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Geological Survey
Suirbhéireacht Gheolaíochta
Ireland | Éireann

Research Programme
- Short Call 2020, Final Report -

Lead Applicant Name	Dr. Neil Ogle
Host Organisation name	Queen's University Belfast
Project Title	Delivering Added Value to the Tellus Survey: A Multi-elemental Isotopic Database of Soil and Streamwater
Contract Number	2020-SC-053

This report covers the period 1st December 2020 to project end date 31st January 2022

2. (a) Project information:

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

Executive summary (lay abstract, approx. 250 words):

Given the thousands of samples that have been collected (and continue to be collected) through iterations of Tellus surveys over the last decade and tens of thousands of geochemical analyses that have been performed, this project served to fill a gap that previous surveys for the most part have overlooked: Stable Isotope Analysis (SIA).

This project aimed to delve into the vast repository of Tellus soil and water samples available and subject them to a suite of isotopic analysis. The objectives were as follows:

1. **Soil**: Perform stable carbon, nitrogen, and sulphur analysis on bulk soil samples
2. **Soil**: Perform stable carbon and oxygen analysis on bulk soil carbonates
3. **Water**: Perform stable carbon isotope analysis on the Dissolved Inorganic Carbon (DIC)
4. **Water**: Perform stable oxygen and hydrogen analysis on water samples
5. To take each suite of data and subject them to geospatial analysis and produce GIS maps of isotopic variation – *Isoscapes*.

Each of these objectives have been achieved and a substantive first database of isotopic values have been created through which to better inform a range of interested parties: climate modellers, protectors of ecosystems, e.g., peatlands, agri-food industry, policy makers etc.

(i) Results, scientific/engineering targets reached beyond the state of the art and conclusions

Isotopic analysis is a versatile analytical tool within the environmental sciences whereby the same techniques can be equally applied to decipher, for example, that a cut of beef did (or did not) originate from a particular area of the country or provide an insight into global temperatures tens of thousands of years ago.

The analytical methods by which this project has been completed is summarised as follows:

Analytical Infrastructure

Bulk soil $\delta^{13}C$ and $\delta^{15}N$ analysis was performed at the Queen's University Belfast's (QUB) Chrono Centre utilizing a Thermo Delta V Advantage Isotope Ratio Mass Spectrometer (IRMS) coupled to a Thermo Flash 1112 Elemental Analyser as depicted in Figure 1

Figure 1 Thermo Delta V IRMS with Elemental Analyser atop

200 samples were measured on this machine and a further 80 were performed by ISO-Analytical on a Europa Scientific 20-20 IRMS with Sercon CNS-EA. All sulphur ($\delta^{34}S$) samples were measured on the Sercon set-up by Iso-Analytical.

All soil carbonate isotope analysis and carbon isotope analysis of DIC in water was performed within the Stable Isotope Facility (SIF) of QUB on an AP2003 IRMS coupled to a Gilson Autosampler (Figure 2).

Figure 2 AP2003 IRMS with autosampler

As the technology behind isotope ratio mass spectrometry advances, there has been a gradual shift in analysis away from the magnetic sector machines as outlined above and towards cavity ring-down spectroscopy. Such a machine was employed by the University of Durham to analyse the waters for their oxygen and hydrogen isotope values.

No matter the infrastructure employed, the final isotope value of a soil or water sample (given the **δ** symbol and denoted by ‰ units) will adhere to the same basic principle governed by the following equation (in this particular case, the oxygen isotopic value of a sample is required):

$$\delta^{18}\mathrm{O} = \left(\frac{\left(\frac{^{18}\mathrm{O}}{^{16}\mathrm{O}}\right)_{sample}}{\left(\frac{^{18}\mathrm{O}}{^{16}\mathrm{O}}\right)_{standard}} - 1 \right) \times 1000$$

Eqn. 1

The oxygen component though can easily be replaced in *Eqn. 1* by any of the elements of interest in this study:

$\delta^{13}C$ $(^{13}C/^{12}C)$
$\delta^{15}N$ $(^{15}N/^{14}N)$
$\delta^{2}H$ $(^{2}H/^{1}H)$
$\delta^{34}S$ $(^{34}S/^{32}S)$

Different isotopes of the same common light elements utilised in this study exist in different proportions (or ratios) throughout the natural world. By measuring how these ratios change (fractionate) over time and space is the foundation through which SIA can function as a solution to interpreting real world questions.

