Stable Isotopes and Hydrogeology in Ireland

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Outline

1. Stable isotope hydrology and “isoscapes”
2. Pathogens and subsurface transport
3. $^{18}O$ isoscape for Ireland and geospatial drivers
4. Pathogen ingress mechanisms
5. Work to complete and direction
Stable Isotopes
Stable isotopes

• 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
Stable isotopes

- Fractionate into light and heavy fractions
- Mainly due to evaporation or heating
- One isotope much more common than other (large difference in mass)

\[
\delta^{18}O = \left( \frac{\frac{^{18}O}{^{16}O}_{\text{sample}}}{\frac{^{18}O}{^{16}O}_{\text{standard}}} - 1 \right) \times 1000 \text{%}
\]

“del”

“permil”

“Heavy O isotope

“SMOW”

[Graph showing enrichment over time with equation: \( y = -0.0003x^2 + 0.1936x - 7.3198 \), \( R^2 = 0.9976 \).]
Stable isotopes

Isotopically lighter than water left behind in ocean

Precipitation isotopically heavier (more H² and O¹⁸)
Stable isotopes

- 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)
Stable isotopes

- 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
“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
ISO-MECH

• First temporal O\textsuperscript{18} 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
ISO-MECH

• 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 long-term annual means from about 700 GNIP stations.


IAEA GNIP Network
- Valencia
- Armagh
ISO-MECH
• Insufficient spatial coverage for isotopes in precipitation hinders investigations of relationship between ground water and precipitation
• Need information to help quantify aquifer replenishment rates

IAEA GNIP Network - Valencia - Armsg
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)
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).
ISO-MECH

- 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)
ISO-MECH

• 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)
ISO-MECH

• 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
Aquifer vulnerability

- Topsoil
- Subsoil
- Bedrock
- Hazard (Source)
- Pathway
- Point of Release
- Unsaturated Zone
- Water Table
- Target
<table>
<thead>
<tr>
<th>Study Area</th>
<th>Name</th>
<th>Bedrock</th>
<th>GW Vuln.</th>
<th>Aquifer Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>S.A. 1</td>
<td>Meath</td>
<td>Limestone</td>
<td>Low</td>
<td>LI</td>
</tr>
<tr>
<td>S.A. 2</td>
<td>Wicklow</td>
<td>Granite</td>
<td>High</td>
<td>LI/PI</td>
</tr>
<tr>
<td>S.A. 3</td>
<td>Kilkenny</td>
<td>Sandstone, Shale, Limestone</td>
<td>Extreme</td>
<td>PI</td>
</tr>
<tr>
<td>S.A. 4</td>
<td>Westmeath</td>
<td>Limestone</td>
<td>High</td>
<td>LI</td>
</tr>
<tr>
<td>S.A. 5</td>
<td>Offaly</td>
<td>Limestone, Sandstone</td>
<td>High</td>
<td>LI/Lm</td>
</tr>
</tbody>
</table>
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 ($\chi^2 = 10.686, p = 0.03$)
• 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%

Well Design Parameters – Liner Clearance & Liner Cap

Antecedent Precipitation – 48-hour & 120-hour
Low Vulnerability LR Model

• Significant hierarchies included:
  • Well Design Parameters – 52.8%
  • Septic Tank Proximity – 24.2%
  • Antecedent Precipitation – 13.2%
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Well Design Parameters – Liner Clearance & Liner Cap

Antecedent Precipitation – 48-hour & 120-hour

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%

**Well Design Parameters** – Liner Clearance; Wellhead Cover; 10m Wellhead Radius Condition

**Antecedent Precipitation** – 30-day
**High/Extreme Vulnerability LR Model**

- Significant hierarchies included:
  - Hydrogeological Setting – 33.1%
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  - Antecedent Precipitation – 13%

