



Research Programme
- Short Calls, Final Report -

Lead Applicant Name	Shane Regan
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Host Organisation name	Trinity College Dublin
Project Title	Iso-Mech (Development of a national groundwater isoscape for mechanistic recharge estimation and bacterial fingerprinting)
Contract Number	2017-SC-004

Date: 6-12-18

This report covers the period November 1st 2017 to October 31st 2018



2. (a) Project information:

Final project report (max 2500 words, excluding figures and headings):

- (i) Progress of objectives and scientific/engineering targets beyond the state of the art & methods used

The ISO-MECH project comprises the following objectives and scientific targets:

1. Development of a temporally significant Irish $\delta^{18}\text{O}$ and δD groundwater isoscape using mean annual values,
2. Quantify the temporal isotopic properties of Irish rainfall, using a network of cumulative rainfall collectors,
3. Determination of temporal and spatial precipitation to groundwater (P/GW) isotopic ratios to assess spatial and temporal groundwater recharge patterns and mechanisms,
4. Elucidation of the primary environmental factors driving seasonal groundwater isotopic composition and overarching isotopic patterns.
5. Calculation of seasonal levels of surface water contribution to sample points, thus permitting inferential modelling of microbial contamination mechanisms.
6. Help validate GSI recharge estimation and provide a basis for an updated sampling strategy.

Monthly rainfall samples were collected between March and October 2018. Groundwater samples were collected by the EPA from their national hydrometric network between July and August 2018. Groundwater samples were also collected from selected EPA monitoring boreholes in March 2018 (~30) and June 2018 (~20). A number of domestic wells were sampled in March 2018 (~40) and June 2018 (~30), and in November 2018 (~40).

$\delta^{18}\text{O}$ analysis was performed using Continuous Flow-Isotope Ratio Mass Spectrometry (Thermo DeltaPlus CF-IRMS) and Gas Chromatography (GC). Samples were transferred to 12.5 ml glass Exetainers® which had been double washed in milliQ deionised water and dried at 70 °C for 12 hrs prior to use. 0.5 ml sub-samples were pipetted into 12 ml flat-bottomed Exetainers, capped and flushed (80 ml/min) with 0.3% CO_2 in a pure He gas mix for 500 seconds, and subsequently equilibrated in a thermostatically controlled sample block at 23 °C for 21 hrs (permitting CO_2 exchange between gaseous and aqueous phases, followed by formation of carbonic acid). The equilibrated headspace gas was sampled by a CTC autosampler before entering a Thermo Gas Bench, comprising an 8-port Valco valve for analyte loading/filling; a 100 μl sample loop, and two Nafion (C7HF13O5S.C2F4 sulfonated tetrafluoroethylene-based fluoropolymer co-polymer membrane) traps for moisture removal. Ten 100 μl aliquots per sample were taken and sent to the CF-IRMS via the GC.

Corrections to the primary Standard Mean Ocean Water (VSMOW) was made using IAEA certified reference materials Standard Light Antarctic Precipitation (SLAP), and Greenland Ice Sheet Precipitation (GISP), allowing characterisation of standard deviations from replicated samples (Gröning et al., 2004). Reference standards characterised by known δ values were run with each block of unknown samples. The first peak was discarded for each sample to condition the GC and to reduce potential carryover. Calculated standard deviations for the remaining peaks from each sample were used to assess IRMS stability during sample runs. Analytical precision was quantified



and maintained via inspection of the degree of reference sample variability (V-SMOW). Results are presented in ‰ with respect to V-SMOW according to:

$$\delta_{sample}(\text{‰}) = \left(\frac{R_{sample}}{R_{standard}} - 1 \right) * 1000 \quad (1)$$

where δ_{sample} is the isotope ratio of sample relative to the V-SMOW and R is the $^{18}\text{O}/^{16}\text{O}$ atomic ratio.

The first round of laboratory analysis was carried out in June 2018 for $\delta^{18}\text{O}$. However, problems with the IRMS meant results were not reliable. Following the collection of EPA groundwater samples in September 2018, laboratory analysis re-commenced on all groundwater and rainfall samples (~ 500) between October and November 2018. Pathogen analysis from domestic wells was carried out using IDEXX field kits; EPA pathogen analysis was carried out in the EPA water quality laboratory in Monaghan.