Eqn. 1 also denotes that known standards (both internationally-accepted and laboratory-calibrated) are required against which the real world δ-values can be calculated and Table 1 summarises those that were used in this study. These will usually be values that will bracket the expected values of samples and are also used to perform 2-or 3-point calibrations to ascertain the true value of the sample.

Analysis	**Standard 1**	**Standard 2**	**Standard 3**
Soil $\delta^{13}C$ QUB$^{\Delta}$	IA-R068 = -25.22‰	IA-R069 = -18.88‰	IA-R006 = -11.64‰
Soil $\delta^{13}C$ Iso-Analytical*	IA-R001 = -26.43‰	IA-R005 = -26.03‰	IA-R006 = -11.64‰
Soil $\delta^{15}N$	IA-R068 = +0.99‰	IA-R069 = +11.60‰	IAEA N2 = +20.30‰
Soil $\delta^{15}N$ Iso-Analytical°	IA-R001 = +2.55‰	IA-R045 = -4.71‰	IA-R046 = +22.04‰
Soil $\delta^{34}S$ Iso-Analytical	IA-R061 = +20.33‰	IA-R025 = +8.53‰	IA-R026 = +3.96‰
Soil Carbonate $\delta^{13}C$ QUB	AR = +2.4‰	IAEA-CO-9 = -47.32‰	
Soil Carbonate $\delta^{18}O$ QUB	AR = -2.60‰	IAEA-CO-9 = -15.32‰	
Water $\delta^{13}C$ DIC QUB	AR = +2.4‰	IAEA-CO-9 = -47.32‰	
Water $\delta^{18}O$ Uni of Durham	IA-R063 = -0.41‰	IA-R064 = -12.34‰	
Water $\delta^{2}H$ Uni of Durham	IA-R063 = +11.26‰	IA-R064 = -98.32‰	

*Table 1. Standards used in this study to calibrate samples. $^{\Delta}$ Standards calibrated against and traceable to IAEA-CH7 (polyethylene, $\delta^{13}C_{V\text{-}PDB}$ = -32.15 ‰). * Standards calibrated against and traceable to IAEA-CH6 (sucrose, $\delta^{13}C_{V\text{-}PDB}$ = -10.449 ‰). ° Standards calibrated against and traceable to IAEA-N1 (ammonium sulphate, $\delta^{15}N_{AIR}$ = 0.4 ‰). AR is an internal laboratory marble standard calibrated against and traceable to IAEA-NBS19 ($\delta^{13}C_{V\text{-}PDB}$ = +1.95‰, $\delta^{18}O_{V\text{-}PDB}$ = -2.20‰). All water standards have been calibrated using equilibration and continuous flow - isotope ratio mass spectrometry against V-SMOW2 and were scale corrected using SLAP2.*

Spatial Analysis

ArcGIS®Pro from the Environmental Systems Research Institute (ESRI) was used to spatially represent the isotope values from the various analyses. Several spatial analyst tools exist within the software and for these initial representations ordinary Kriging was selected. The co-ordinate system was "TM75 Irish Grid" and the plot boundary was defined by "IRL_Country".

Kriging spatial analysis is widely used in the "isoscaping" community. It is possible within ArcGIS however to adjust variables such as *cell size*, *search radii* and *minimum neighbours* etc. to formulate subtly different interpolations for the same measured data. In essence, different Kriging algorithms will change the value range of the classes used for visual representation. For this baseline report however, Kriging *default* parameters were utilised:

- Ordinary Kriging
- Spherical Semi-Variogram Model
- Variable Search Radius
- Number of Points: 12, default max distance
- Cell Size: Maximum of Inputs
- Tile Size :128x128

While the results of spatial analysis are presented in part (iii), the datasets are presented by analytical type in Section 3.

