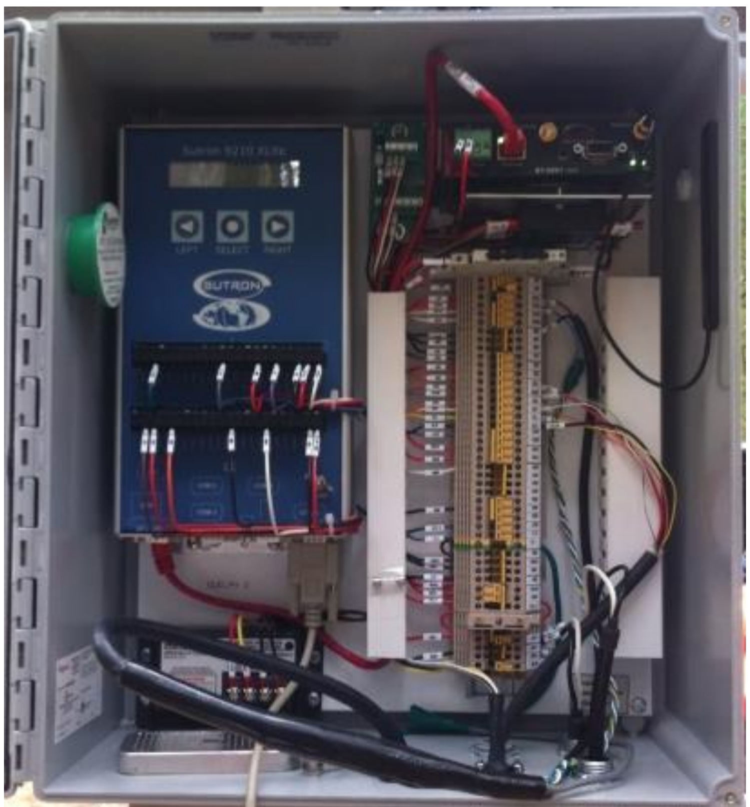
Research locations



Sensor equipment

EXO™ Water Quality Sonde – YSI Inc. (Yellow Springs, OH)

Submersible Ultraviolet Nitrate Analyzer (**SUNA™**) – Satlantic Inc. [Sea-Bird Scientific] (Halifax, NS)



Integrated Telemetry System – Hoskin Scientific Ltd. (Burlington, ON)

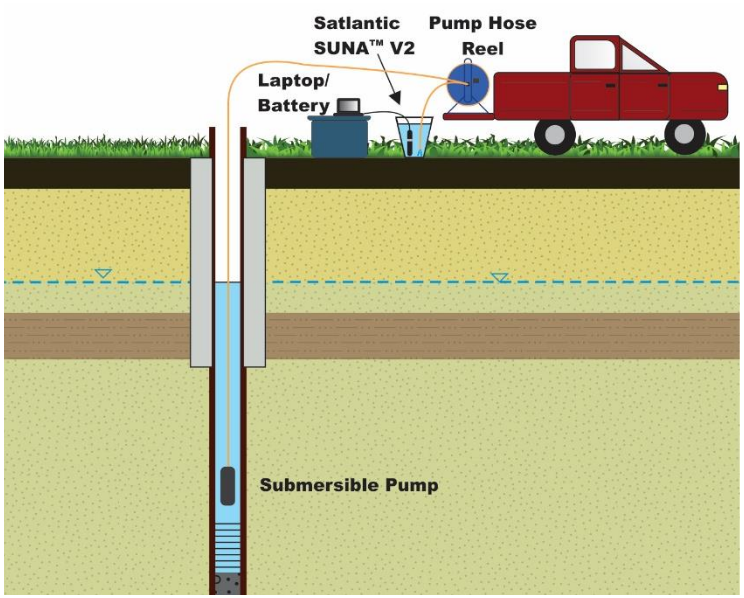
Testing methods

Flow Cell Testing

Vertical Profiling

Real-time Remote Monitoring (RTRM)

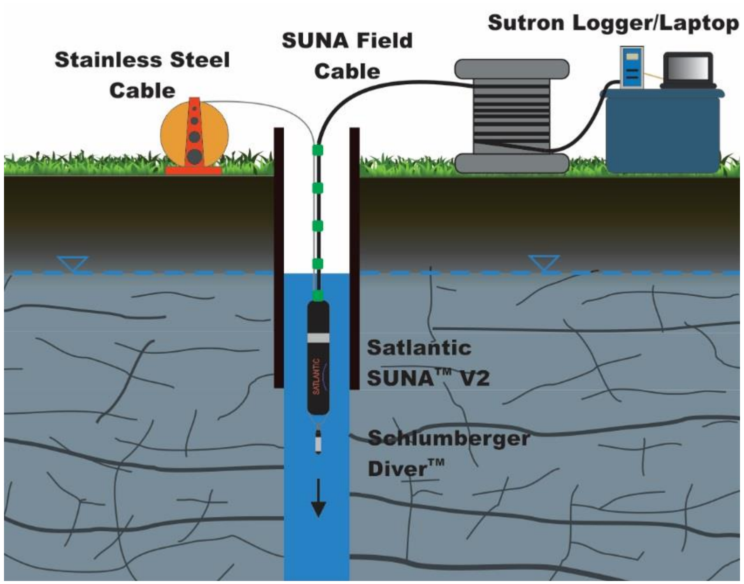
Testing methods



Flow Cell Testing

- Nine MWs in Norfolk County tested over four periods (Jul 2014 – Feb 2015)
- Purged water discharged through flow cell bucket containing SUNA
- SUNA obtained measurements of NO_3^- near continuously (i.e. every second)
- Compared SUNA readings to lab concentrations – how precise are they relative to one another?

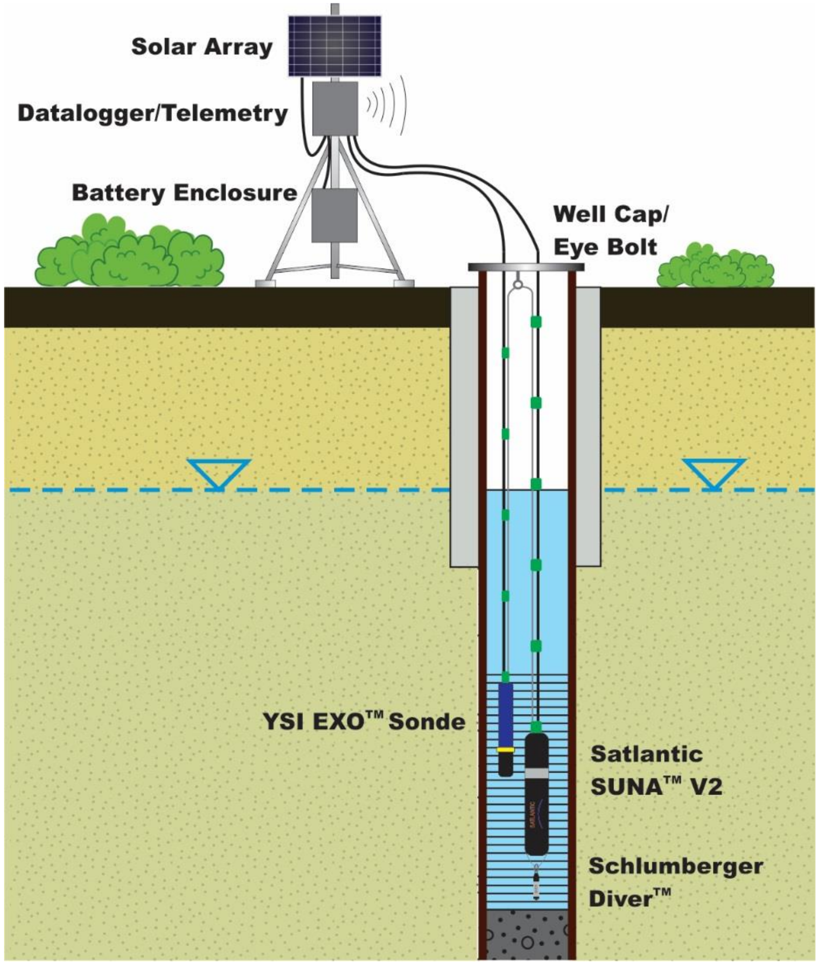
Testing methods



Vertical Profiling

- Eight PWs tested over two periods (Aug 2014 – Oct 2014)
- SUNA/EXO lowered down-hole and retrieved; measurements obtained at specified rates
- Can changes in geochemistry be observed at different hydrostratigraphic intervals?
- Are NO_3^- concentrations variable along OB well screen? In open bedrock boreholes?

Testing methods

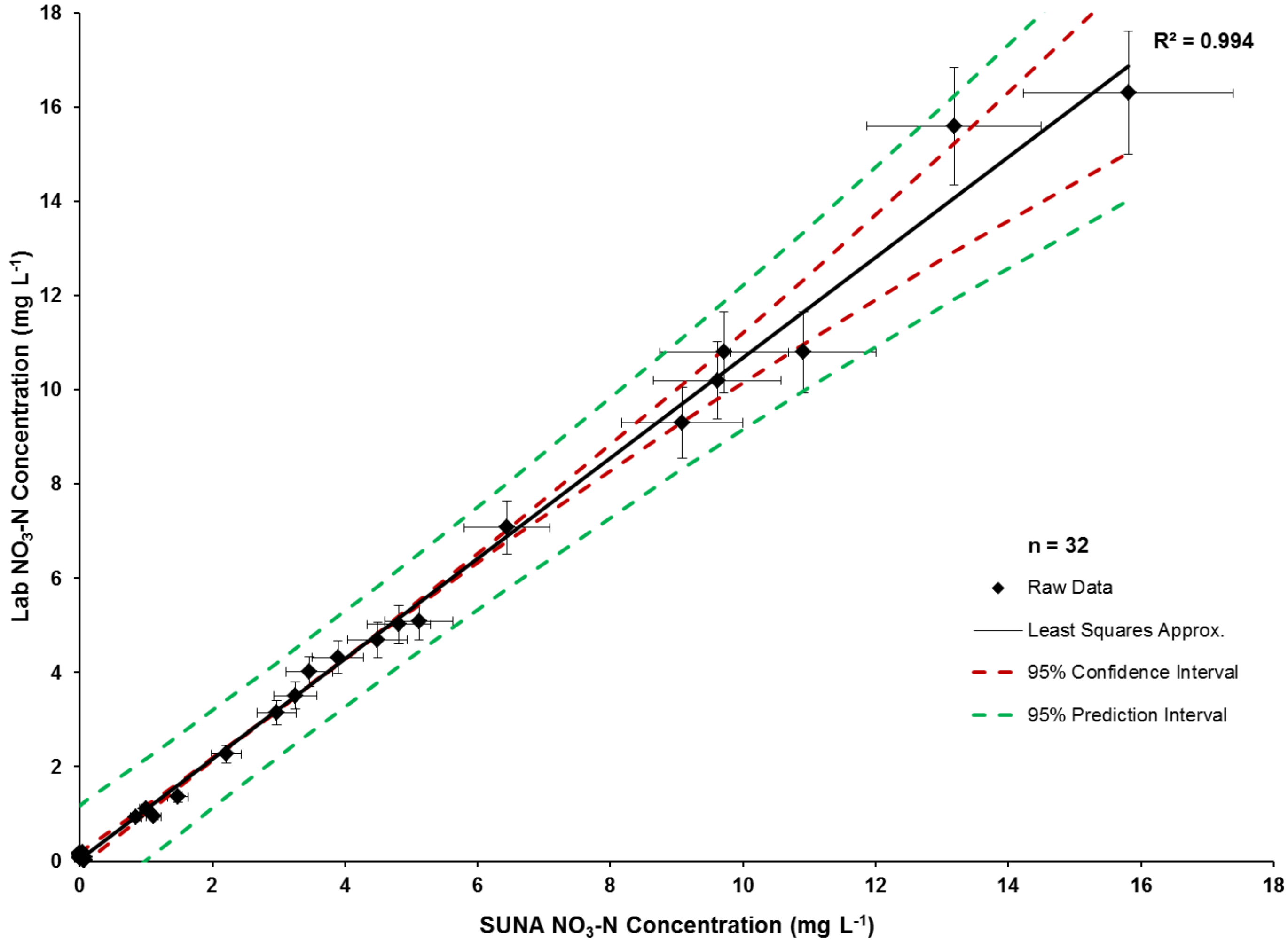


Samples: NO_3^-, temp., pH, EC, DO, turbidity, GW levels

Real-time Remote Monitoring (RTRM)

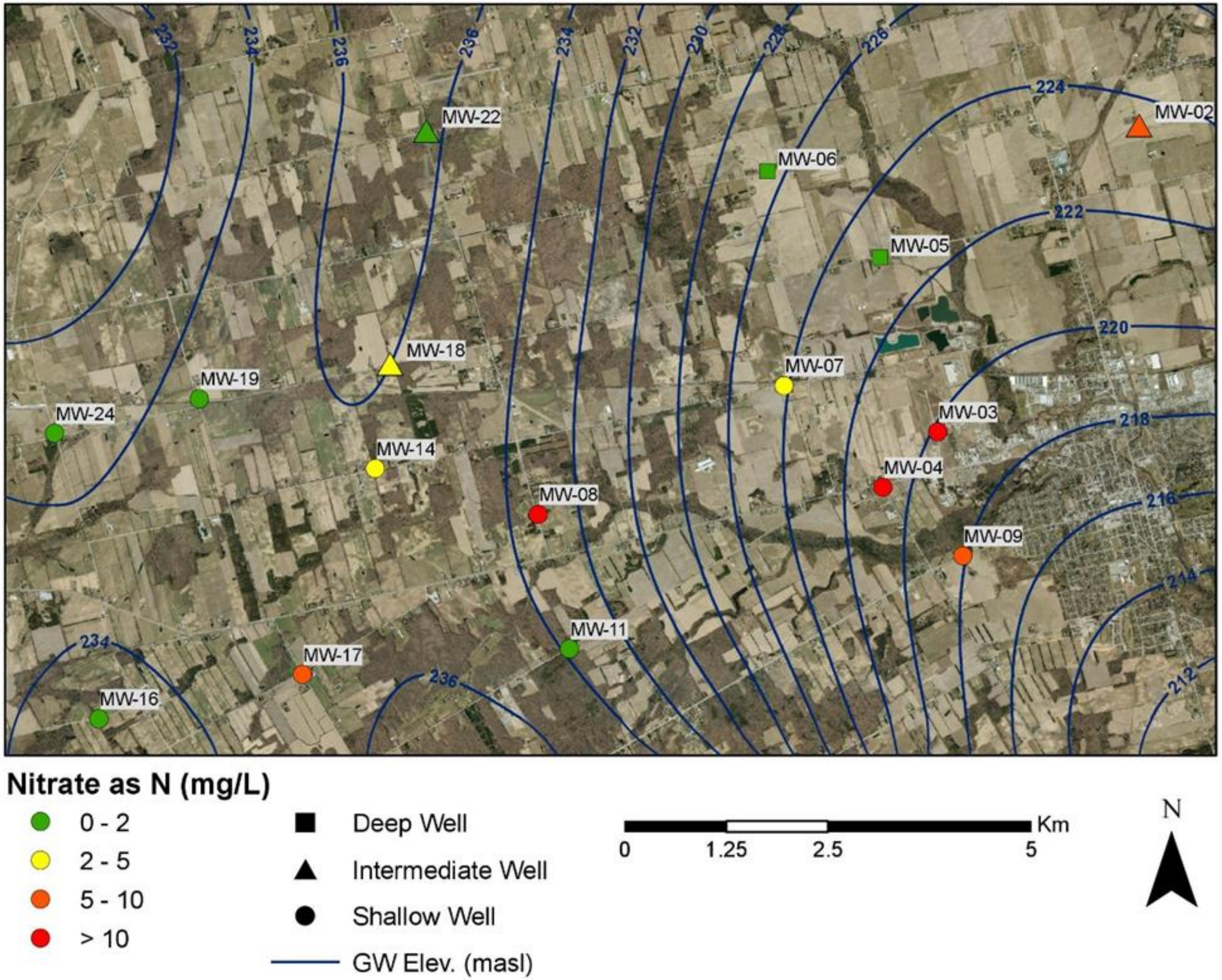
- Two PWs in Port Rowan tested (Nov 2014-Aug 2015)
- SUNA and EXO sensors suspended in screened interval
- Measurements obtained every 15 minutes and then averaged hourly
- Climate data (precipitation, air temp.) collected hourly from UoG research station
- Can groundwater quality changes be correlated to recharge events (i.e. precipitation/GW levels)?