- (ii) Implementation (please include any issues with timelines, milestones, management etc. or deviations from the original implementation plan)

Rain Samplers for rainfall collection were ordered from Palmex Ltd and installed at four sites:

- Climate monitoring station at Clara Bog: 26-1-18 at 11:00
- Met Éireann climate synoptic station at Fermoy: 30-1-18 at 10:00
- Met Éireann climate synoptic station at Claremorris: 30-1-18 at 14:00 (Figure 1)
- Met Éireann climate synoptic station at Phoenix Park: 7-2-18 at 16:00

The first round of rainfall samples were collected in the second week of March 2018, due to the adverse weather conditions experienced across most of Ireland in early March 2018.





Figure 1. Rainfall Sampler in Claremorris

EPA groundwater monitoring was delayed and commenced in July 2018. The project team received the first round of EPA samples in the first week of September, 6 months later than scheduled. However, in early March 2017 the project team undertook independent groundwater sampling at a selection of EPA borehole nest sites (Figure 2) and domestic wells in Meath, Westmeath and Cork (~100 samples). This was repeated in June 2018, following the ‘drought’, and again in November 2018. The second EPA monitoring period will be completed in early December 2018.



Figure 2. Borehole sampling at Dripsey, Co. Cork

The significant delay in the EPA groundwater monitor schedule, resulted in the delay in laboratory stable isotope analysis. The laboratory analysis was also delayed by equipment and analytical problems. These were resolved in November 2018 and results for analysis of Oxygen-18 were available at the end of November. The equipment for Deuterium analysis has yet to arrive in the TCD IRMS laboratory. All water samples are stored and will be analysed when the equipment arrives (early 2019); including the second round of EPA groundwater sampling.

(iii) Outputs (please provide a short description and complete the table below)

1. O18 Groundwater Isoscape

The summer of 2018 was one of the worst recorded ‘droughts’ in Ireland. The EPA groundwater monitoring schedule coincided with the end of this drought and provided a unique opportunity to measure the stable isotopic concentration of groundwater and its response to a sustained period of little to no precipitation and groundwater recharge. The $\delta^{18}\text{O}$ groundwater isoscape, from



groundwater samples collected between July and August 2018, is presented in Figure 3:

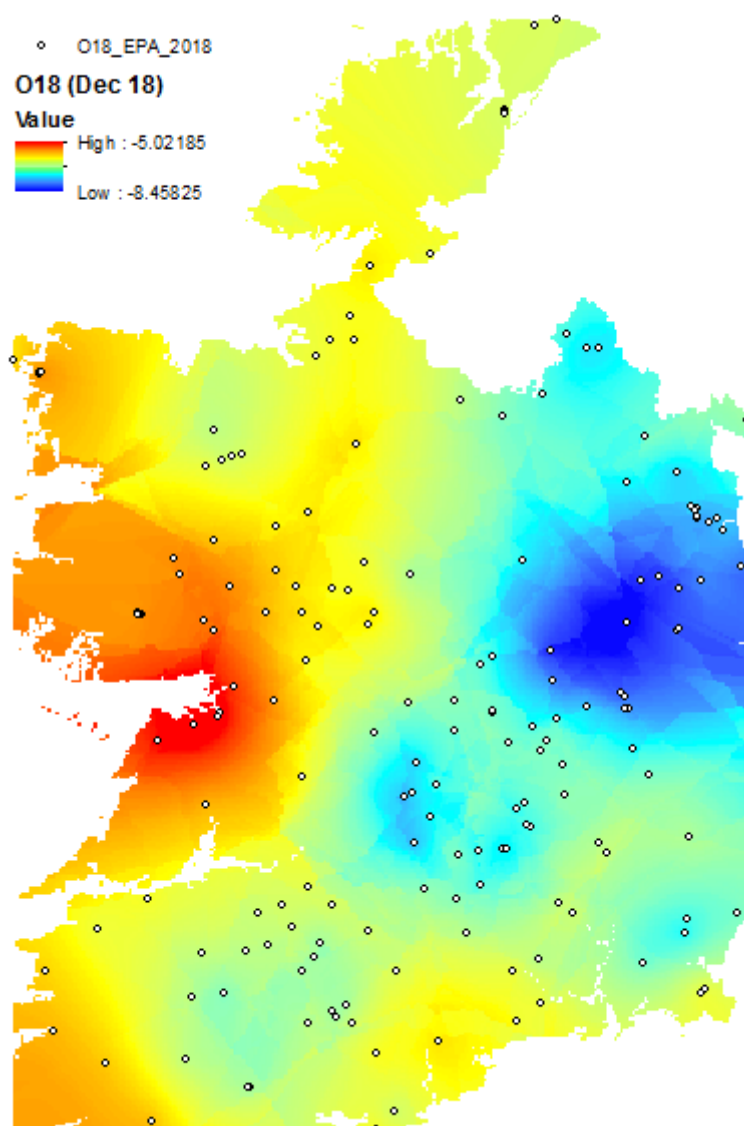


Figure 3. $\delta^{18}\text{O}$ groundwater isoscape (Summer 2018)

A previous isoscape study from groundwater samples collected in the summer of 2013 (Regan *et al.*, 2017), permits a comparison of the drought study to a baseline study. The differences in the isoscape are presented in Figure 4. It is apparent that a marked depletion (> 1 mil) is recorded in the east of Ireland, which recorded extremely low rainfall amounts, while a moderate enrichment is recorded in the west of Ireland, which had slightly more rain. The western region also coincides where karst bedrock is mapped. The inference is that a greater level of groundwater – surface water interaction in the karst environment gives a more temporally variable isotope signature (i.e. responds much more rapidly to fluctuations in precipitation and surface runoff generation). In contrast, slower soil matrix groundwater and diffuse recharge in the east is gradually depleting the groundwater reservoir.

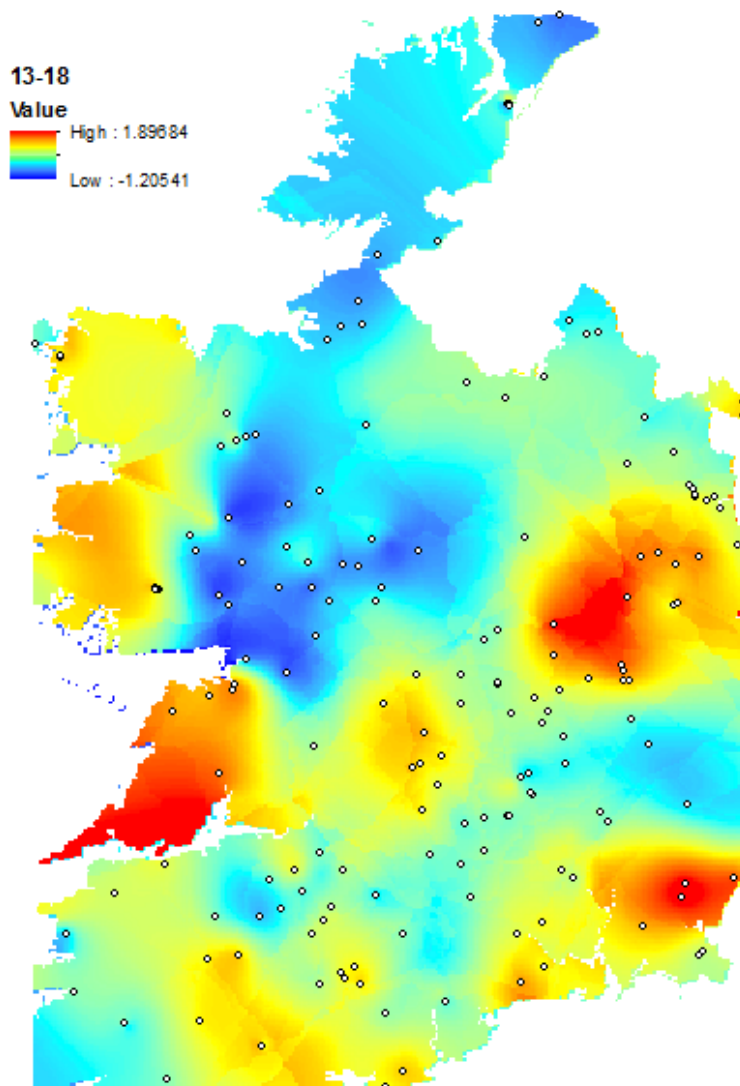


Figure 4. Difference in $\delta^{18}\text{O}$ groundwater isoscape between Summer 2013 and Summer 2018

2. Regional precipitation $\delta^{18}\text{O}$ gradient

Measured $\delta^{18}\text{O}$ in precipitation from regional rain gauges is shown in Figure 5. A distinct seasonal pattern is observed at all gauges, with the most enriched concentration occurring in the summer months, and becoming markedly more depleted in the winter months. The most depleted concentration is associated with snow, collected in March 2018 (< -10 mil).