**Well Design Parameters** – Liner Clearance; Wellhead Cover; 10m Wellhead Radius Condition

**Antecedent Precipitation** – 30-day
<table>
<thead>
<tr>
<th>Vulnerability Model Comparison</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Low Vulnerability</strong></td>
</tr>
<tr>
<td>• Local hydrogeology not found to be significant</td>
</tr>
<tr>
<td>• Well design highly significant (52.8%)</td>
</tr>
<tr>
<td>• Septic tank proximity significant (24.2%)</td>
</tr>
<tr>
<td>• Short-term precipitation significant (13.2%)</td>
</tr>
<tr>
<td>• Agriculture significant (9.5%)</td>
</tr>
<tr>
<td><strong>High/Extreme Vulnerability</strong></td>
</tr>
<tr>
<td>• Local hydrogeology significant (33.1%)</td>
</tr>
<tr>
<td>• Well design significant (29.8%)</td>
</tr>
<tr>
<td>• Septic tank proximity significant (22.1%)</td>
</tr>
<tr>
<td>• Medium-term precipitation significant (13%)</td>
</tr>
<tr>
<td>• Agriculture not found to be significant</td>
</tr>
</tbody>
</table>
Vulnerability – Recharge – Runoff – Precipitation - Susceptibility

The link between subsoil permeability, recharge, runoff and vulnerability

<table>
<thead>
<tr>
<th>Subsoil</th>
<th>Permeability</th>
<th>Thickness</th>
<th>Recharge</th>
<th>Runoff</th>
<th>Aquifer vulnerability</th>
</tr>
</thead>
<tbody>
<tr>
<td>High</td>
<td>High</td>
<td>1-3 m</td>
<td>High</td>
<td>Low</td>
<td>Extreme</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt;3 m</td>
<td>High</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Moderate</td>
<td>High</td>
<td>1-3 m</td>
<td>High</td>
<td>Low</td>
<td>Extreme</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3-10 m</td>
<td>Intermediate</td>
<td>Intermediate</td>
<td>High</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt;10 m</td>
<td>Intermediate</td>
<td>Intermediate</td>
<td>Moderate</td>
</tr>
<tr>
<td>Low</td>
<td>Intermediate</td>
<td>1-3 m</td>
<td>Intermediate</td>
<td>Low</td>
<td>Extreme</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3-5 m</td>
<td>Low</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5-10 m</td>
<td>Low</td>
<td>High</td>
<td>Moderate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt;10 m</td>
<td>Low</td>
<td>High</td>
<td>Low</td>
</tr>
</tbody>
</table>

The “Ontario Dataset”
The “WELLness” Project

Dual Receptor Model

QMRA
Fate and Transport Model
KAP Assessment

Microbial Risk Profile
Well Owner Risk Profile

Comprehensive Risk Assessment Tool
Water Well Information System

"Raw" (Unprocessed) Datasets

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

Well Testing Information System

- Years: 2010-2016 inclusive
- ~1,250,000 records
- E. coli and Total Coliforms
- Source Address
WWIS
- ~720,000 records (2016)
- Well ID
- Source Construction
- Local Hydrogeology
- UTM Coordinates (Source)

```
# UTM Coordinate Separation
* rgdal

# UTM Coordinate Conversion
* rgdal
```

**Geocoded WWIS Dataset**

```
# Data Processing
```

```
# Source Address Cleaning
+ tidyverse, stringr
* placement

# Clean Address Conversion via Google AF
```

**Geocoded WTIS Dataset**

```
# Data Merging
```

```
# Calculate distances between geocodes via Haversine Distance Calculation

# Filter distances >1.5km
```

**WTIS**
- Years: 2010-2016 inclusive
- ~1,250,000 records
- E. coli and Total Coliforms
- Source Address

```
# Merged WWIS-WTIS Dataset
```

```
* tidyverse,
doParallel,
foreach,
fuzzyjoin
```

**Merged WWIS-WTIS Dataset**
- Years: 2010-2016 inclusive
- 938,854 records
- E. coli and Total Coliforms
- Well Construction; Hydrogeological Setting
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)
Distance Analysis of Merged Dataset

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

Approximately 62,000,000 datapoints!!!
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\textsuperscript{18} isoscape for Ireland and geospatial drivers
O$^{18}$ 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\textsuperscript{18} Isoscape drivers

- Variation of $\sim 3\%$ (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
O$^{18}$ Isoscape drivers