Results: flow cell testing

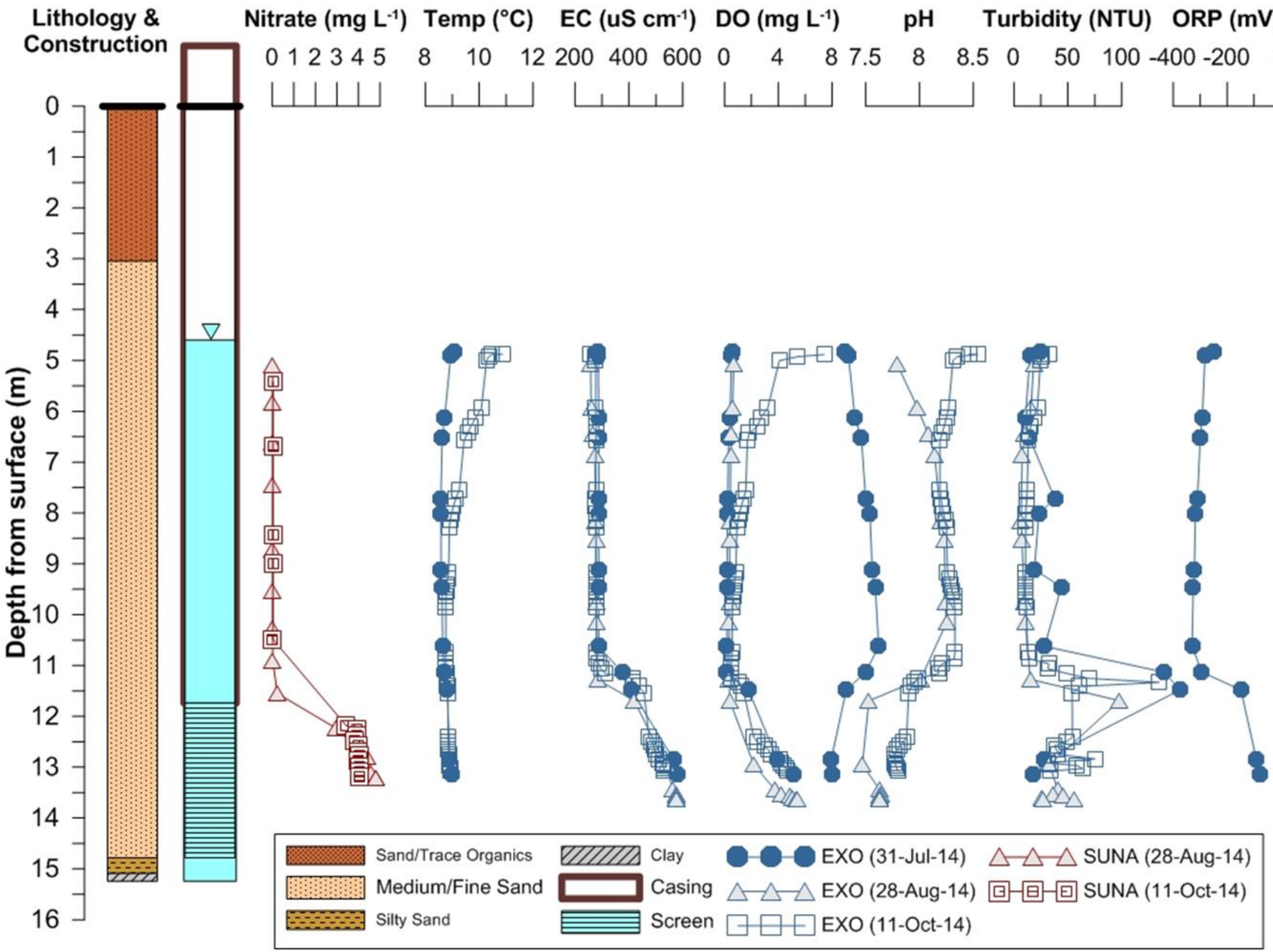


Error (mg/L): -0.25 │**Error**│ **(mg/L):** 0.28

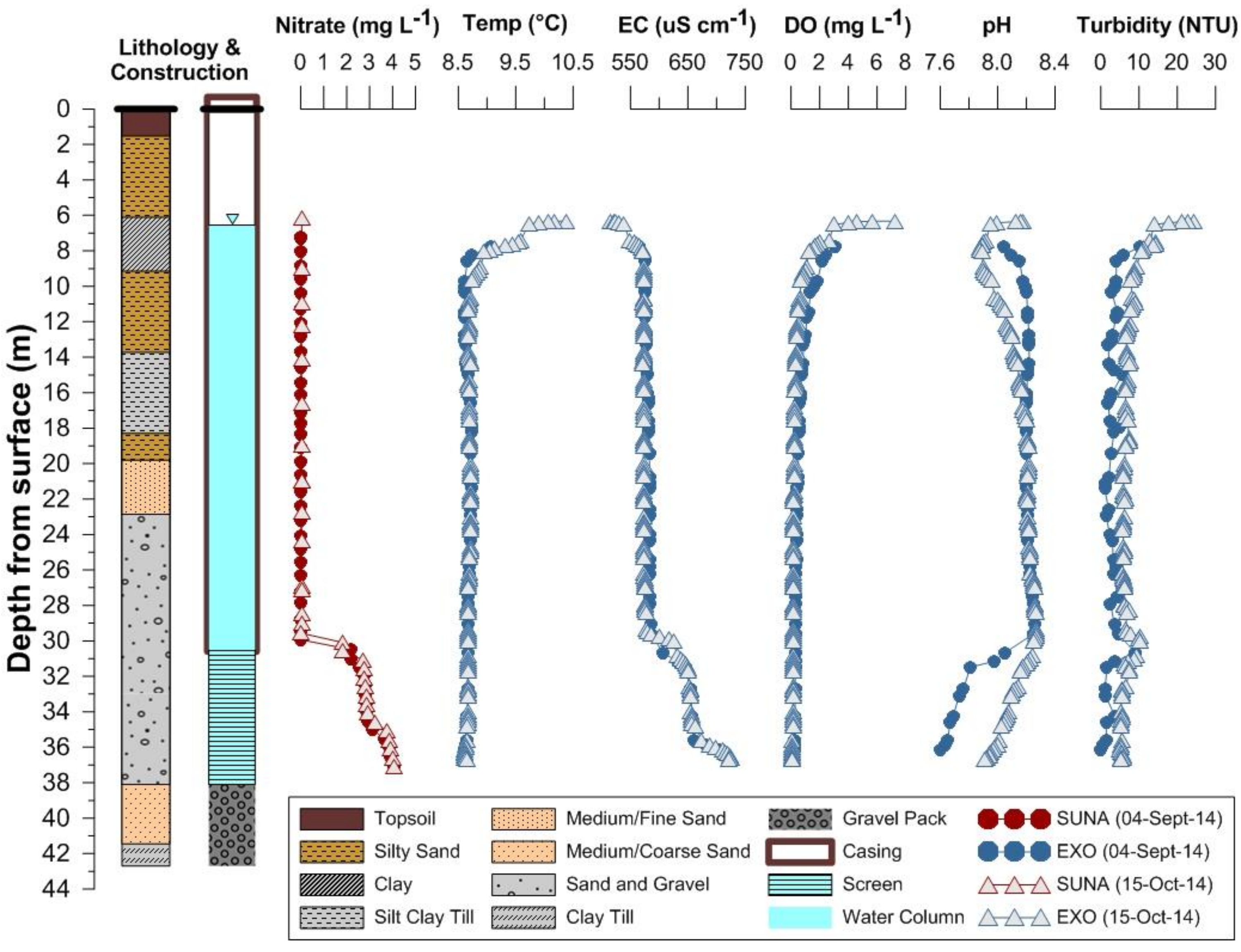
Results: flow cell testing



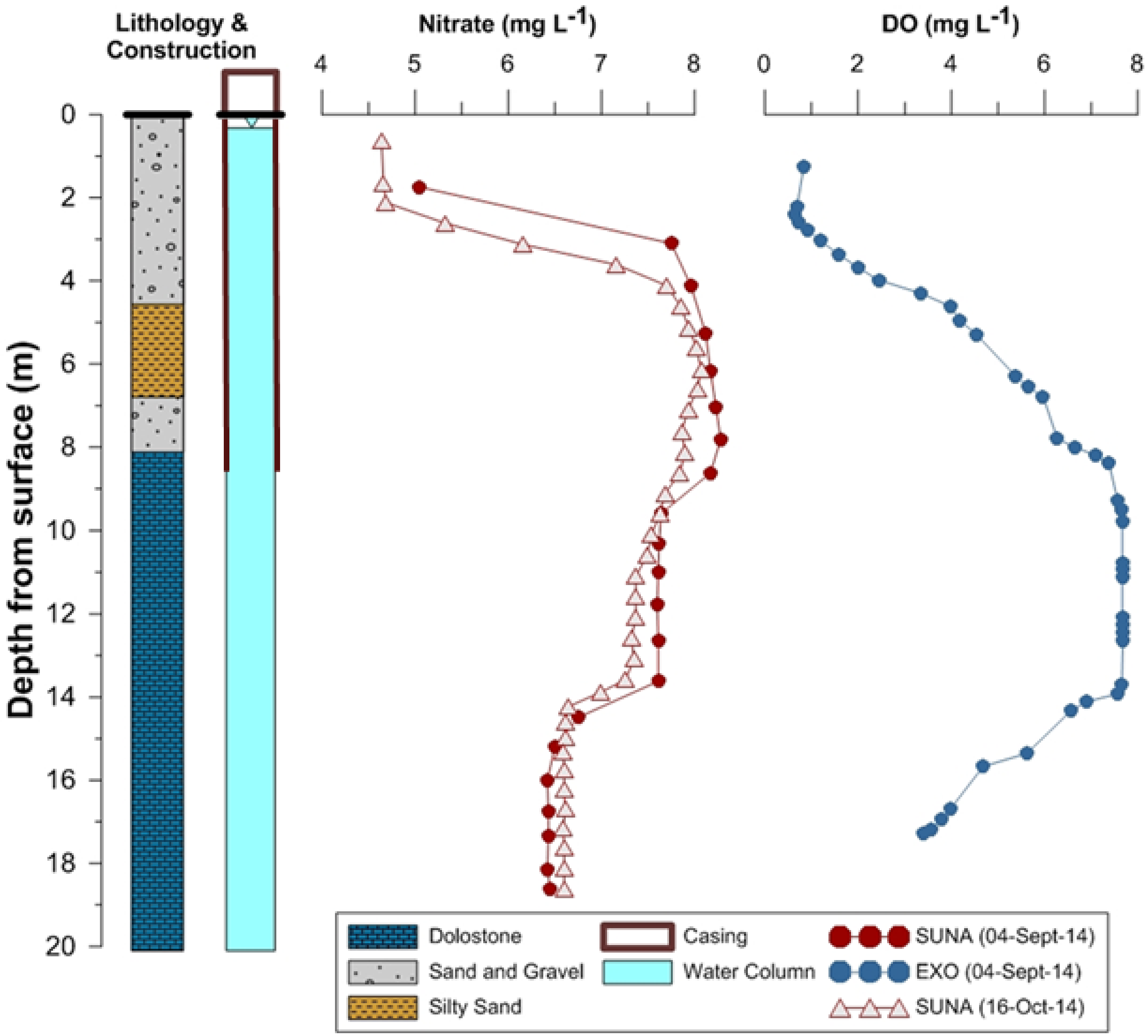
Results: vertical profiling



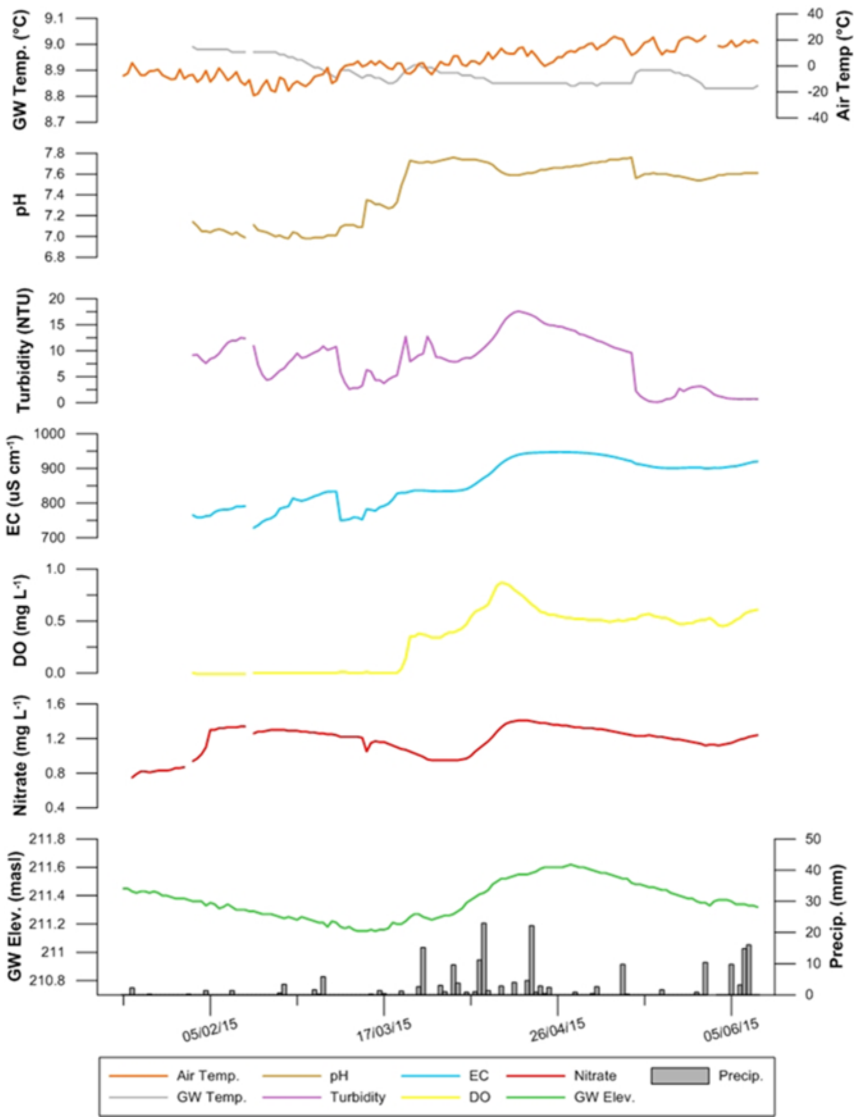
Results: vertical profiling



Results: vertical profiling



Results: real-time remote monitoring



PR8

- Noticeable increases in turbidity, EC, nitrate with spring recharge (Mar 9-)
- Increase in DO with spring recharge
- Magnitude of changes much larger for turbidity, EC compared to PR11
- Noticeable increase in pH preceding spring recharge

Conclusions

1. Flow cell testing allows SUNA to measure NO_3^- concentrations in the field at high precision relative to purging techniques (R^2=0.99, |Error| = 0.28 mg/L)

2. Vertical profiling provides a down-hole method of measuring nitrate concentrations with depth in the water column

3. RTRM methods provide unique groundwater quality datasets at fine temporal resolution

Conclusions

4. Nitrate and DO have distinct changes in concentration with depth at the Stone Well (open bedrock borehole)

5. Noticeable changes in turbidity, EC, nitrate were observed at two RTRM stations and appear to result from spring recharge

6. Turbidity may serve as best indicator of recharge; aquifer response time on the order of 2 days in Port Rowan

Two recent studies

Developing novel techniques for measuring in situ groundwater nitrate concentrations, vertical geochemical profiling, and real-time remote groundwater quality monitoring

MacDonald (2015)

Neonicotinoids in groundwater: presence and fate in two distinct hydrogeologic settings in Ontario, Canada

