

International Association of Hydrogeologists (IAH/AIH)



### Stable Isotopes and Hydrogeology in Ireland

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December 4<sup>th</sup> 2018

### Outline

- 1. Stable isotope hydrology and "isoscapes"
- 2. Pathogens and subsurface transport
- 3. O<sup>18</sup> isoscape for Ireland and geospatial drivers
- 4. Pathogen ingress mechanisms
- 5. Work to complete and direction

- Same atomic number but different atomic weight due to varying numbers of neutrons in nucleus
- Stable isotopes not involved in any natural radioactive decay process
- Naturally occurring

Used to study geologic processes that affect ground and surface water





- Fractionate into light and heavy fractions
- Mainly due to evaporation or heating



 One isotope much more common than other (large difference in mass)





- Global meteoric water line
- Ocean water falls below line isotopically enriched
- Deviations from MWL changes in precipitation in warmer or colder climate or geochemical (geothermal water)

**Composition affected only by physical processes** 

**Temperature dependence – history** 





Matiatos and Wassenaar (2018, JoH)

### "Isoscapes"

- Describes large-scale spatiotemporal stable isotope distributions within natural environments
- Investigates the hydrological connectivity between water resource and hydro-climatic sources
- Large scale mapping of the stable isotopic composition of phreatic aquifers are used as a proxy for revealing recharge zones to enable sustainable management of water resources



http://wateriso.utah.edu/waterisotopes

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http://wateriso.utah.edu/waterisotopes

- First temporal O<sup>18</sup> and D groundwater isoscapes for Ireland
- Sampled EPA groundwater monitoring network (> 290 sites) – 2 periods (plus 2013 study)
- Plus domestic well study areas utilised in on-going pathogen studies



- Insufficient spatial coverage for isotopes in precipitation hinders investigations of relationship between ground water and precipitation
- Need information to help quantify aquifer replenishment rates
- Installed rain collector gauges



Global distribution of oxygen-18 (per mil, ‰) in precipitation produced by interpolation of longterm annual means from about 700 GNIP stations.

http://wwwnaweb.iaea.org/napc/i h/documents/other/G NIP%20brochure.pdf

www.iaea.org

#### IAEA GNIP Network - Valencia

Armagh



### IAEA Helps Brazil Strengthen Isotope Monitoring of Precipitation

Aleksandra Peeva, IAEA Department of Nuclear Sciences and Applications



www.iaea.org



The CPRM team after the set-up of the Recife Isotope monitoring station. This rainfall totalizer will be used to collect samples, whose isotopic signature will provide valuable additional data for the Global Network of Isotopes in Precipitation (GNIP). (Photo: R. Kirchheim/CPRM)

#### **Related Stories**



How Climate Change Affects Water Resources in Costa Rica



New Findings Unlock Climate Change Information Stored in Rain Samples

#### Related Resources

% Water

% Precipitation

- Climate Change: Making a Difference Through Nuclear Technologies, IAEA Bulletin (Vol. 56/2, June 2015)
- Global Network of Isotopes in Precipitation (GNIP)
- % Isotope Hydrology Section

Interpreting changes in isotope ratios in precipitation allows scientists to determine changes in rainfall patterns and learn where, when and how groundwater is recharged. Rainfall patterns and their relationship with groundwater recharge is essential for understanding the impact of climate change on water availability (see Isotope hydrology).

- P/GW ratios
- Used to identify dominant groundwater recharge processes
- E.g. rapid recharge/ preferential flow versus slower soil matrix processes



Sanchez et al (2016, GRL)

- Groundwater isoscapes driven by precipitation shallow groundwater typically considered to represent annual precipitation
- Shallow regional groundwater indicator for long-term seasonally weighted precipitation inputs
- Can hydrogeological factors also effect concentration?
- Ground water systems can differ from mean annual precipitation due to seasonally biased recharge, infiltration evaporative processes, event-driven recharge, or by mixing with older ground water (Jasechko et al., 2014)

- Seasonal monitoring of  $\delta^{18}$ O and  $\delta$ D variations from spatially distributed groundwater and rainfall stations across Ireland
- Aims: i) improve the understanding of precipitation origin, evaporative effects and estimated recharge rates, and ii) use results to conservatively trace bacterial (*E. coli*) ingress mechanisms
- Will improve knowledge of recharge mechanisms in the Irish subsurface environment and pilot a novel method for microbial source attribution and transport in the aquatic environment