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

![Graph showing precipitation dynamic with data points for Phoenix Park, Clara, Claremorris, Fermoy, and Bell Harbour. The graph includes a map of Ireland with precipitation data visualized in different colors. The graph shows the dO18 values for each location over time from 31.12.17 to 16.12.18.](image-url)
Enteric Microbes and Isotopes - Mechanistic Inference
Contamination Mechanisms

Mechanism affects:
- Incidence
- Frequency
- Seasonality
- Concentration
- Predictive Accuracy
- Likelihood of Infection
- Acquired Immunity
- Ability to design interventions
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 $^{18}O$ to appear at the municipal well; B, time for surface water enriched in $^{18}O$ to appear at piezometer. River stages estimated from US Army Corps of Engineers’ Pool 7 tailwater elevation data are also shown.

<table>
<thead>
<tr>
<th>Isotope time series</th>
<th>$^3$H-$^3$He age dating</th>
<th>HAV cell culture</th>
<th>Temperature time series</th>
<th>Groundwater model</th>
</tr>
</thead>
</table>

NA, not analyzed.
The Irish Situation (Beauty and the Beast)

<table>
<thead>
<tr>
<th></th>
<th>No Event</th>
<th>“The Beast”</th>
<th>Drought (Beauty!!)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC Absent</td>
<td>83.8%</td>
<td>69.2%</td>
<td>46.15%</td>
</tr>
<tr>
<td>EC Present</td>
<td><strong>16.2%</strong></td>
<td><strong>30.8%</strong></td>
<td><strong>53.85%</strong></td>
</tr>
</tbody>
</table>

Pearson Chi-Square = 7.007, P = 0.030
The Irish Situation (Beauty and the Beast)

ANOVA

<table>
<thead>
<tr>
<th></th>
<th>Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F</th>
<th>Sig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Between Groups</td>
<td>43.264</td>
<td>2</td>
<td>21.632</td>
<td>24.866</td>
<td>.000</td>
</tr>
<tr>
<td>Within Groups</td>
<td>59.156</td>
<td>68</td>
<td>.870</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>102.420</td>
<td>70</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Multiple Comparisons

Dependent Variable: O18
Bonferroni

<table>
<thead>
<tr>
<th>(I) Event</th>
<th>(J) Event</th>
<th>Mean Difference (I-J)</th>
<th>Std. Error</th>
<th>Sig.</th>
<th>95% Confidence Interval</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>The Beast</td>
<td>1.28218*</td>
<td>.25483</td>
<td>.000</td>
<td>.6567 to 1.9077</td>
</tr>
<tr>
<td></td>
<td>Drought</td>
<td>1.87848*</td>
<td>.30072</td>
<td>.000</td>
<td>1.1403 to 2.6166</td>
</tr>
<tr>
<td>The Beast</td>
<td>None</td>
<td>-1.28218*</td>
<td>.25483</td>
<td>.000</td>
<td>-1.9077 to -0.6567</td>
</tr>
<tr>
<td></td>
<td>Drought</td>
<td>.59630</td>
<td>.32916</td>
<td>.223</td>
<td>-.2117 to 1.4043</td>
</tr>
<tr>
<td>Drought</td>
<td>None</td>
<td>-1.87848*</td>
<td>.30072</td>
<td>.000</td>
<td>-2.6166 to -1.1403</td>
</tr>
<tr>
<td></td>
<td>The Beast</td>
<td>-.59630</td>
<td>.32916</td>
<td>.223</td>
<td>-1.4043 to .2117</td>
</tr>
</tbody>
</table>

*. The mean difference is significant at the 0.05 level.
The Irish Situation (Beauty and the Beast)

Independent-Samples Kruskal-Wallis Test

<table>
<thead>
<tr>
<th>Event</th>
<th>Total N</th>
<th>Test Statistic</th>
<th>Degrees of Freedom</th>
<th>Asymptotic Sig. (2-sided test)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>The Beast</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drought</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1. The test statistic is adjusted for ties.
“THE MODEL”
(3-D Incl EC Pres, Event, Depth and O18)

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\textsuperscript{nd} EPA groundwater sampling round (Oct-Dec 2018), incl. pathogen analysis

• Precipitation isoscapes

• P/GW ratios