Browne (2017)

Neonics

- Group of insecticides developed and introduced to commercial use in 1990s, early 2000s
- Rapidly widespread due to ease of use and perception that they are environmentally friendly
  - Used as seed coatings for corn, soybeans
- Despite widespread application, knowledge surrounding environmental fate not comprehensive
  - Field studies largely focused on soil, soil dust and surface water bodies
  - Research about neonics in groundwater less robust

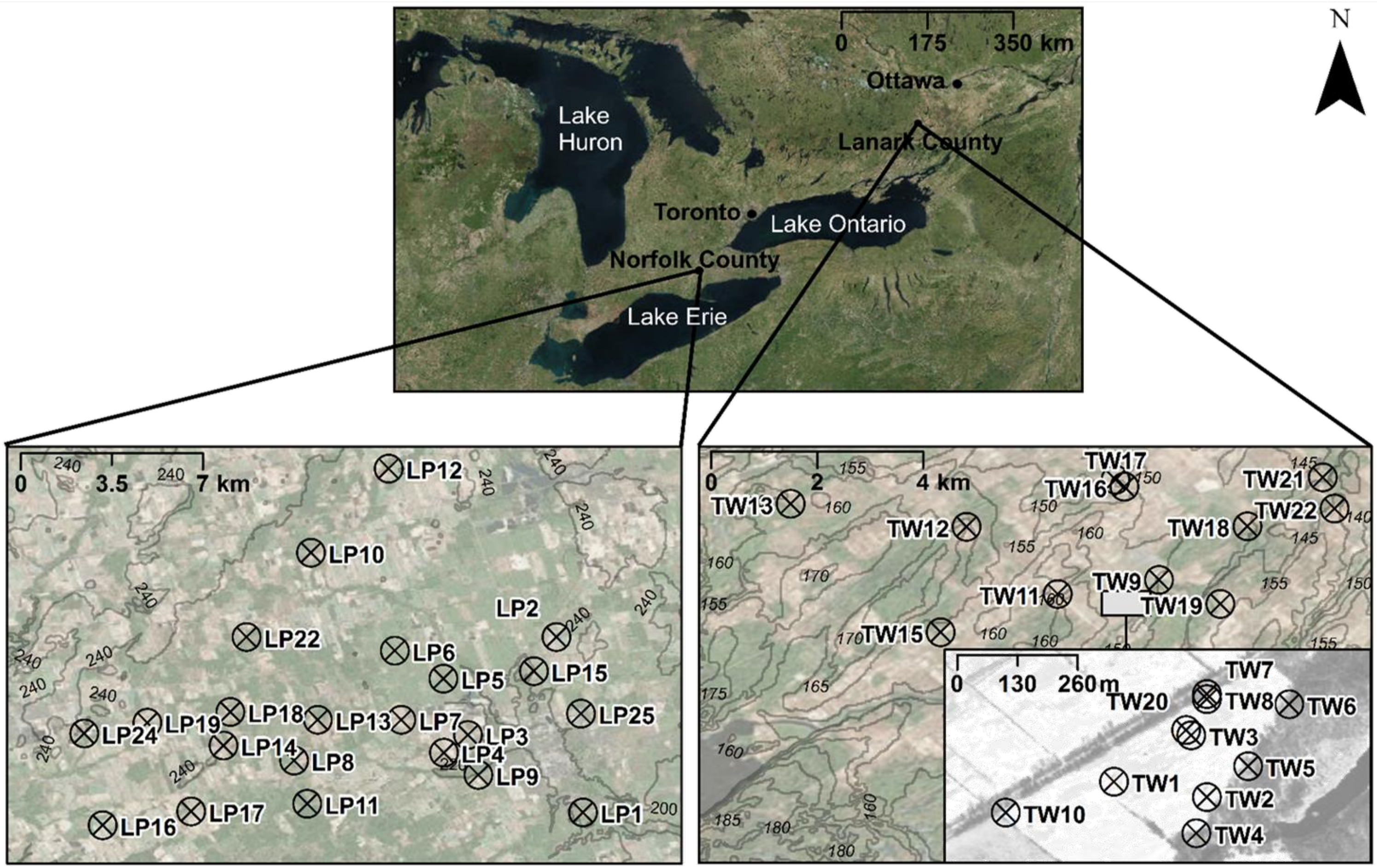
Objectives

- Investigate the presence and fate of neonicotinoids in Ontario groundwater
  - Compare results in distinct hydrogeologic settings (shallow, sandy aquifer versus a crystalline fractured bedrock aquifer)
  - Clothianidin and thiamethoxam are the most commonly used neonicotinoids at each research site

Browne et al. (2017) Submitted

Research sites

- Five seasonal sampling rounds conducted using 18 to 26 monitoring intervals at each research site



Norfolk County

- Unconfined quaternary aquifer
- Rich in groundwater that is characterized as highly vulnerable [1]
- Intensive agriculture
  - 78% of land is actively cultivated[1]
  - Maize, soybeans, ginseng, tobacco, and wheat

- 26 multi-level wells (58 monitoring intervals) drilled for Tier 3 water budget study between 2010 and 2011
- Past studies at this site have examined groundwater contamination caused by nitrate[2,3,4,5]

[1] LPRCA (2008)
[2] Gardner (2017)
[3] Hollingham (2011)
[4] Macdonald (2015)
[5] Saleem et al. (2016)

Lanark County

- Thin, till overburden underlain by fractured, crystalline rock
- Predominantly forested
  - 29% of land is actively cultivated [1]
  - Small-scale maize and soybean farms (largest farm is 121 ha)

- 21 multilevel wells (52 monitoring intervals) progressively drilled between 2004 and 2008
- Past studies at this site have shown groundwater to be vulnerable to land-applied contaminants [2,3,4,5]

[1] Agriculture and Agri-Food Canada (2017)
[2] Levison et al. (2012)
[3] Levison and Novakowski (2009)
[4] Praamsma (2016)
[5] Trimper (2010)

Methods

Measuring Device	Parameter
YSI 556 Handheld Device	Dissolved Oxygen Electrical Conductivity Oxidation-Reduction Potential pH Temperature
Satlantic SUNA[1]	Nitrate-N

[1] Satlantic (2017)

Methods

Measuring Device	Parameter	
Pressure Transducers[1]	Groundwater elevations	
Rain Gauge[2,3]	Precipitation	
LC-ESI(+)-MS/MS Analysis	Acetamiprid Clothianidin Dinotefuran Imidacloprid Thiacloprid Thiamethoxam	Atrazine Azoxystrobin Cyantraniliprole Mefenoxam Metochlor

[1] Solinst Canada Ltd. (2015)
[2] Environment and Climate Change (2017)
[3] Hoskin Scientific (2017)

Methods

- Crop survey
- Soil sampling
- River sampling
- Mathematical modelling

Results

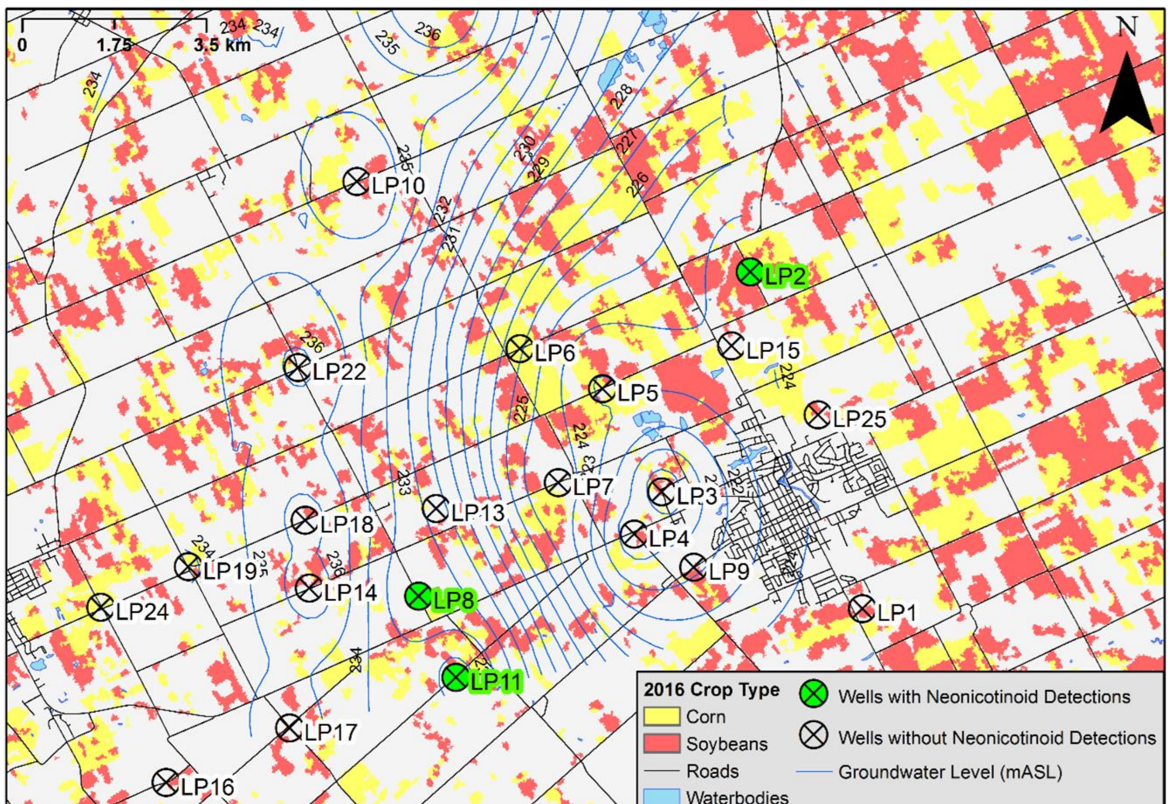
- Clothianidin peak at several wells at both sites in August
- Low imidacloprid concentrations in the summer of 2016
- Thiamethoxam peak at one Lanark County well during April sampling rounds

Sampling Round	Clothianidin (µg/L)	Imidacloprid (µg/L)	Thiamethoxam (µg/L)	Number of samples
April 2016	TW17 (0.095)	---	TW17 (0.46)	50
July 2016	---	LP-MW-08S (0.07)	TW17 (0.061)	44
August 2016	LP-MW-02D (1.68) LP-MW-08D (2.09) LP-MW-11D (1.67) TW1D (1.16)	LP-MW-08S (0.03)	---	51
November 2016	---	---	---	41
April 2017	---	---	TW17 (0.42)	42
Detection Frequency (%)*	2.2	0.9	1.3	228

** Above level of quantitation*

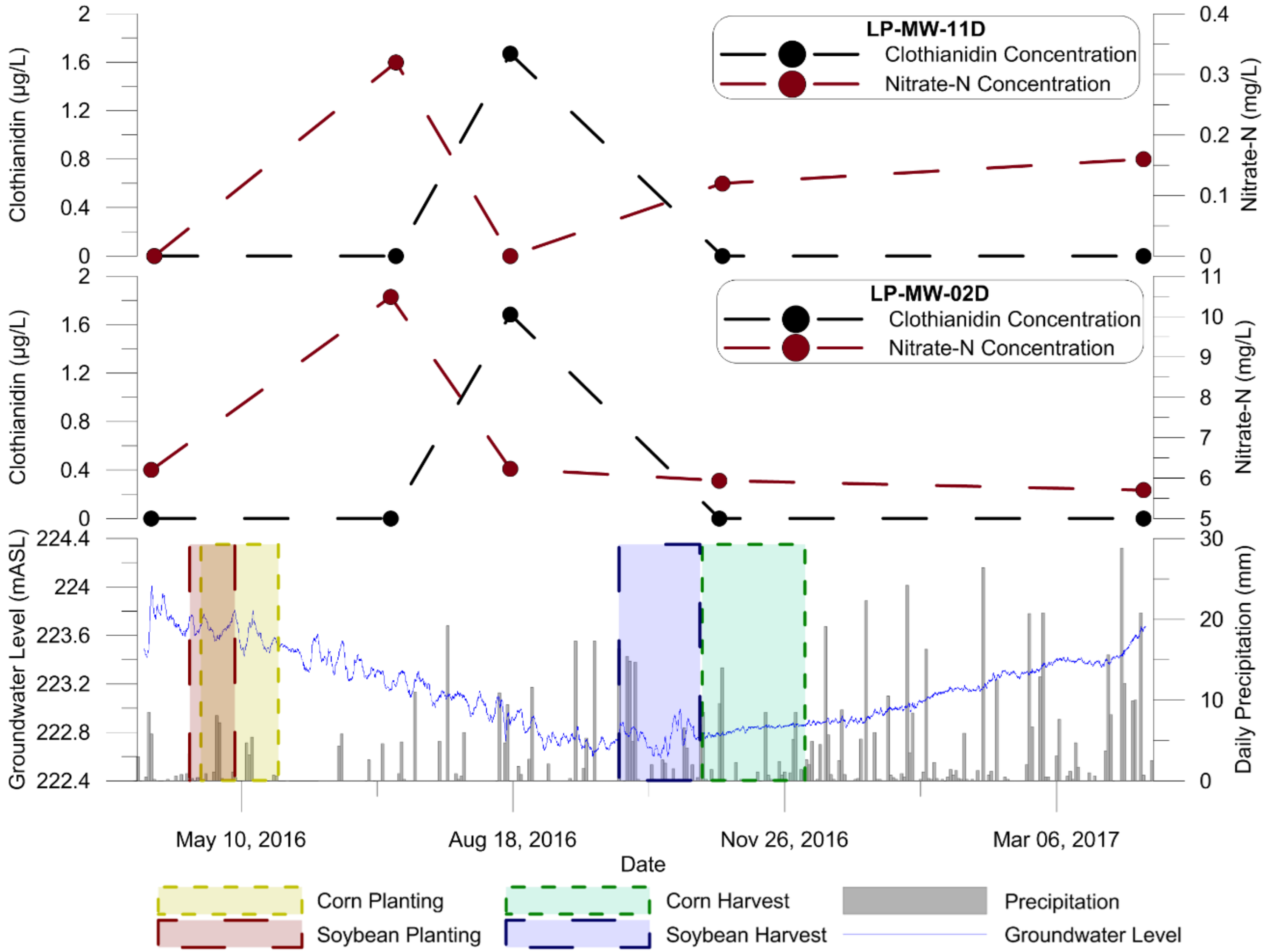
Norfolk County crop map

Location	Crop	Neonicotinoid	Treatment Rate (mg a.i./seed)[1]	Seeding Rate (seeds/ha)	Neonicotinoid Application Rate (g a.i./ha)
Norfolk County	Corn	Clothianidin	0.25	74,000	18.5
	Soybeans	Thiamethoxam	0.076	432,000	32.8