# **Microbial Subsurface**

# Transport

## **Objectives**

- Investigate the presence/absence of thermo-tolerant coliforms (>90%
  E. coli) with respect to all potential risk factors and develop multivariate "well susceptibility models for Republic of Ireland;
- Develop machine learning models for a very large integrated Ontarian dataset (940,000 groundwater samples);
- Infer subsurface microbial incidence and transport

### Sampling . . . . Lots and lots of sampling



### **Contaminant Source Investigation**



PLAN

### **Aquifer vulnerability**



Topsoil

Subsoil

Bedrock

### **Study Areas**



### **Study Areas**

Study Area	Name	Bedrock	GW Vuln.	Aquifer Type
S.A. 1	Meath	Limestone	Low	LI
S.A. 2	Wicklow	Granite	High	LI/PI
S.A. 3	Kilkenny	Sandstone Shale Limestone	Extreme	PI
S.A. 4	Westmeath	Limestone	High	LI
S.A. 5	Offaly	Limestone Sandstone	High	Ll/Lm

### **Risk Factor Analysis – Vulnerability**

- E. coli presence variable among study areas
  - *High/Extreme* Vuln 11% (SA3) to 44 % (SA5)
  - *Low* Vuln 45% (SA1)

Lower than expected *E. coli* presence within *High/Extreme* vulnerability areas, while higher than expected within *Low* vulnerability area ( $\chi^2 = 10.686$ , p = 0.03)

### **Risk Factor Analysis - Precipitation**



- 14/15 private wells positive for *E. coli* during monthly sampling
- Increased presence & magnitude
- during late summer & early winter
- 42.5% *Low* Vuln
  - 32% *High/*Ex Vuln
  - Correlation between 120h precip and
    *E. coli* (r = 0.785)

### **Hierarchical Logistic Regression**

- 11 models in total
- Classification Cutoff point = 0.5
- Susceptibility models were developed to 90% predictive accuracy
- Will present Low and High Vuln. Models



### Low Vulnerability LR Model

- Significant hierarchies included:
  - Well Design Parameters 52.8%
  - Septic Tank Proximity 24.2%
  - Antecedent Precipitation 13.2%
  - Agricultural Landuse 9.5%

<u>Well Design Parameters</u> – Liner Clearance & Liner Cap

Antecedent Precipitation – 48-hour & 120-hour

### Low Vulnerability LR Model

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### WHAT'S MISSING?

#### **HYDROGEOLOGY!**

# *High/Extreme* Vulnerability LR Model

- Significant hierarchies included:
  - Hydrogeological Setting 33.1%
  - Well Design Parameters 29.8%
  - Septic Tank Proximity 22.1%
  - Antecedent Precipitation 13%

<u>Well Design Parameters</u> – Liner Clearance ; Wellhead Cover; 10m Wellhead Radius Condition

<u>Antecedent Precipitation – 30-day</u>

# *High/Extreme* Vulnerability LR Model

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<u>Antecedent Precipitation – 30-day</u>

### **Vulnerability Model Comparison**

*Low* Vulnerability

- Local hydrogeology not found to be significant
- Well design highly significant (52.8%)
- Septic tank proximity significant (24.2%)
- Short-term precipitation significant (13.2%)
- Agriculture significant (9.5%)

High/Extreme Vulnerability

- Local hydrogeology significant (33.1%)
- Well design significant (29.8%)
- Septic tank proximity significant (22.1%)
- Medium-term precipitation significant (13%)
- Agriculture not found to be significant

### Vulnerability – Recharge – Runoff – Precipitation -Susceptibility

Subsoil Recharge Runoff Aquifer vulnerability Permeability Thickness Extreme High 1-3 m High Low < High High >3 m Low Moderate 1–3 m High Low Extreme 3-10 m Intermediate Intermediate High >10 m Intermediate Intermediate Moderate 1–3 m Intermediate Intermediate Low Extreme 3-5 m High High Low High 5–10 m Moderate Low High >10 m Low Low

The link between subsoil permeability, recharge, runoff and vulnerability

Source: Misstear et al.; Hydrogeology Journal (2009) 17: 275-285

## The "Ontario Dataset"



# Public

# Public | Santé Health | publique Ontario | Ontario





# The "WELLness" Project



Assessment

### Water Well Information System

### "Raw" (Unprocessed) Datasets

### Well Testing Information System

### WWIS

- ~720,000 records (2016)
- Well ID
- Source Construction
- Local Hydrogeology
- UTM Coordinates (Source)