(ii) Implementation

Almost immediately after being funded at the end of November 2020, the global COVID-19 pandemic forced the population into lockdown. University staff were prohibited from entering the premises for approximately 3 months. This time however was spent selecting those soil and water samples from the Tellus repository that could be analysed once lockdown was lifted or the university deemed some staff as essential to return. The original proposal was to select 400 water and soil samples. To minimise storage issues at QUB and facilitate time for the GSI to locate samples, an initial batch of 200 soil samples (Shallow Topsoil A) from the G1 and G3 survey areas was selected along with a selection of peri-urban Dublin samples. Whilst measurement was ongoing, the next 200 soil samples from G5 could be finalised, as well as the water samples from G1, G3 and G4.

With such a vast repository, time was taken to ensure that the initial batch of soil samples selected were geographically representative and would encompass an array of soil types. Constant communication with GSI however, would reveal that some selected samples were either missing, used up or within the possession of other researchers and so more time was spent seeking replacements. Eventually an initial batch of 200 was arrived at and despite some initial courier problems they were delivered to QUB mid-March. These samples and their locations (along with those that were selected at a later date) are listed in Section 3.

Ahead of sample arrival, consumables required for analysis were ordered and delivered. Lockdown also allowed the formation of a mini-website within the QUB site. Initially visible, the site has been hidden after a campus wide redesign. Once this report has been accepted the results will be made visible once again on this site.

Deemed as essential staff, personnel could return to QUB and laboratory analysis could begin in SIF in mid-March. However, immediately upon return in March 2021 it was noticed that the machine dedicated to carbon, nitrogen and sulphur analysis as well as oxygen and hydrogen on waters had malfunctioned over lockdown and the funds available to have it repaired were prohibitive. Fortunately, an almost duplicate of this machine resided within the same School in QUB (the Chrono Centre) and this unit was able to analyse the 200 soil samples for carbon and nitrogen. After receiving quotes from other enterprises, sulphur analysis on soils was performed outside the University by Iso-Analytical in England. In both these cases though, the cost per analysis had risen with the result that eventually the original 400 earmarked for analysis would have to be reduced. Carbon and oxygen analysis of soil carbonate and latterly $\delta^{13}C_{DIC}$ within the waters, was still able to proceed within SIF.

While this first batch of samples was being analysed between late March and early June both within and outside QUB, the next batch of 200 soil and water samples were selected and Covid restriction easing meant collection was done in person from GSI HQ in Dublin in early July 2021. The Chrono Centre were unable to analyse the soil samples at this time, but fortunately Iso-Analytical could do so. Price variance meant that to keep within budget only a further 80 samples could be measured for bulk carbon and nitrogen from the G5 survey area as well as soil carbonate. A further 100 samples for sulphur analysis were also selected from this batch of 200.

337 water samples from the G1, G3 and G4 sampling areas were selected at this time and collected from GSI. As mentioned, they were measured by another outside body – University of Durham (Dr. Darren Gröcke, Department of Earth Sciences). These samples and their locations are also included in Section 3.

(iii) Outputs to date

The principal objective of this project was to add value to the already existing database of Tellus geochemical data. This has been achieved with the creation of the following GIS "Isoscapes" and accompanying isotope data (with their locations) in Section 3.

Bulk Soil δ^{13}C and δ^{15}N Analysis

Isotopic analysis of soils can provide an insight into soil health - essential for maintaining plant and food production. Also, as both sources and sinks of carbon, soil isotope analysis can provide information for climate mitigation and for modification of climate models. Indeed, the list of topics to which soil isotopic analysis can contribute is long: tracking changes in vegetation cover, nutrient cycling, assessing the effect of fertilizer treatment etc. In this study a total of 279 δ^{13}C and δ^{15}N bulk soil values were measured (Section 3) from the G1, G3, G4, G5 and peri-urban Dublin sampling areas. Two samples went unrecorded for both carbon and nitrogen: 615156A and 650216A. 650384A only returned a carbon value. The generated bulk carbon and nitrogen isoscapes are presented in Figures 3 and 4. Actual isotopic values of carbon ranged from -4.72‰ (sample number 610563A) to -30.48‰ (611675A). 610563A, however is recorded as being a sand sample and is by far the most enriched, the next being 583733A at -17.27‰ (silty in texture). Most samples occupied