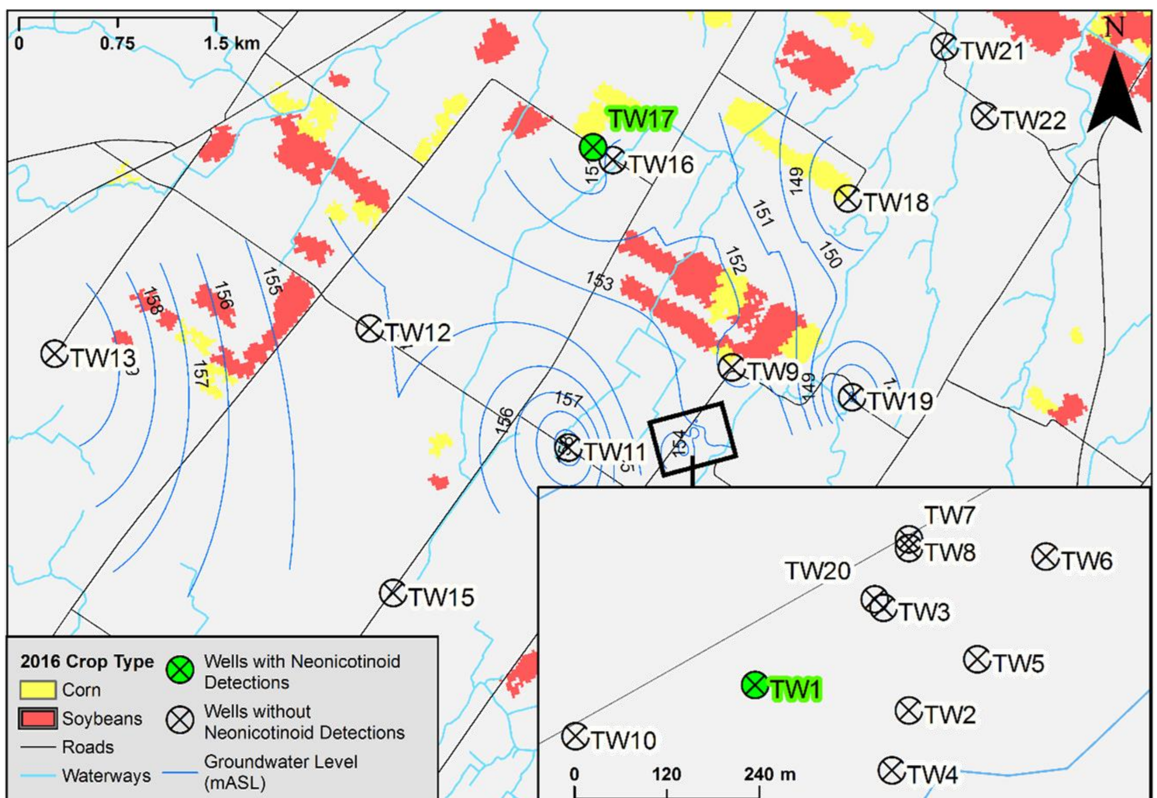
[1] OMAFRA (2016)
Crop map obtained from Agriculture and Agri-Food Canada (2017)

Clothianidin and nitrate in Norfolk County



Lanark County crop map

Location	Crop	Neonicotinoid	Treatment Rate (mg a.i./seed)[1]	Seeding Rate (seeds/ha)	Neonicotinoid Application Rate (g a.i./ha)
Lanark County	Corn	Thiamethoxam	0.25	79,000	19.8
	Soybeans	Thiamethoxam	0.076	402,000	30.6



[1] OMAFRA (2015)
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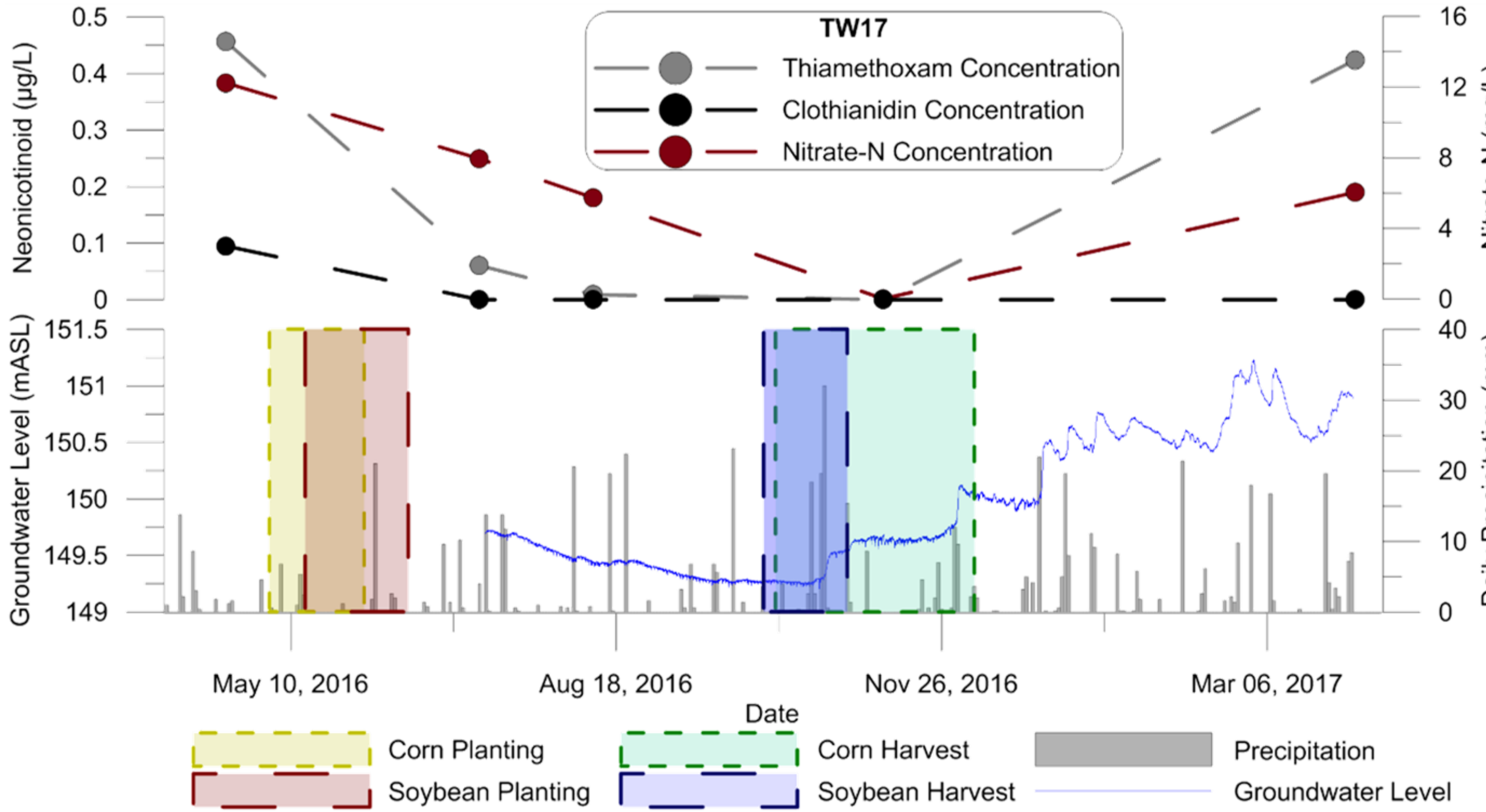
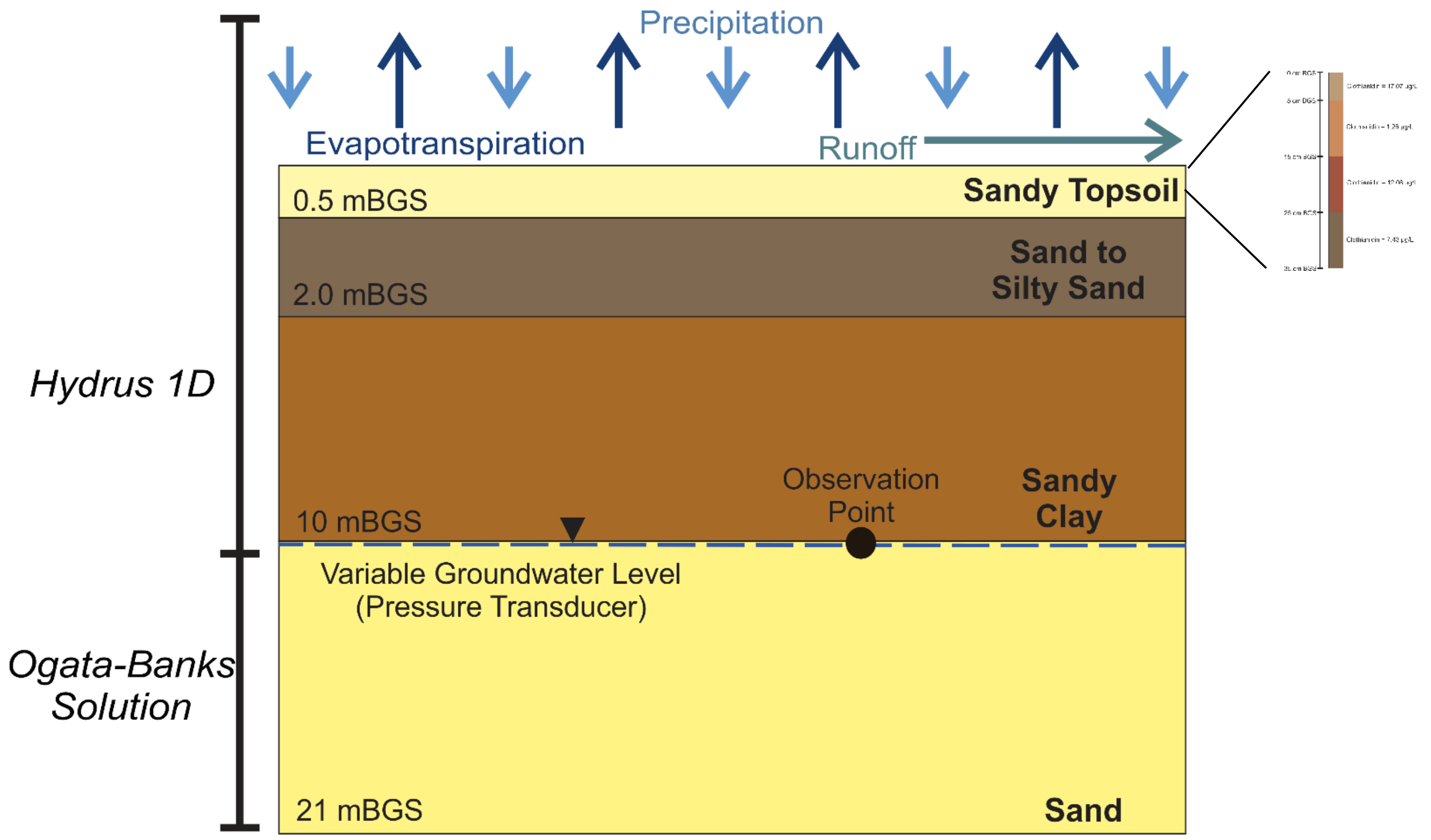
Thiamethoxam and nitrate in Lanark County

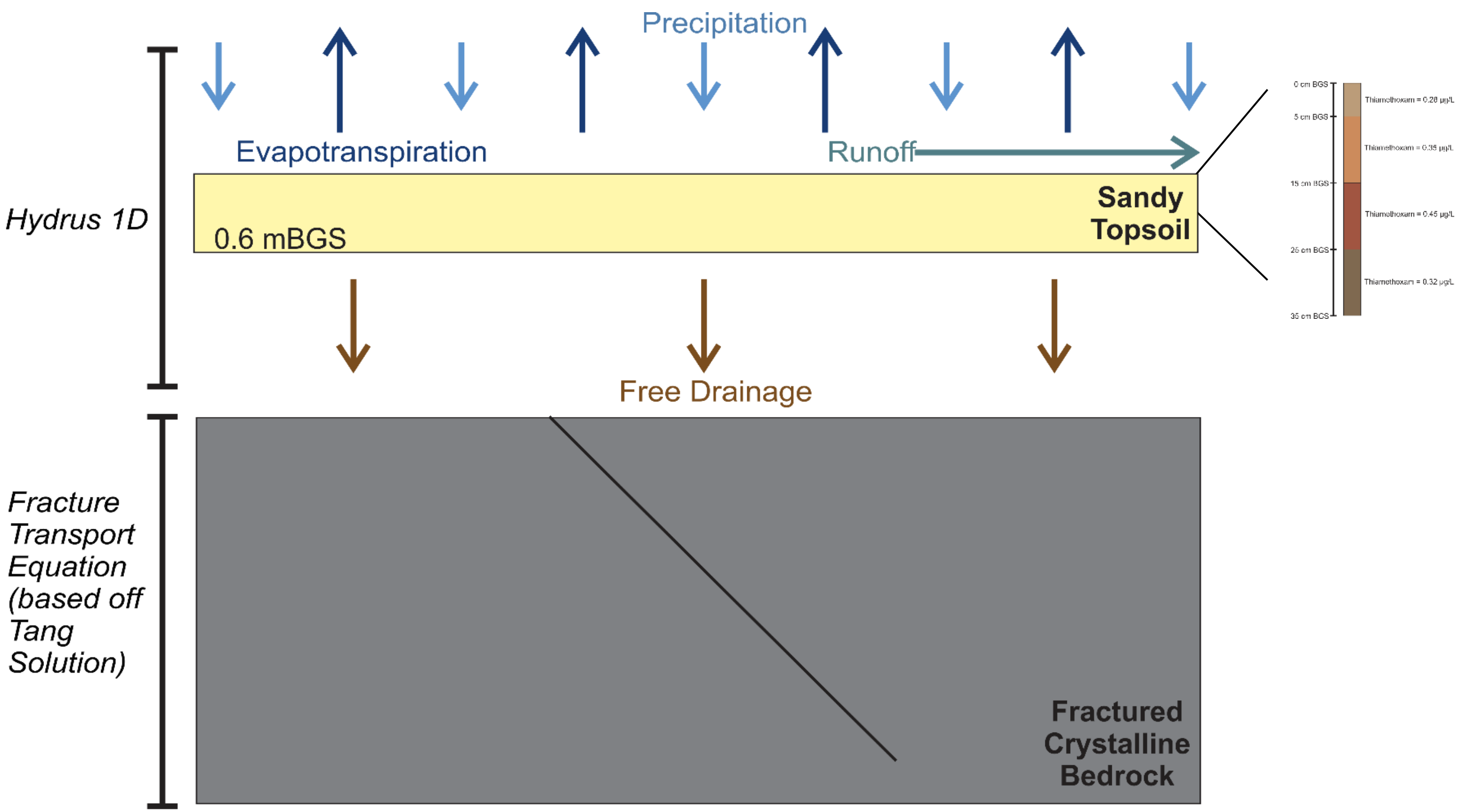


Norfolk County (LP2) mathematical modelling



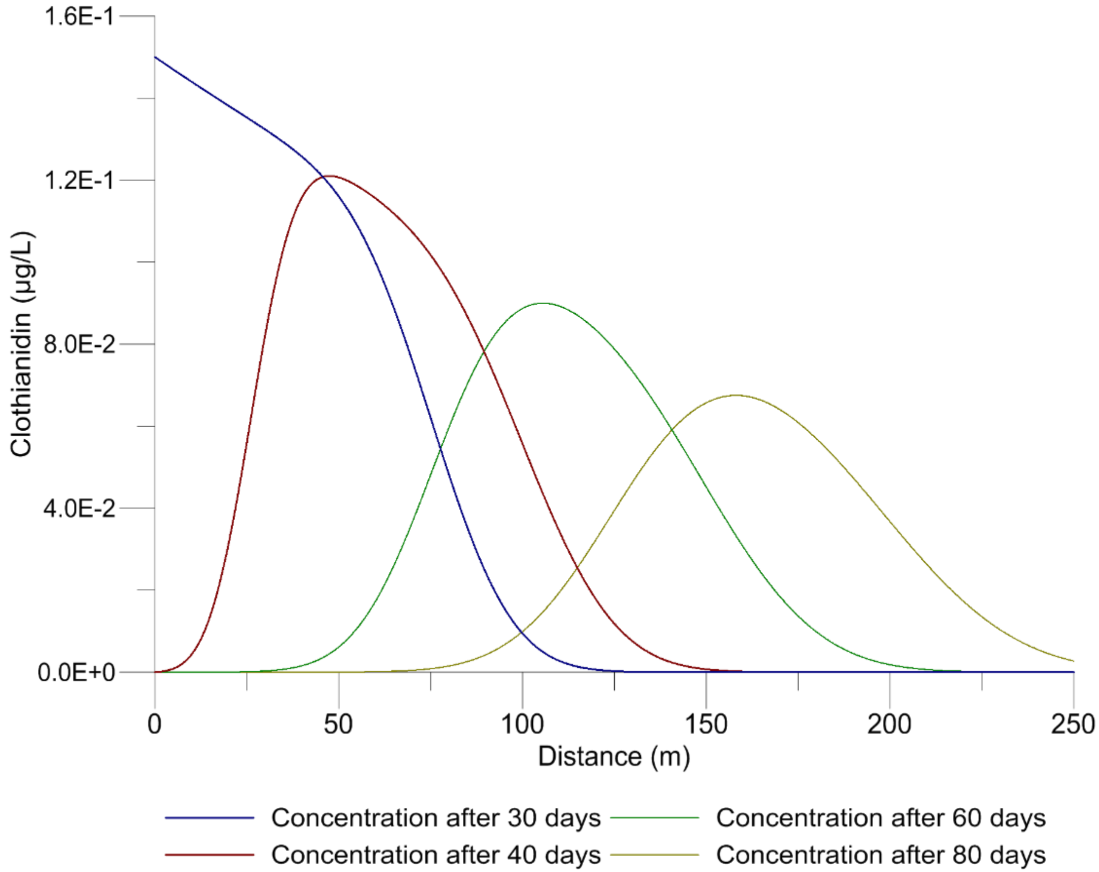
Šimůnek et al. (2013)
Ogata and Banks (1961)
Van Genuchten (1981)