Years: 2010-2016 inclusive

WTIS

- ~1,250,000 records
- E. coli and Total Coliforms
- Source Address



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- Years: 2010-2016 inclusive
- ~1,250,000 records
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- Source Address



gdalinfo ~/openev/utm.tif Driver: GTiff/GeoTIFF Size is 512, 512 Coordinate System is: PROJCS["NAD27 / UTM zone 11N", GEOGCS["NAD27", DATUM["North American Datum 1927", SPHEROID["Clarke 1866",6378206.4,294.978698213901]], PRIMEN["Greenwich",0], UNIT["degree",0.0174532925199433]], PROJECTION["Transverse Mercator"], PARAMETER["latitude of origin",0], PARAMETER["central meridian",-117], PARAMETER["scale factor",0.9996], PARAMETER["false easting", 500000], PARAMETER["false northing",0], UNIT["metre",1]] Origin = (440720.000000,3751320.000000) Pixel Size = (60.000000,-60.000000) Corner Coordinates: Upper Left ( 440720.000, 3751320.000) (117d38'28.21"W, 33d54'8.47"N) 440720.000, 3720600.000) (117d38'20.79"W, 33d37'31.04"N) Lower Left ( Upper Right ( 471440.000, 3751320.000) (117d18'32.07"W, 33d54'13.08"N) Lower Right ( 471440.000, 3720600.000) (117d18'28.50"W, 33d37'35.61"N) 456080.000, 3735960.000) (117d28'27.39"W, 33d45'52.46"N) Center

Band 1 Block=512x16 Type=Byte, ColorInterp=Gray



### tidyverse/stringr

Whitespace Tools Patterns Matching Functions

### **Fuzzy Logic Joining/Merging**

Join tables together based not on whether columns match exactly, but whether they are similar by some comparison. Implementations include string (Calculated Haversine) distance and regular expression matching (Address; BR Geology)





Precision

**Boolean Logic** 

Significance

Fuzzy Logic

### **Distance Analysis of Merged Dataset**

M	lin. 🍦	1st Qu.	Median $^{\circ}$	Mean 🔅	3rd Qu.®	Max.	1
6	078e-05	0.0383	0.07531	0.1266	0.158	1	
				0			
	Ω. –						
stance(Km)	0. e						
Dis	4.0 -						
	0.2						
	0.0				1		

Approximately 62,000,000 datapoints!!!

WWIS WTIS 2010 2016 Dataset

- 938 854 testing records from 159 531 unique wells
  1-404 observations/well (averaging 11 observations/well)
- January 2010 December 2016



**Greater Toronto Area** 



● 10-15% Occurrence ● 5-10% Occurrence ● 1-5% Occurrence ● <1% Occurrence



■ 10-15% Occurrence ■ 5-10% Occurrence ■ 1-5% Occurrence ■ <1% Occurrence</p>



### Conclusions

- Developed models seem to work logically as predictive tools;
- Private well susceptibility is a product of a number of factors including; well type, well design and construction, hazard source proximity, geological setting (*High/Extreme* vuln), precipitation and aquifer vulnerability;
- Significance of short-term precipitation (*Low* vuln) suggests rapid by-pass contamination mechanisms and very specific point/zone of ingress;

### Conclusions

- Significance of medium-term antecedent precipitation (High Vuln) suggests slower contamination pathways;
- Significance of hydrogeo setting within High Vuln cohort and source characteristics within total cohort suggests multiple mechanisms;
- Vulnerability/susceptibility/risk probability are extremely fluid concepts and depend on multiple variables and variable interactions
- Contamination mechanisms (well and aquifer) are as unique as the well or aquifer they are associated with.

# O<sup>18</sup> isoscape for Ireland and geospatial drivers

### O<sup>18</sup> Isoscape study

- Uplands Pre Cambrian to Lower Palaeozoic igneous, metamorphic and sedimentary rocks
- West and Midlands Carboniferous rocks (karstified)
- Groundwater generally unconfined
- Aquifer classification based on productivity, potential yield and extent



### O<sup>18</sup> Isoscape drivers

- Variation of ~ 3‰ (Min 7.5 ‰, Max 4.1‰)
- Progressive depletion to eastern coast
- Primary determinants?
- Location with respect to orographically influenced rainfall
- Annual precipitation volume
- Dominance by winter recharge

#### Modern groundwater recharge

#### Table 2

Univariate association analyses between measured groundwater  $\delta^{10}$ O and continuous (scale) variables; Non-parametric Spearman R<sub>sp</sub>, Two-tailed tests of significance with cases excluded on pair-wise basis.