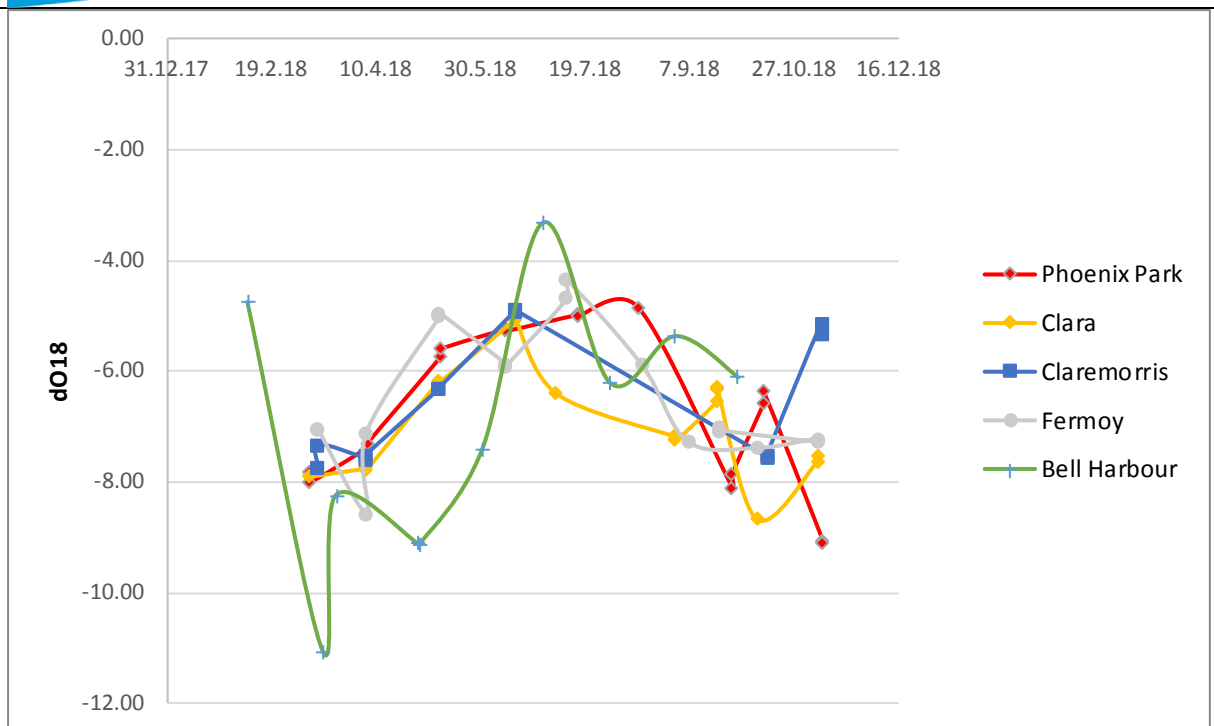


Figure 5. $\delta^{18}\text{O}$ in precipitation

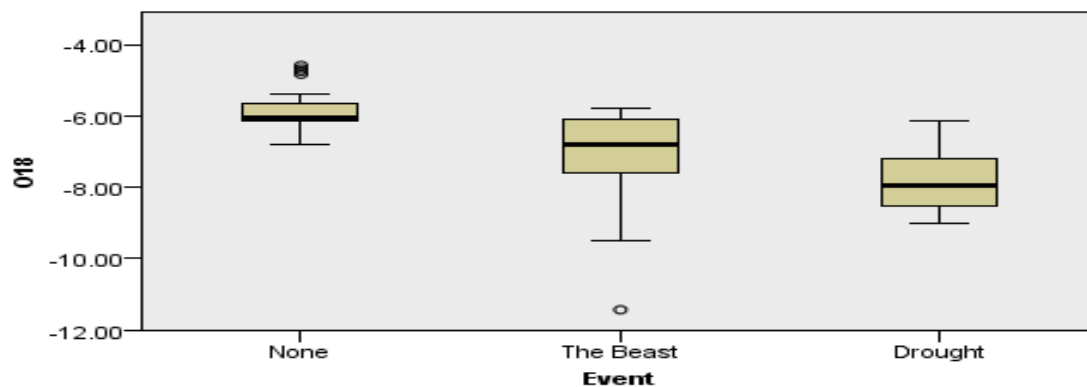
3. O18 and e-coli association in domestic wells

The statistical difference in $\delta^{18}\text{O}$ from domestic groundwater wells sampled in March 2018, following the snow event 'The Beast', in June 2018 during 'The Drought', and in times outside these periods, is shown in Figure 6. A significant difference is found between the three periods, with isotopic concentration being depleted following snow, and becoming more depleted during the drought and absence of groundwater recharge.