Lanark County (TW17) mathematical modelling

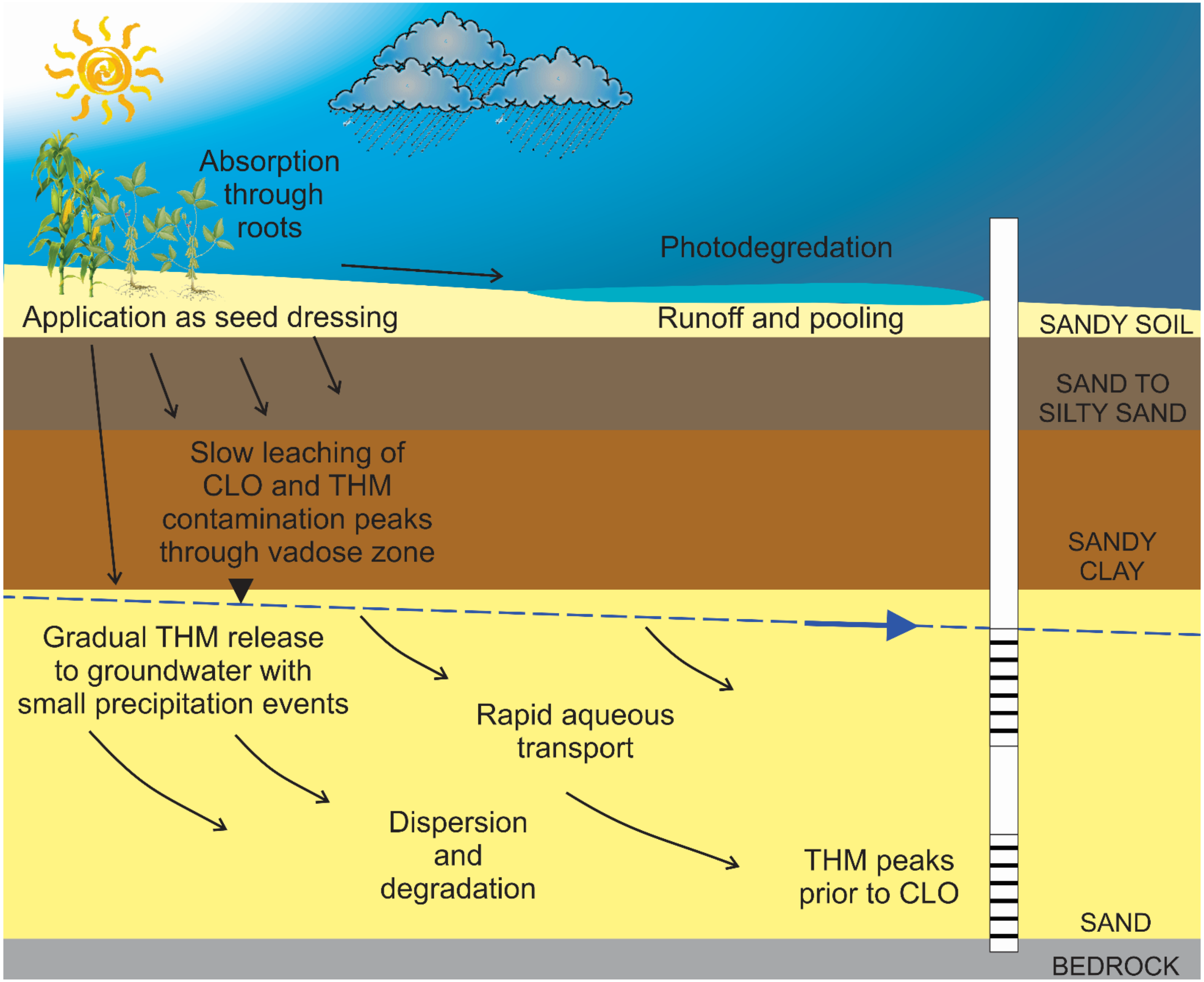


Šimůnek et al. (2013)
Sudicky (1988)

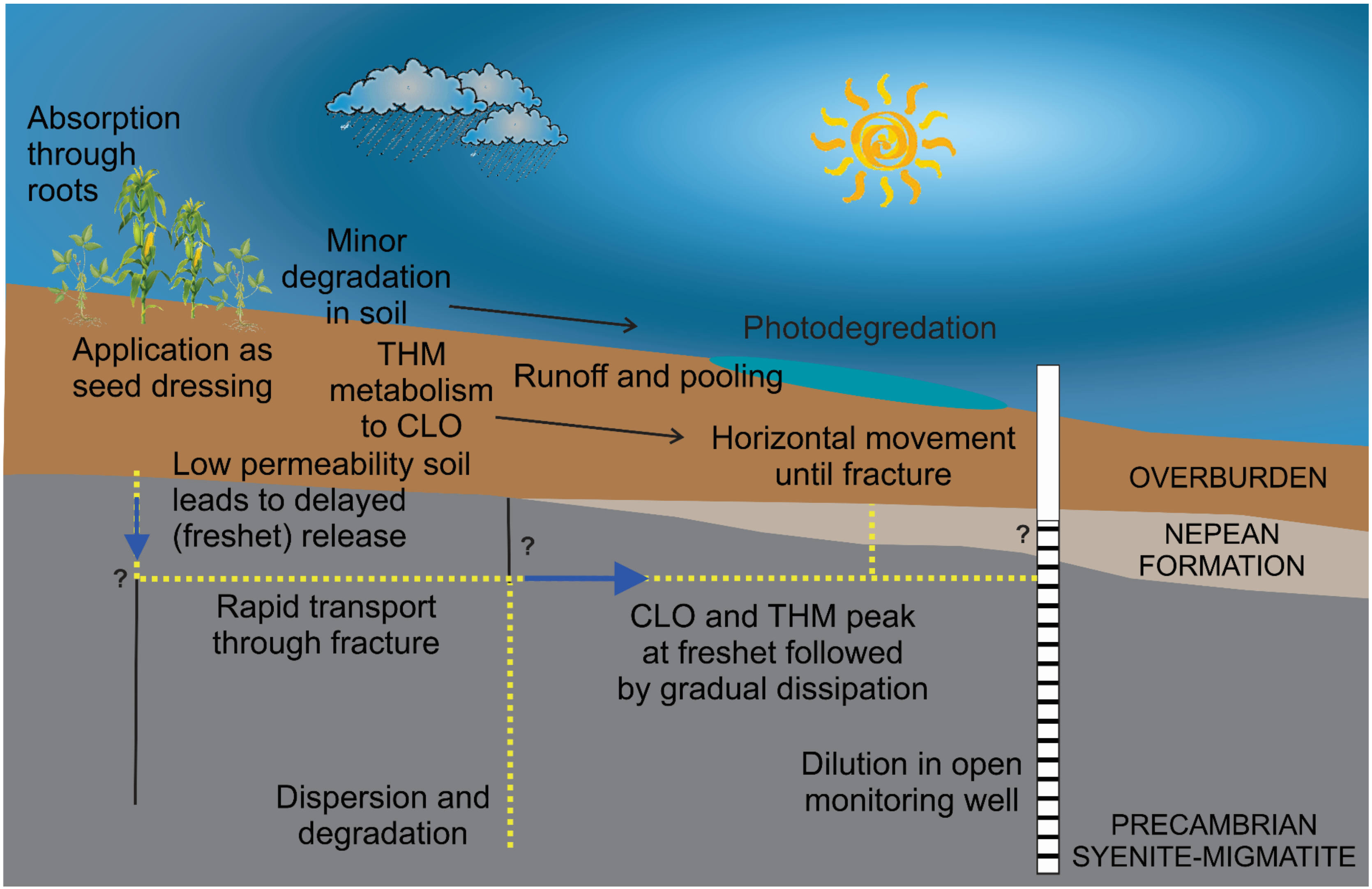
Transport through saturated subsurface in Norfolk County



Norfolk County (LP2) conceptual diagram



Lanark County (TW17) conceptual diagram



Recommendations

- Further research into how neonics move in groundwater within different climatic settings and hydrogeologic settings is recommended
  - Could also analyze effects of crop rotations on neonic movement
- Further research to analyze the movement of acetamiprid, dinotefuran, nitenpyram, and thiacloprid to groundwater
- Future focus on the presence and fate insecticides that will be used in lieu of neonics

Acknowledgements

Dr. Beth Parker, UofG

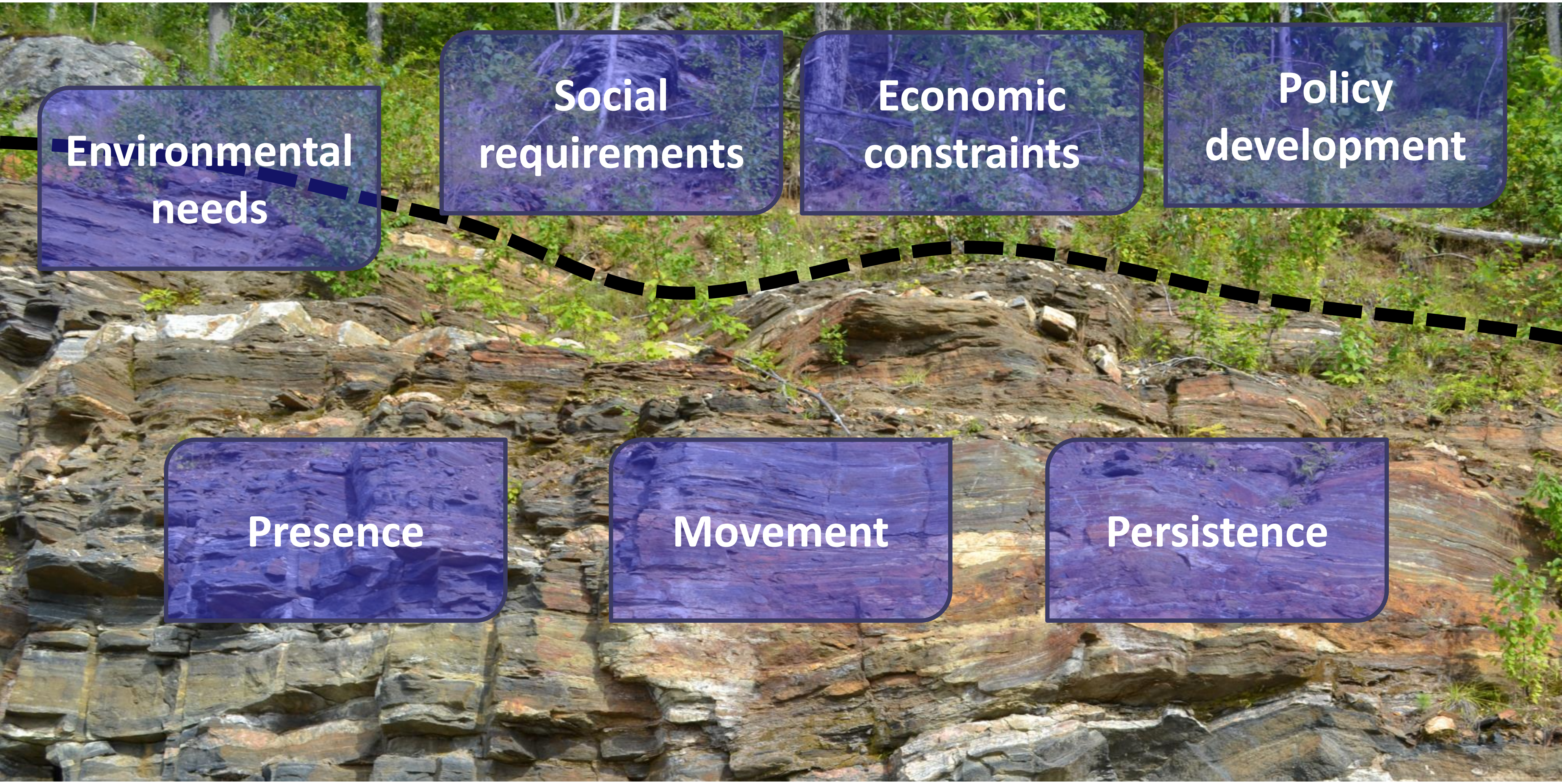
Dr. Kent Novakowski, Queen's
Dr. Victor Limay-Rios, UofG
Dr. Art Schaafsma, UofG

Numerous graduate and summer students!


Merci!
jlevison@uoguelph.ca
www.uoguelph.ca/engineering/jlevison/home

Extra slides

How do our activities impact water quality & how can we mitigate them?

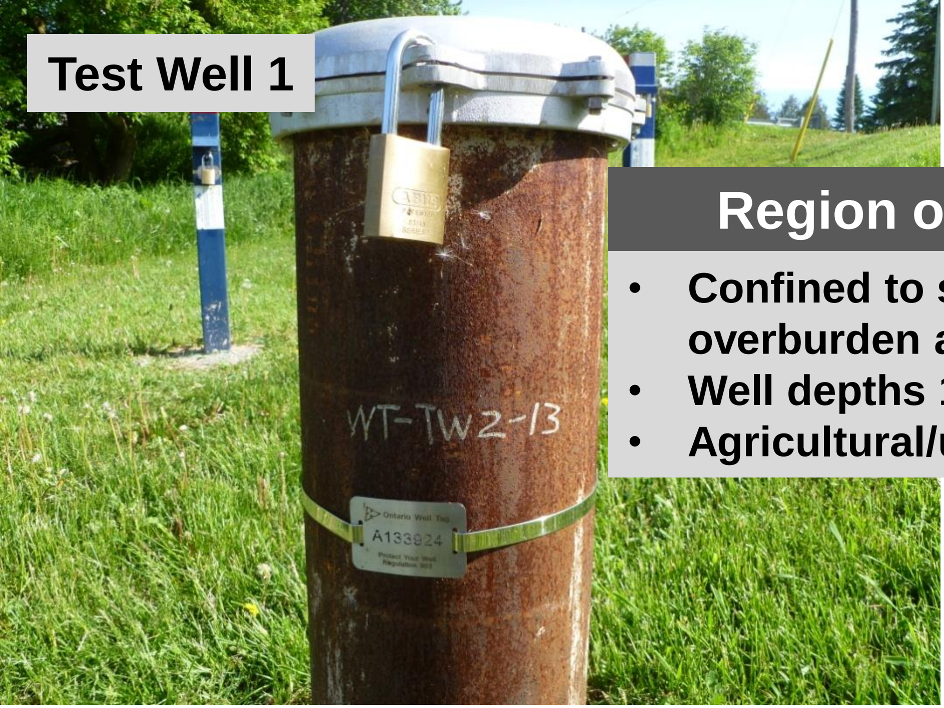


Long Point Tier 3

- Unconfined and confined overburden aquifers
- Well depths 10-40 m BGS
- Agricultural land use
- 9 monitoring wells

Port Rowan

- Unconfined overburden aquifer
- Well depths 10-15 m BGS
- Forested land use
- 4 production wells, 9 monitoring wells



Test Well 1


Test Well 2

Region of Waterloo

- Confined to semi-confined overburden aquifer
- Well depths 15-35m BGS
- Agricultural/urban land use