	N	Rap	р
Location:			
X-Coordinate	142	-0.438	< 0.001
Y-Coordinate	142	-0.408	< 0.001
Elevation (m)	142	-0.052	0.540
Recharge:			
Recharge Coefficient (mm/year)	141	0.153	0.053
Recharge Capacity (mm)	141	0.046	0.590
Estimated Recharge (mm)	141	0.167	0.048
Seasonal Climate:			
Mean Annual Precipitation	142	0.530	< 0.001
Spring Mean Precipitation	142	0.483	< 0.001
Summer Mean Precipitation	142	0.425	< 0.001
Autumn Mean Precipitation	142	0.561	< 0.001
Winter Mean Precipitation	142	0.519	< 0.001
Mean Annual Temperature	142	0.414	< 0.001
Spring Mean Temperature	142	0.372	< 0.001
Summer Mean Temperature	142	0.156	0.063
Autumn Mean Temperature	142	0.449	< 0.001
Winter Mean Temperature	142	0.536	< 0.001
Antecedent Precipitation			
24-h	142	0.110	0.223
48-h	142	0.171	0.019
120-h	142	-0.033	0.617
10-day	142	-0.078	0.321
30-day	142	0.265	0.002
60-day	142	0.211	0.011
90-day	142	0.349	< 0.001
120-day	142	0.470	< 0.001
150-day	142	0.250	0.001

Note: Spring – March, April, May; Summer – June, July, August; Autumn – September, October, November; Winter – December, January, February.

### O<sup>18</sup> Isoscape drivers

- Logit modelling of locational clusters
- Local/regional (hydro)geological setting exerts a secondary influence on  $\delta^{18}O$  composition

#### Table 4

Multinomial Logit model for developed groundwater 8180 clusters.

Effect	-2 Log Likelihood of Reduced Model	Chi-Square*	df	Sig.
Model Intercept	196.861	0.000	0	
AnnRainfall*AnnTemp	270.960	74.099	3	< 0.001
Sample Source	217.526	20.664	3	< 0.001
Gen_Aquifer_Type	214.097	17.236	6	0.008
Drainage (Dry/Not Dry)	205.847	8.986	3	0.029

The chi-square statistic is the difference in -2 log-likelihoods between the final model and a reduced model. The reduced model is formed by omitting an effect (variable) from the final model.



### O<sup>18</sup> Isoscape drivers

- High productivity bedrocks (e.g. karst limestone), bedrock aquifers with little or no soil/subsoil cover, and regions characterised by High/Extreme groundwater vulnerability, found to be more likely to attenuate the seasonal precipitation  $\delta^{18}$ O composition.
- Groundwater from poorly productive bedrocks, regions with high groundwater residence times (e.g. bedrocks capped with significant subsoil depths), and Low/Moderate aquifer vulnerability areas, were more likely to reflect the long-term mean annual precipitation  $\delta^{18}$ O composition.





### 2018 'Drought'





### 2018 'Drought'

- Increase ~ 1 mil in karst area (e.g. from -6.3 to -5.6) – Karst aquifers
- Decrease in east ~ 1 mil in karst area (e.g. from - 6.6 to -7.9) – Ll aquifers
- Faster recharge to west? GW-SW interaction in karst systems
- East more representative of annual rainfall concentration





## Enteric Microbes and Isotopes -Mechanistic Inference

### **Contamination Mechanisms**





### **Microbes and Isotopes – The Theory**

- Surface water (and "new" groundwater) can be a source of contamination in a drinking water well, an understanding of the volume of surface water and travel time to the well is needed to assess a well's vulnerability/susceptibility/risk prob,
- Seasonal, spatio-temporally distinct isotopic signals could be used as an indicator,
- Stable Isotopes are DEFINITELY not suitable as a tracker/tracer, but may shed light on source- or aquifer-specific mechanisms