The statistical association between $\delta^{18}\text{O}$ from the same domestic groundwater wells and presence of E-Coli, is shown in Figure 7. The occurrence of E-Coli is statistically significant during the snow and drought periods, but not in the 'normal' period. This implies that during the snow event, groundwater is locally recharged quickly (meltwater), whereas during the drought, there is little or no recharge, and the E-Coli mass that is present increases due to the absence of diluting (real) groundwater. Two processes are thereby occurring.



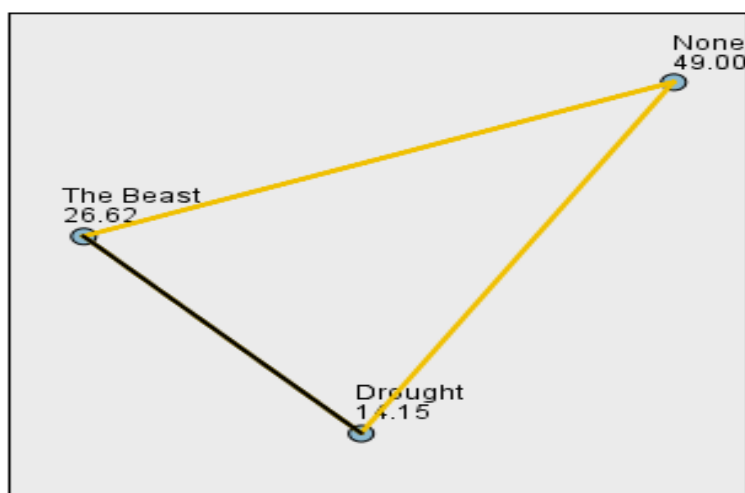
Independent-Samples Kruskal-Wallis Test



Total N	71
Test Statistic	33.584
Degrees of Freedom	2
Asymptotic Sig. (2-sided test)	.000

1. The test statistic is adjusted for ties.

Figure 6. Statistical analysis of groundwater samples from snow and drought events



Each node shows the sample average rank of Event.

Sample1-Sample2	Test Statistic	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.

Figure 7. Statistical association of groundwater samples from snow and drought events with E-Coli presence

Task No.	Deliverable description	Planned delivery (as per proposal)	Expected delivery
WPA	Site selection and field instrumentation	Month 1	Complete
WPB	Rainfall and groundwater sampling	Month 12	Month 12/ Post Contract
WPC	Laboratory analysis	Month 10	Month 12/ Post Contract
WPD	Data analysis and isoscape development	Month 10	Month 12/ Post Contract



Publications to date:

[Conference Publication] Regan, S. and Hynds, P. (2018) ISO-MECH: Development of a groundwater isoscape for mechanistic recharge estimation and bacterial fingerprinting *EGU General Assembly 2018 – Geophysical Research Abstracts* Vol 20, EGU2018-15322 Vienna, Austria, , APR-18

[Conference Publication] Regan, S. and Hynds, P. (2018) ISO-MECH: Development of a groundwater isoscape for mechanistic recharge estimation and bacterial fingerprinting *45th International Association of Hydrogeologists Congress 2018 –Daejeon, South Korea, SEPT-18*



4. Data/outputs submitted with final report *(please list the documents, presentations, datasets etc. submitted with this report)*

- a. Presentation given to IAH Irish Group in the Geological Survey December 4th 2018
- b. Presentation given at the IAH International Congress, South Korea, September 7th 2018
- c. *Compiled databases of O18 and Deuterium from groundwater and precipitation
- d. *Compiled databases of pathogens from groundwater
- e. *EPA database of water quality analysis from collected groundwater samples
- f. *Groundwater and precipitation raster isoscapes
- g. *GIS shapefiles of all monitoring locations

Note: *Completion following delivery of final results