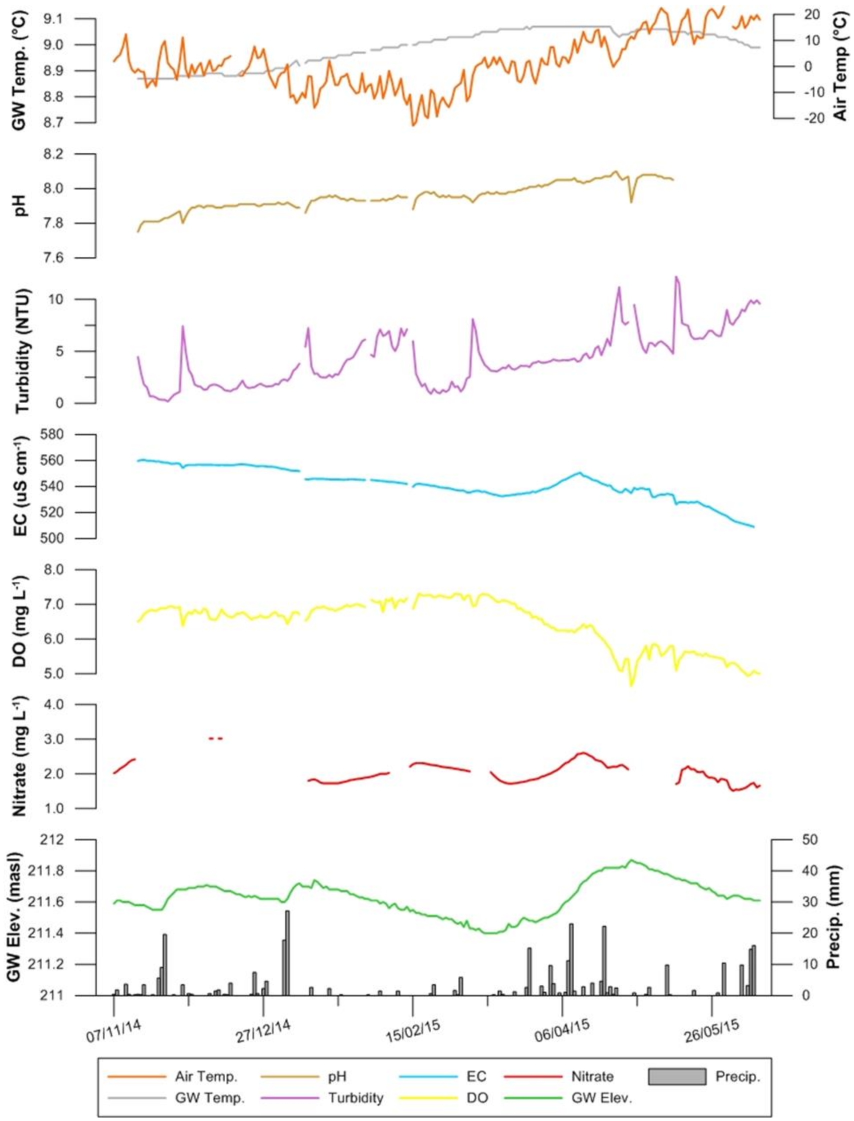

Stone Well


BAFF

Guelph Area

- Shallow to deep confined bedrock aquifers
- Well depths 20-75m BGS
- Golf course/natural land use

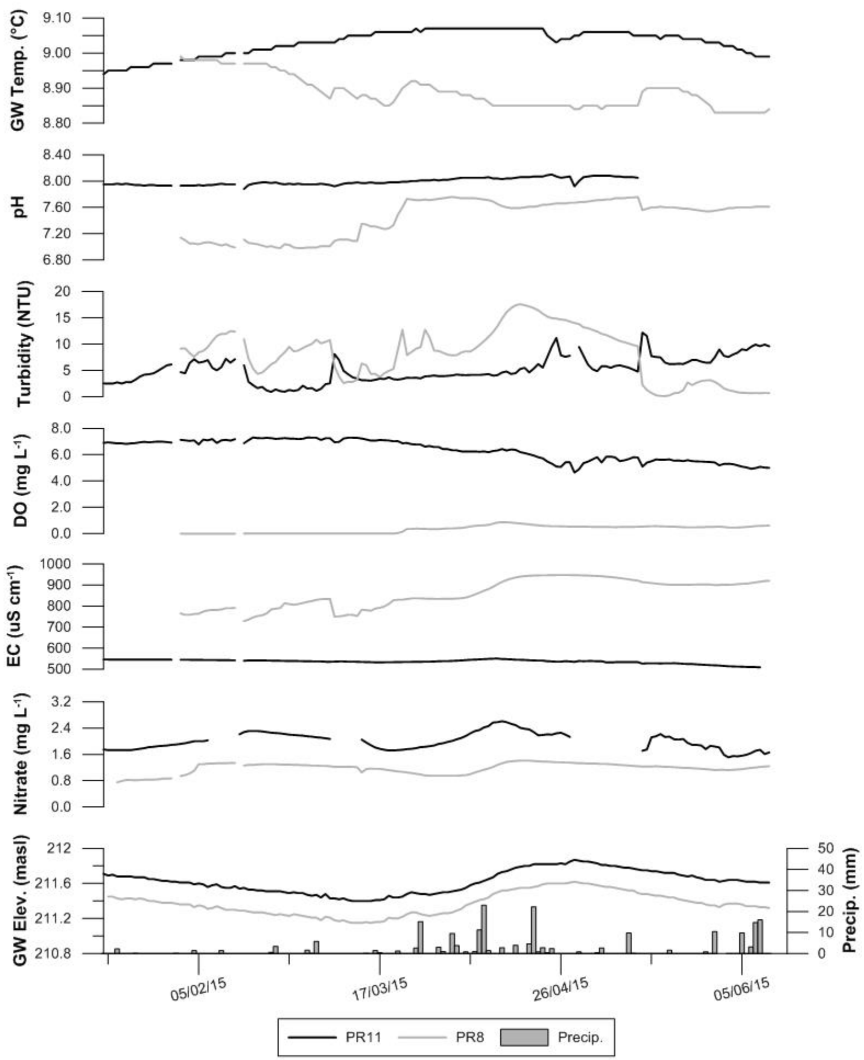
Results: real-time remote monitoring



PR11

- Noticeable increases in turbidity, EC, nitrate with spring recharge (Mar 9-)
- Decrease in DO with spring recharge
- Turbidity pulses after fall and spring recharge events (Nov 24, Jan 3/4)
- No noticeable responses in pH or temperature

Results: real-time remote monitoring



PR11 and PR8

- Similar responses in turbidity, nitrate between PR11 and PR8
- Groundwater levels appear to be strongly connected
- EC, DO, pH difficult to interpret because of scale
- How can we evaluate spatial/temporal relationships between variables?

Recommendations

1. Conduct flow cell testing at a municipal supply well
2. Monitor nitrate concentrations during a pumping test to evaluate effects of pumping on transport
3. Extend length of RTRM (i.e. multi-year) to evaluate seasonal behaviour
4. Expand profiling and RTRM testing to include more bedrock boreholes
5. Compare results from vertical profiling with multilevel sampling from same borehole
6. Isolate sensors for RTRM using packer equipment or FLUTe liners (if possible)

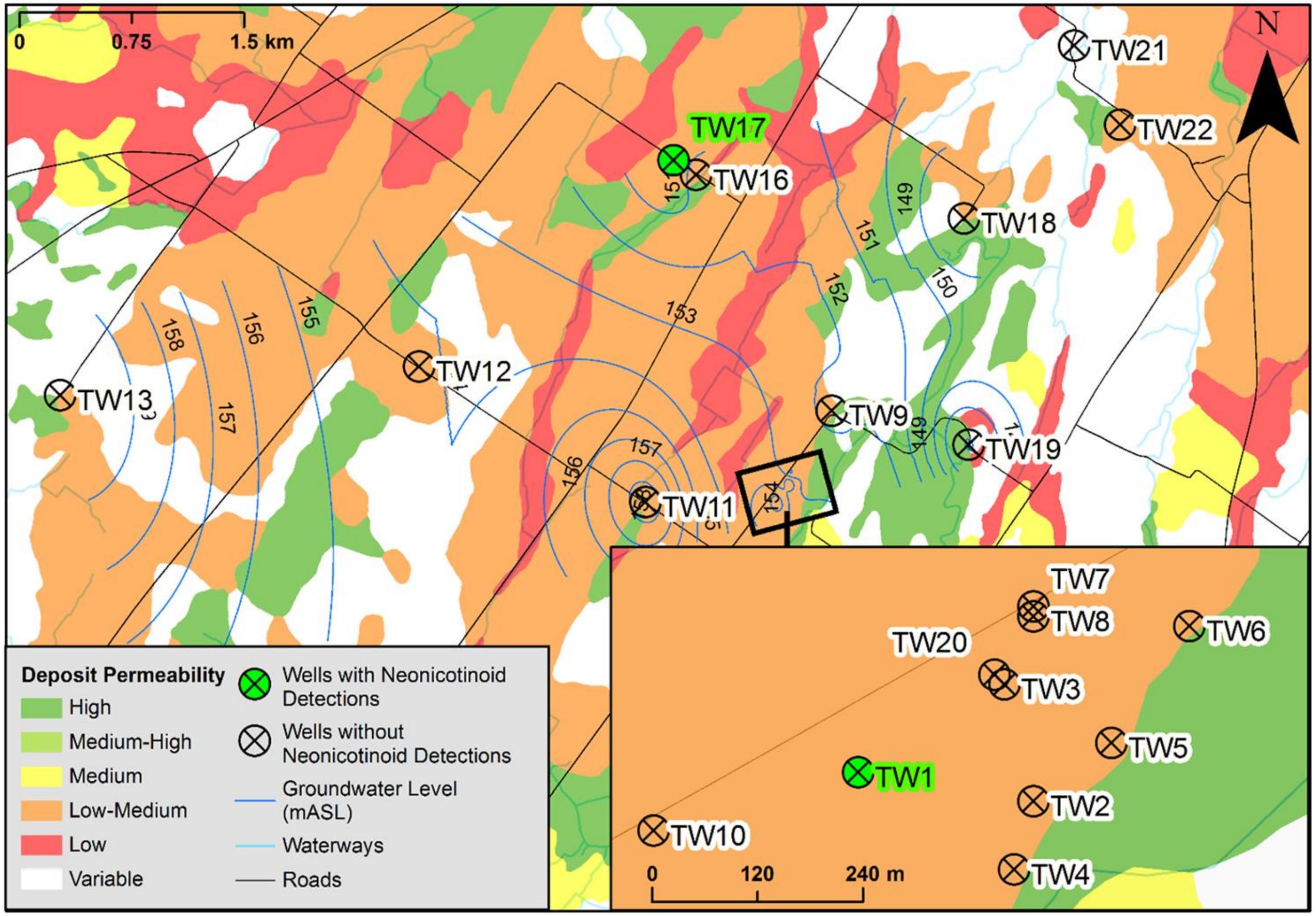
Past Studies

- Half-life in soil is sensitive to soil type, exposure to sunlight, moisture, temperature, pH, and cropping practice[2]
- Correlates positively with silty soil and negatively with sandy soil[1]
- Frequently detected in runoff from agricultural fields[1]
- Highly photodegradable in water[3,4,5]

Neonicotinoid	Soil Degradation Half-Life (d) [3,4,5]	*Log* K_{OC} [3,4,5]	Solubility in Water at 20°C at pH 7 (mg/L) [3,4,5]	Aqueous Photolysis Half-Life at pH 7 (d) [3,4,5]	Aqueous Dissipation Half-Life (d) [3,4,5]
Clothianidin	545	2.1	340 (moderate)	0.1	40.3
Imidacloprid	191	2.1-2.5	610 (high)	0.2	30
Thiamethoxam	50	1.8	4100 (high)	2.7	30.6

[1] Schaafsma et al. (2015)
[2] Browne et al. (2017)
[3] Bonmatin et al. (2015)
[3] Hladik et al. (2014)
[4] Morrissey et al. (2015)

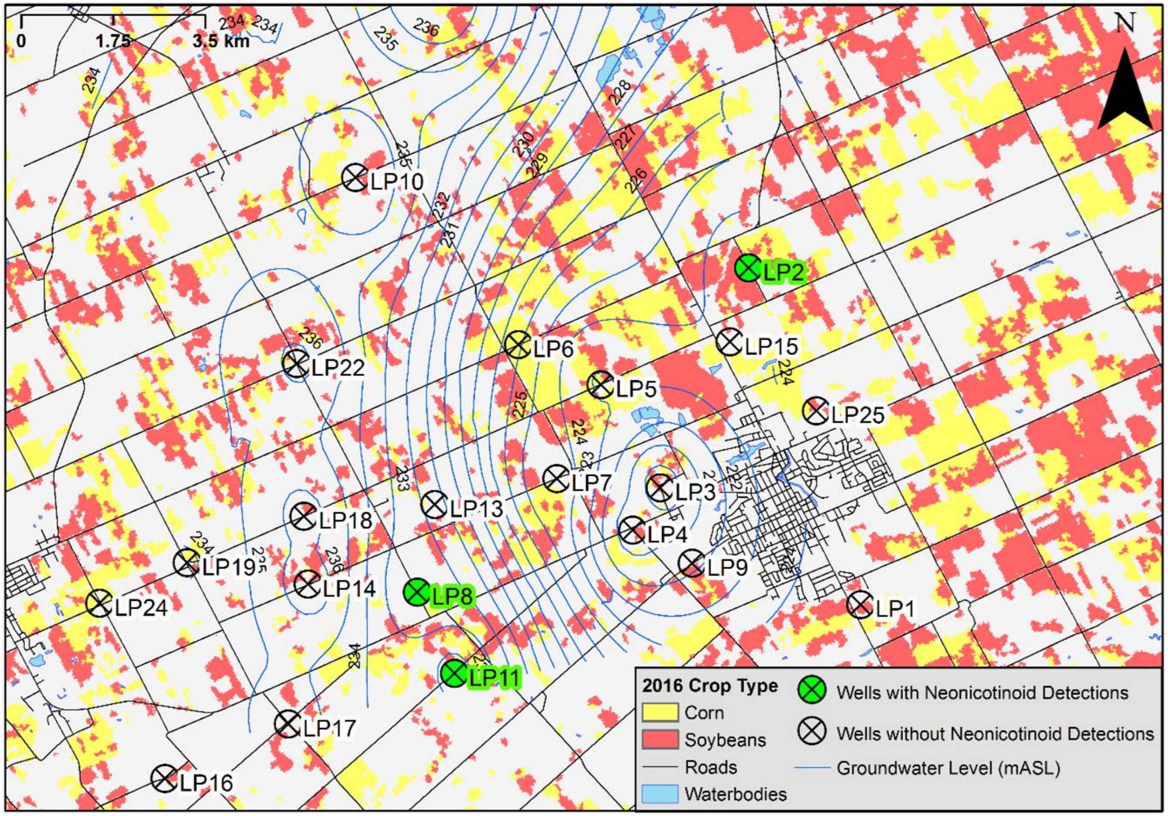
Lanark County Deposit Permeability



Permeability map obtained from Ontario Geological Survey (2010)

Norfolk County crop map

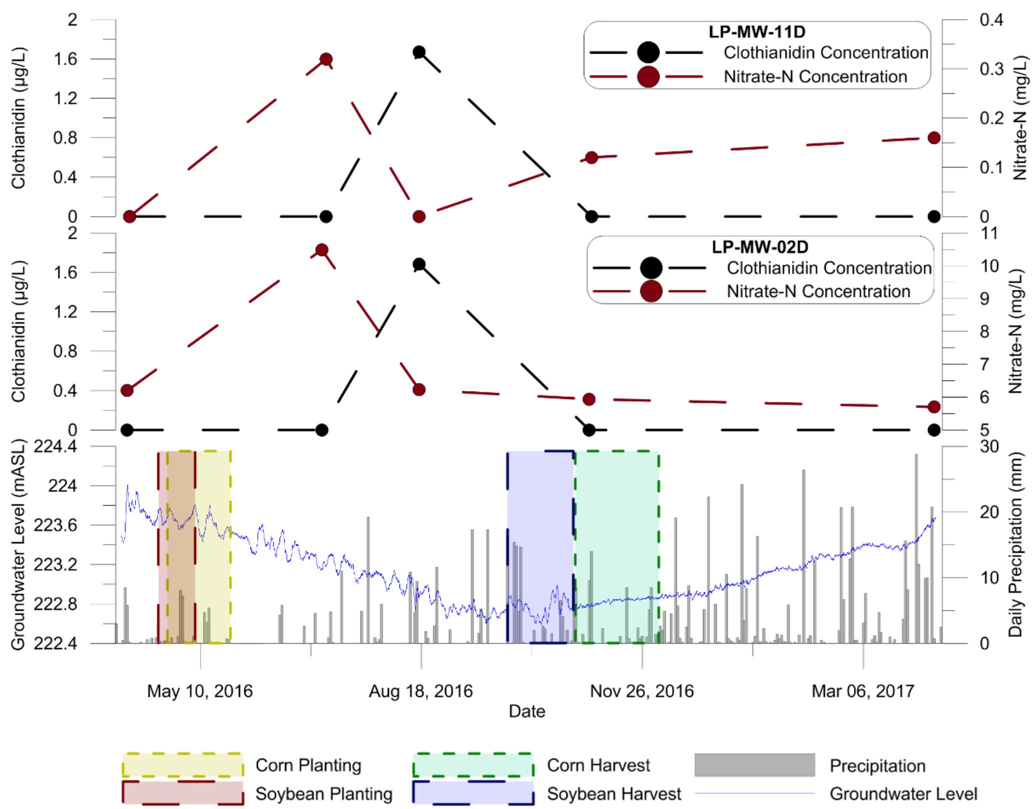
Neonicotinoid	Soil Degradation Half-Life (d)[1,2,3]	Solubility in water at 20°C at pH 7 (mg/L)[1,2,,3]	Aqueous Dissipation Half-Life (d) [1,2,,3]
Clothianidin	545	340 (moderate)	40.3
Thiamethoxam	50	4100 (high)	30.6