### Hunt et al., 2005; Journal of Hydrology

- Stable isotope ratios of oxygen in river water at the City of La Crosse, Wisconsin; peak to peak seasonal variation over 2 years,
- 13 urban (public) wells sampled over same period,
- 12-month time-series from 1 well and piezometer located between river,
- Time of travel (TOT) of floodwater assessed using 4 methods; GW Temp, Virus culture, Particle tracking (Model), and Age Dating (3H–3 He)
- NB: No precipitation isotopes





Fig. 4. Plot of the  $\delta^{18}$ O time series from the municipal well, river, and piezometer installed between the river and the municipal well. Two periods are labeled in the figure: A, time required for floodwater depleted in <sup>18</sup>O to appear at the municipal well; B, time for surface water enriched in <sup>18</sup>O to appear at piezometer. River stages estimated from US Army Corps of Engineers' Pool 7 tailwater elevation data are also shown. Table 4

Summary of time of travel estimates (river to municipal Well 24)

	Isotope time series	<sup>3</sup> H- <sup>3</sup> He age dating	HAV cell culture	Temperature time series	Groundwater model
Flood conditions Non-flood con- ditions	2 Months (2001) 9 Months (2001)	NA 11–12 Years	NA <1 Year	3 Months (2002) 3 Months (2002)	NA 4.5 Months

NA, not analyzed.



### The Irish Situation (Beauty and the Beast)

	No Event	"The Beast"	Drought (Beauty!!)
EC Absent	83.8%	69.2%	46.15%
EC Present	16.2%	30.8%	53.85%

**Shallow Wells** 

**Deeper Wells** 

Pearson Chi-Square = 7.007, P = 0.030

### The Irish Situation (Beauty and the Beast)

		ANOVA			
018					
Between Groups	Sum of Squares 43.264	df 2	Mean Square 21.632	F 24.866	Sig. .000
Within Groups	59.156	68	.870		
Total	102.420	70			

Multiple Comparisons							
Dependent Vari	able: O18						
Bonferroni							
		Mean				95% Confide	nce Interval
(I) Event	(J) Event	Difference (I-J)	Std. Error	Sig.		Lower Bound	Upper Bound
None	The Beast	$1.28218^{*}$	.25483	.0	000	.6567	1.9077
	Drought	$1.87848^{*}$	.30072	.0	000	1.1403	2.6166
The Beast	None	$-1.28218^{*}$	.25483	.0	000	-1.9077	6567
	Drought	.59630	.32916	.2	223	2117	1.4043
Drought	None	$-1.87848^{*}$	.30072	.0	000	-2.6166	-1.1403
	The Beast	59630	.32916	.2	223	-1.4043	.2117
*. The mean diffe	*. The mean difference is significant at the 0.05 level.						

### The Irish Situation (Beauty and the Beast)



# Total N71Test Statistic33.584Degrees of Freedom2Asymptotic Sig. (2-sided test).000

1. The test statistic is adjusted for ties.

### "THE MODEL" (3-D Incl EC Pres, Event, Depth and O18)



Each node shows the sample average rank of Event.

Sample1-Sample2	Test Statistic <sup>⊜</sup>	Std. Error ⊜	Std. Test⊜ Statistic	Sig. 🍣	Adj.Sig.⇔
Drought-The Beast	12.465	7.284	1.711	.087	.261
Drought-None	34.846	6.654	5.237	.000	.000
The Beast-None	22.381	5.639	3.969	.000	.000

Each row tests the null hypothesis that the Sample 1 and Sample 2 distributions are the same.

Asymptotic significances (2-sided tests) are displayed. The significance level is .05.

Normal Conditions: Shallow Source (Infiltration), SW & GW

Drought Conditions: Deep Source, High Concentration (Dilution), "Real Groundwater"

Snow Conditions: Shallow Source (Top Melt), Low Concentration (Dilution), All meltwater after 24hrs

Currently, isotopes (O18) 65-75% effective at predicting E. coli presence during all events

Precipitation not employed to date

### Results to date

- Rare snow event March 2018 opportunity to track groundwater recharge (followed by worst recorded drought)
- E-Coli encountered in depleted groundwater (~10‰) indicating rapid recharge/ ingress

# Work to complete and direction

### Conclusions

- Recharge biased towards winter months
- 3-5 month recharge time
- Hydrogeology secondary influence
- Early results indicate potential to track pathogens in 'vulnerable' aquifer areas

### To do

- Deuterium analysis
- 2<sup>nd</sup> EPA groundwater sampling round (Oct-Dec 2018), incl. pathogen analysis
- Precipitation isoscapes
- P/GW ratios