[1] Bonmatin et al. (2015)
[2] Hladik et al. (2014)
[3] Morrissey et al. (2015)
Crop map obtained from Agriculture and Agri-Food Canada (2017)

Clothianidin and nitrate in Norfolk County

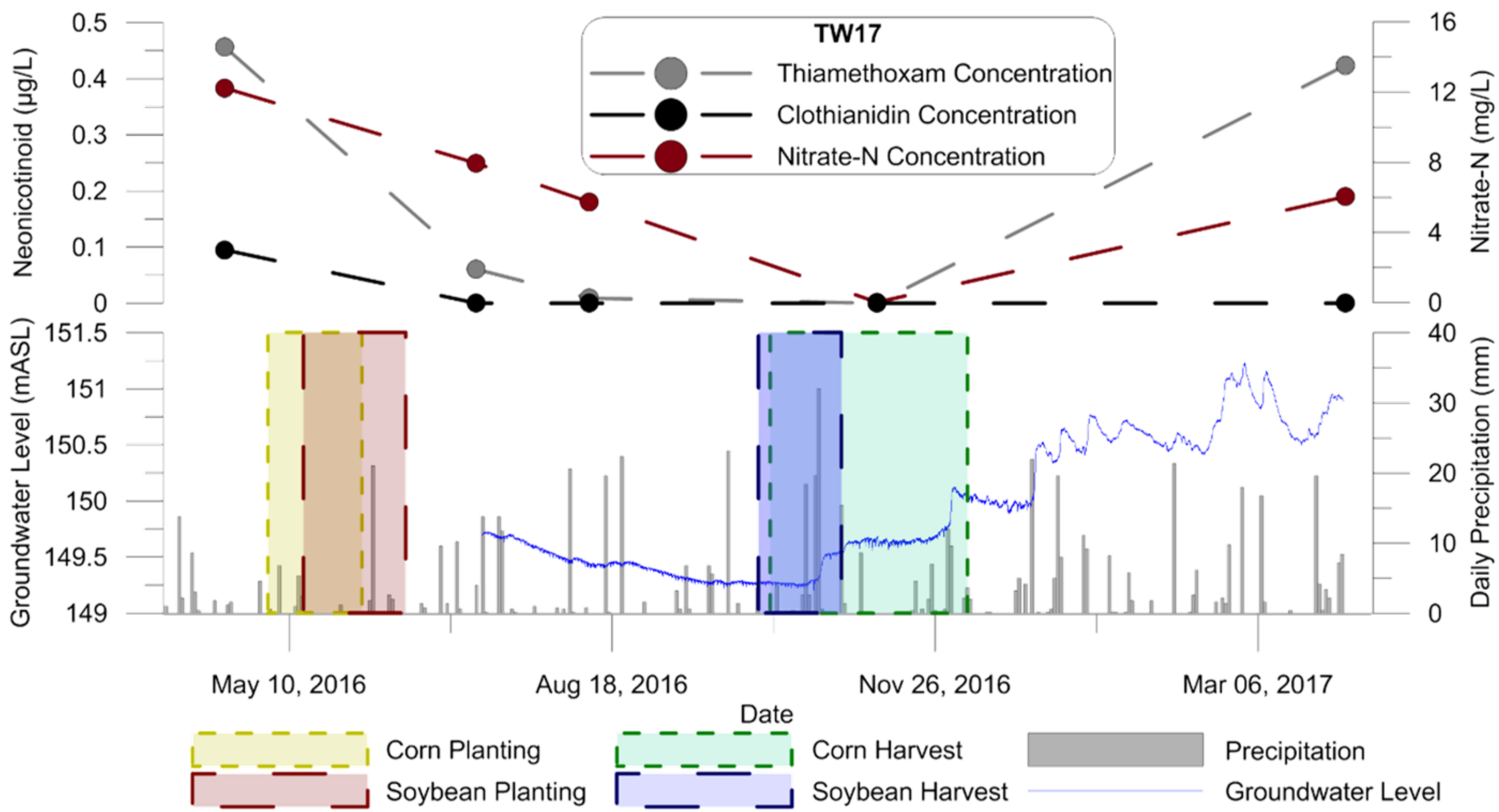
Property	Clothianidin[1,2,3]	Nitrate[4]
Log K_{OC}	2.1	1.16
Solubility in water at 20°C at pH 7 (mg/L)	340 (moderate)	90900 (high)



[1] Bonmatin et al. (2015)
[2] Hladik et al. (2014)
[3] Morrissey et al. (2015
[4] Royal Society of Chemistry (2015)

Thiamethoxam and nitrate in Lanark County

Property	Thiamethoxam[1,2,3]	Nitrate[4]
Log K_{OC}	1.8	1.16
Solubility in water at 20°C at pH 7 (mg/L)	4100 (high)	90900 (high)



[1] Bonmatin et al. (2015)
[2] Hladik et al. (2014)
[3] Morrissey et al. (2015
[4] Royal Society of Chemistry (2015)

Vadose Zone Numerical Modelling

- Hydrus 1D[1]

$$\frac{\delta\theta}{\delta t} = \frac{\delta}{\delta z}\left(k\left(\frac{\delta h}{\delta z} - 1\right)\right) - S$$

  - Advection-dispersion equations for solute transport
- Uses:
  - 1D movement of water, heat, and solutes
  - Variably-saturated media

[1] Šimůnek et al. (2013)

Saturated Zone Analytical Modelling

- Ogata-Banks Solution[1,2]

$$C(x,t) = \frac{1}{2}C_o\left[erfc\left(\frac{x-\frac{v}{R}t}{\sqrt{4\frac{D}{R}t}}\right)+e^{v\frac{x}{D}} * erfc\left(\frac{x-\frac{v}{R}t}{\sqrt{4\frac{D}{R}t}}\right)\right]$$

- Uses:
  - Water and solute movement in variably-saturated porous media

[1] Ogata and Banks (1961)
[2] Van Genuchten (1981)

Fracture Transport Analytical Model

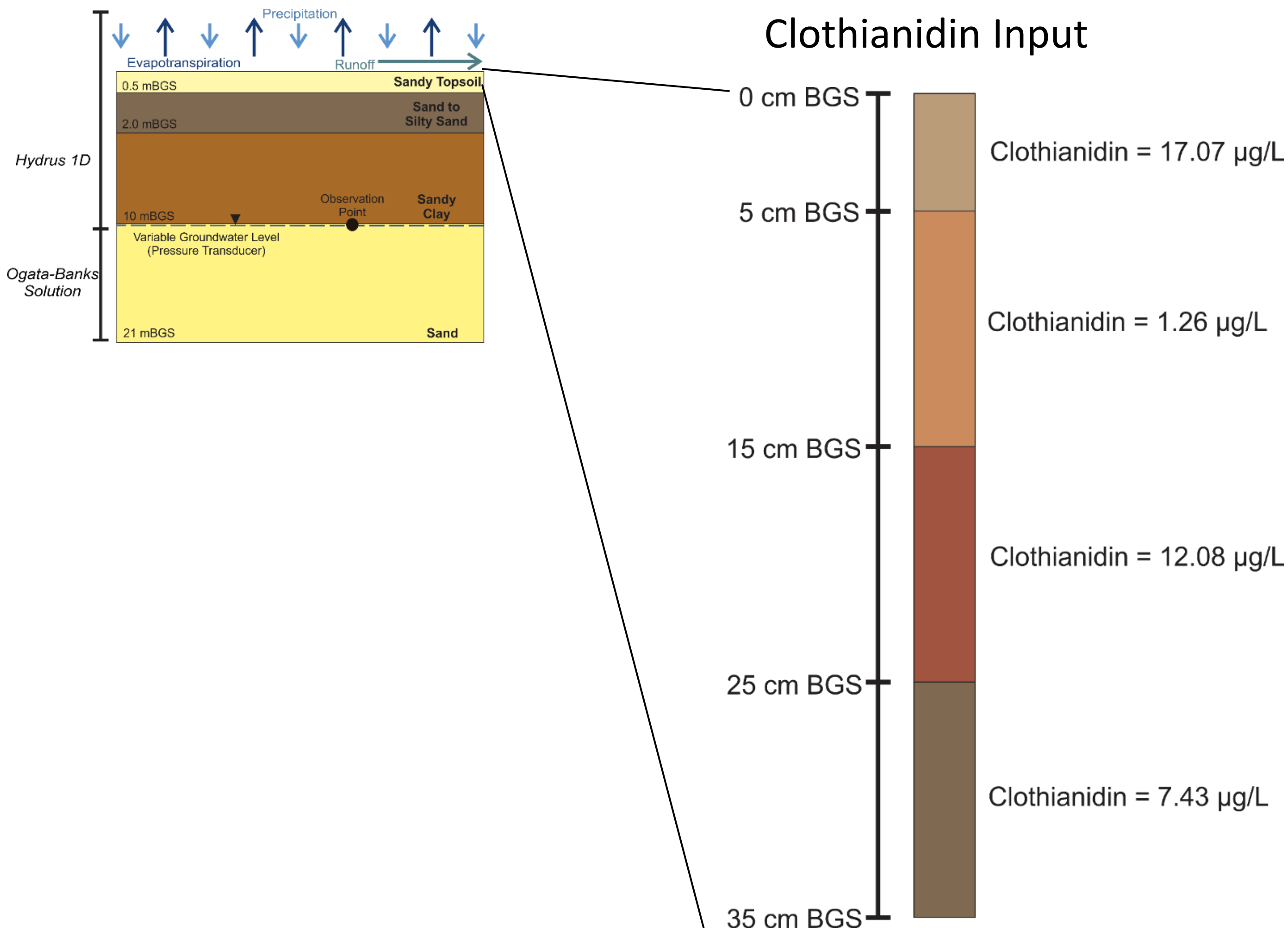
- Analytical Solution for One-Dimensional Advection with Matrix Diffusion[1]

$$C(x,t) = \frac{1}{2} C_o \left[e^{-\frac{\lambda R x}{v}} \right] \left[\begin{array}{c} e^{\left(-\frac{\sqrt{\lambda} R x}{v A}\right)} erfc\left(\frac{x}{2vAT'} - \sqrt{\lambda} T'\right) \\ + e^{\left(-\frac{\sqrt{\lambda} R x}{v A}\right)} erfc\left(\frac{x}{2vAT'} + \sqrt{\lambda} T'\right) \end{array} \right]$$

- Uses:
  - Water and solute movement through a fracture network

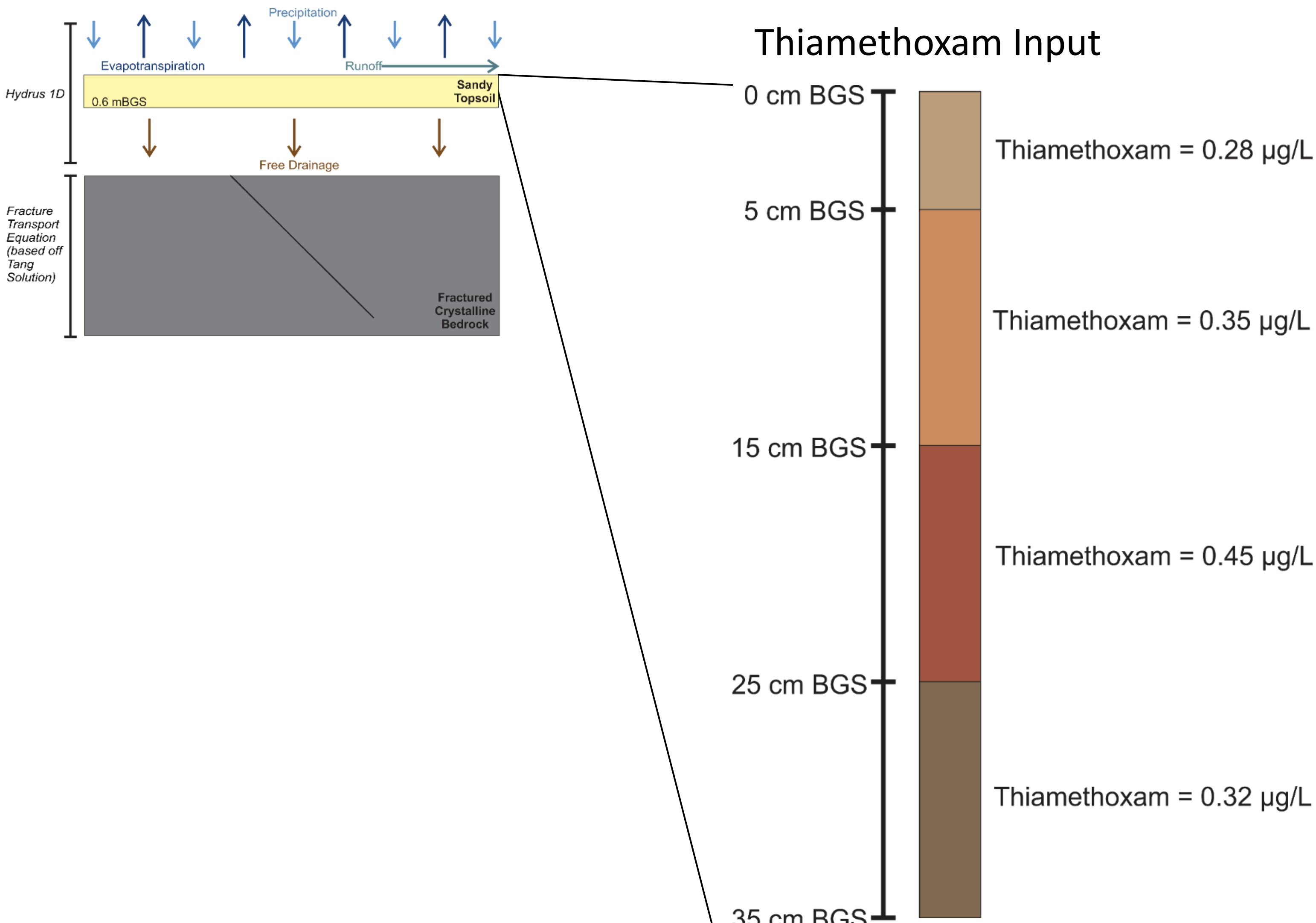
[1] Sudicky (1988)

Norfolk County (LP2) Mathematical Modelling



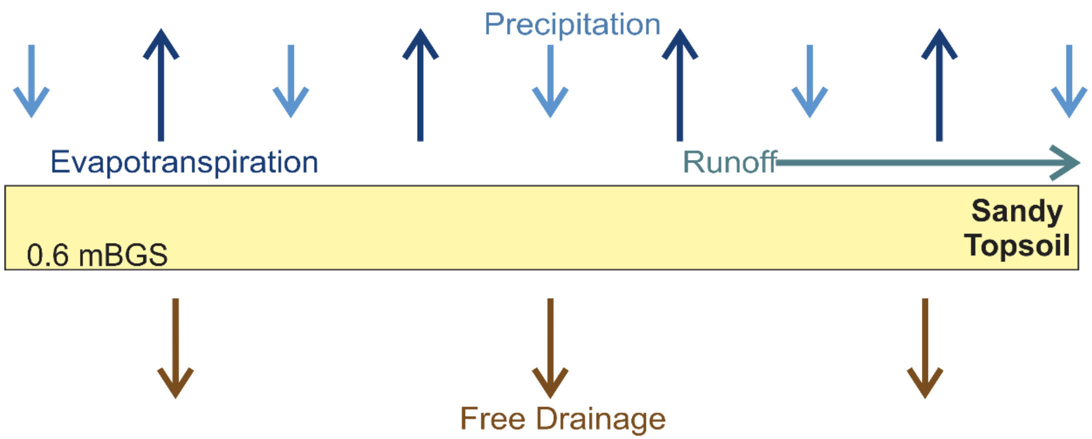
Forero et al. (2017)

Lanark County (TW17) Mathematical Modelling



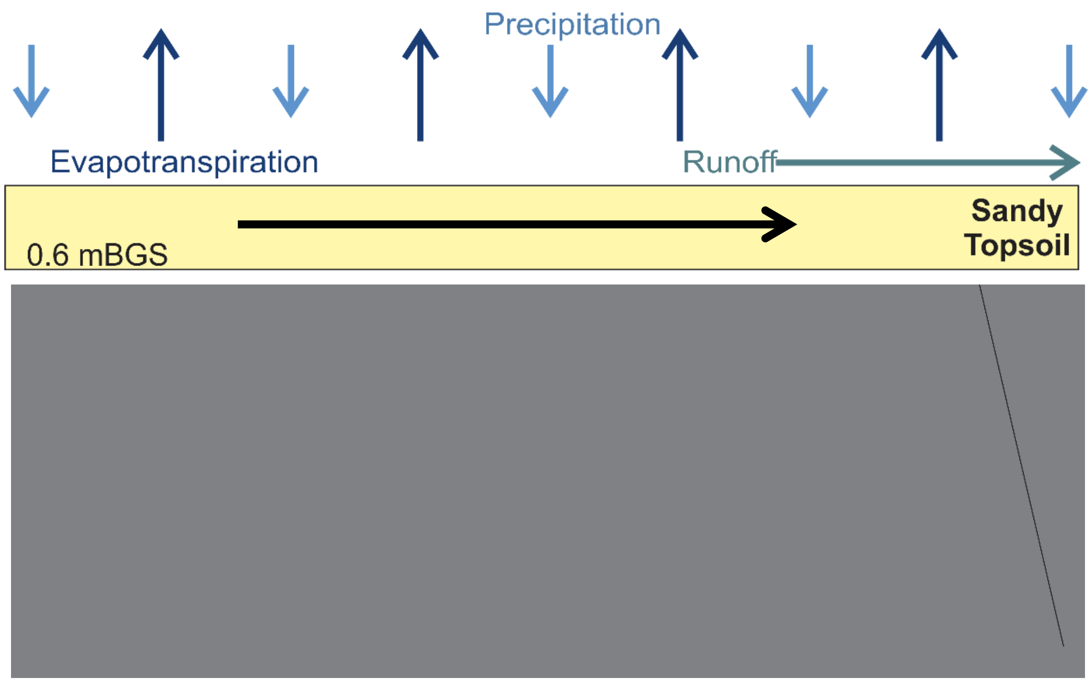
Forero et al. (2017)

Mathematical Modelling



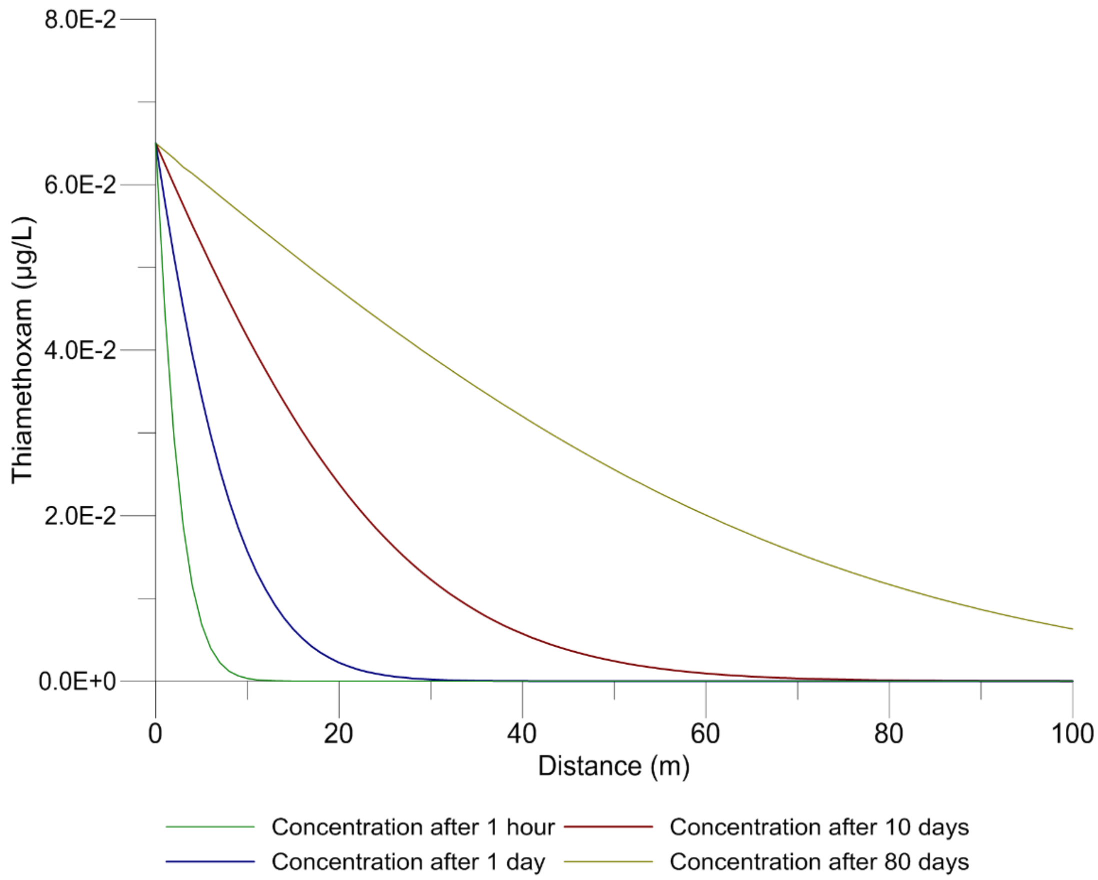
Šimůnek et al. (2013)
Sudicky (1988)

Mathematical Modelling



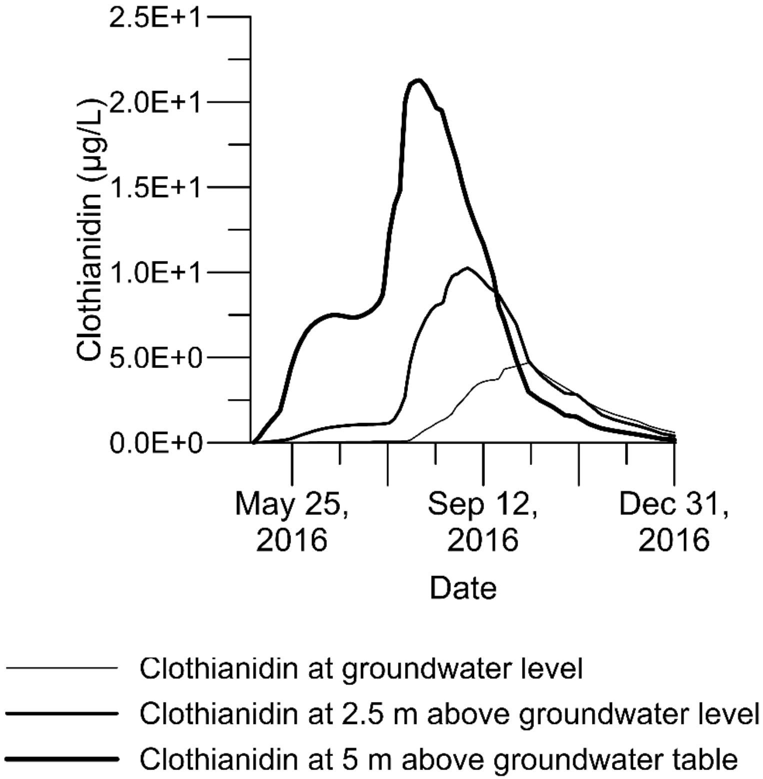
Šimůnek et al. (2013)
Sudicky (1988)

Transport through Fracture Network in Lanark County

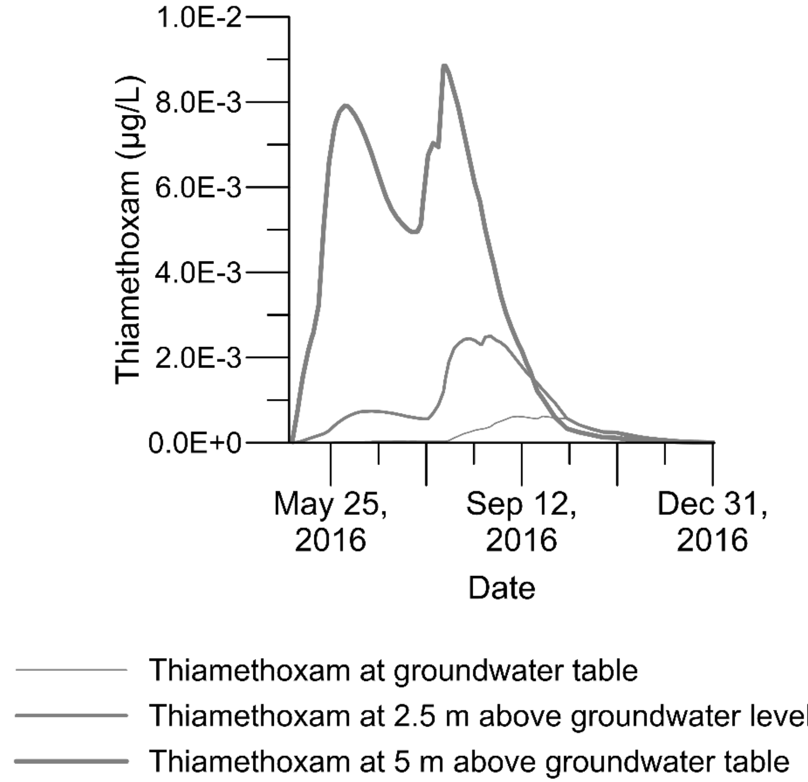


Mathematical Modelling

LP-MW-02 (Norfolk County)

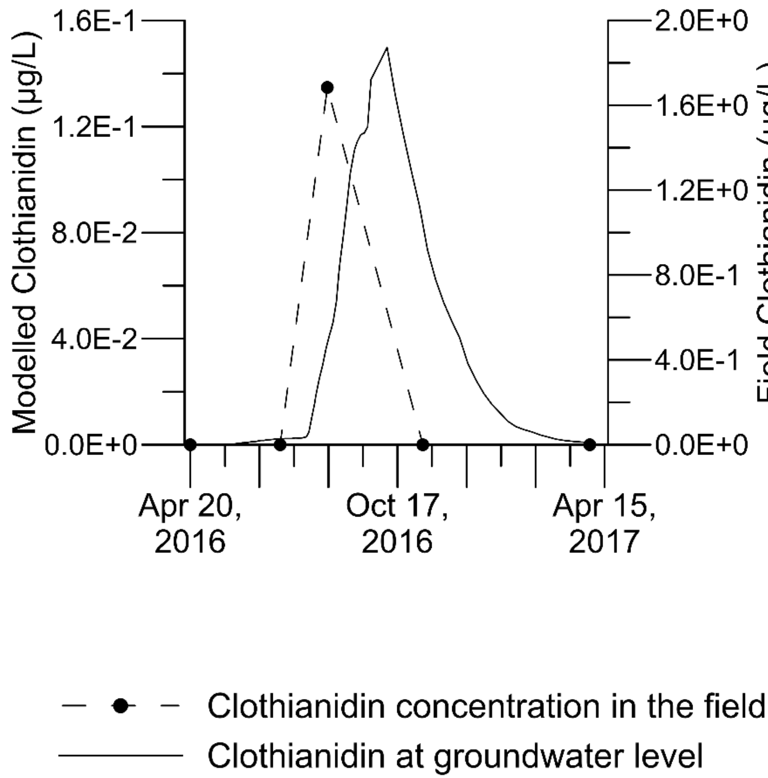


LP-MW-02 (Norfolk County)

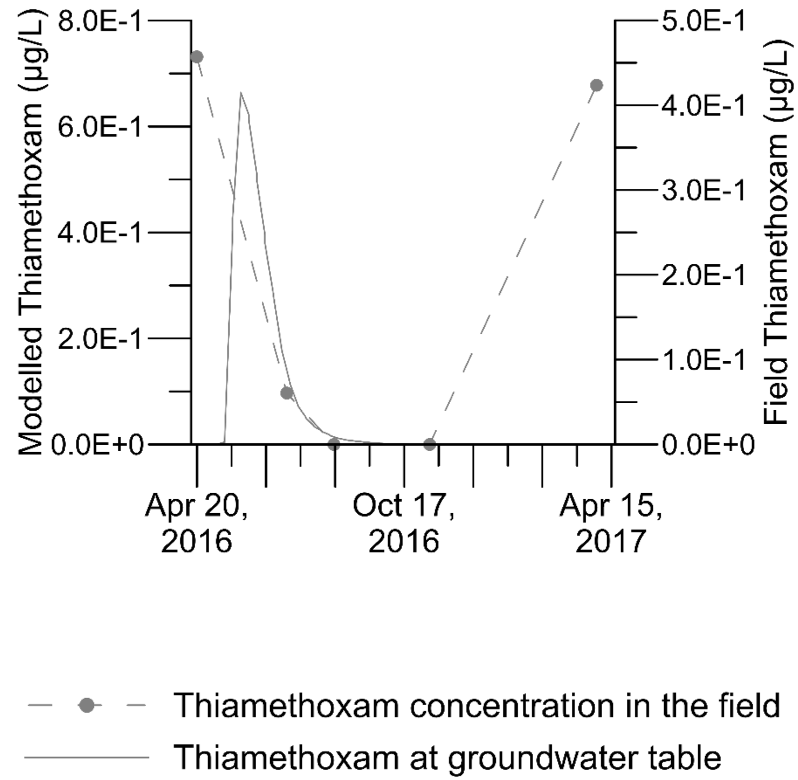


Mathematical Modelling

LP-MW-02 (Norfolk County)



TW17 (Lanark County)



Effects on Vulnerable Species

Neonicotinoid	Toxicological Endpoint	Honeybees (µg a.i./bee)	Bumblebees (µg a.i./bee)	Solitary Bees (µg a.i./bee)	Aquatic Invertebrates (mg/L)
Clothianidin	Acute	3.79×10^{-3}	1.91×10^{-3}	3.79×10^{-4}	> 40
	Chronic	1.38×10^{-3}	1.38×10^{-4}	1.38×10^{-4}	0.12
	Maximum Exposure		2.30×10^{-5}		2.09×10^{-3}
Imidacloprid	Acute	3.79×10^{-3}	3.8×10^{-2}	3.7×10^{-4}	85
	Chronic	$> 2.82 \times 10^{-3}$	$> 2.82 \times 10^{-4}$	$> 2.82 \times 10^{-4}$	1.8
	Maximum Exposure		7.70×10^{-7}		0.07×10^{-3}
Thiamethoxam	Acute	5.0×10^{-3}	5.0×10^{-3}	5.0×10^{-4}	> 100
	Chronic	N/A	N/A	N/A	> 100
	Maximum Exposure		5.06×10^{-6}		0.46×10^{-3}

European Food Safety Authority (2016a, 2016b, 2015)
Pesticide Properties Database (2017)