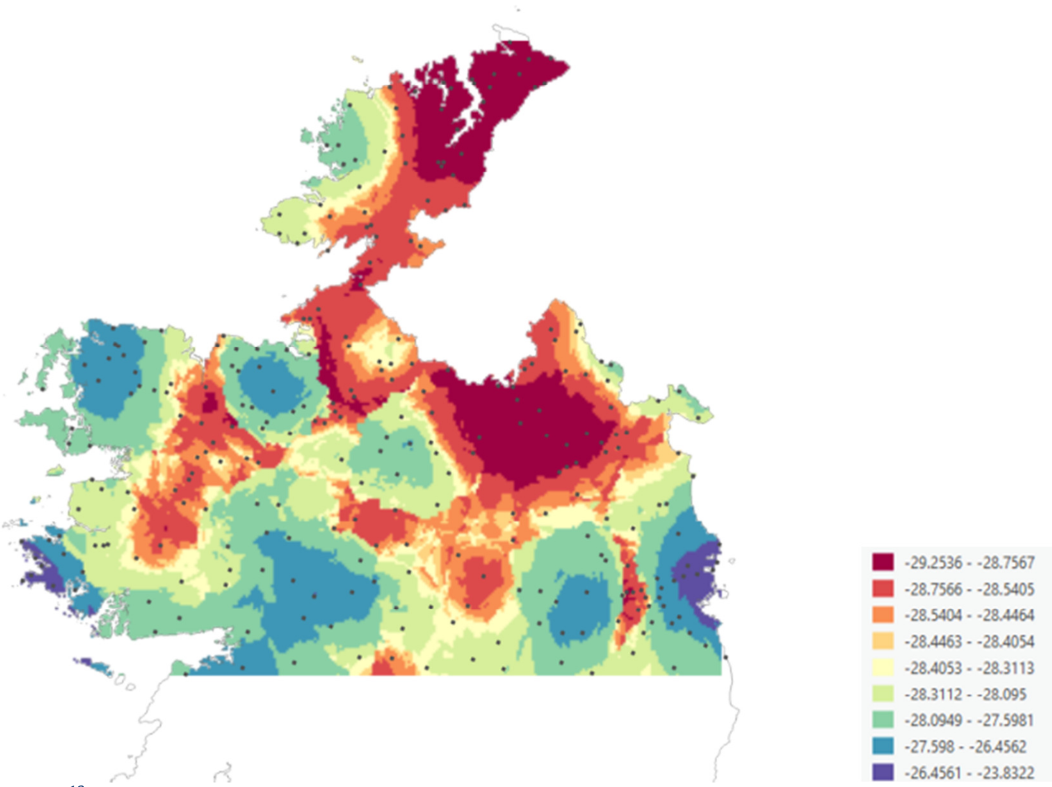

Figure 3 Bulk Soil $\delta^{13}C$ Isoscape. Black dots are sampling locations

a window between approximately -25‰ - -30‰. However, Figure 3 does reveal that most Kriging-derived depleted (more negative) values occupy the border counties and the most enriched (more positive) values were either around Dublin or the western tip of county Galway.

Soil carbon isotope values are reflective of the isotopic signature of its carbon inputs: overlying vegetation, soil type, biological breakdown etc. Soil type distribution in Ireland is incredibly complex but according to the Teagasc Soil Information System, Monaghan, Cavan and Leitrim are dominated by fine loams and peat and north Donegal predominantly by peat. Bulk soil carbon isotope chemistry can perhaps therefore contribute to the understanding of differing peat statuses within these areas – restored, degraded, pristine etc.

Bulk $\delta^{15}N$ values ranged from -1.92‰ (613647A) to 8.60‰ (582926A). The isoscape derived from this data (Figure 4) would suggest that most enriched nitrogen values were to be found in the western most counties (northwest Mayo specifically), again dominated by peatland and the most depleted within and to the north of Dublin. This east-west demarcation of isotope values is a theme that recurs with the remaining analyses.

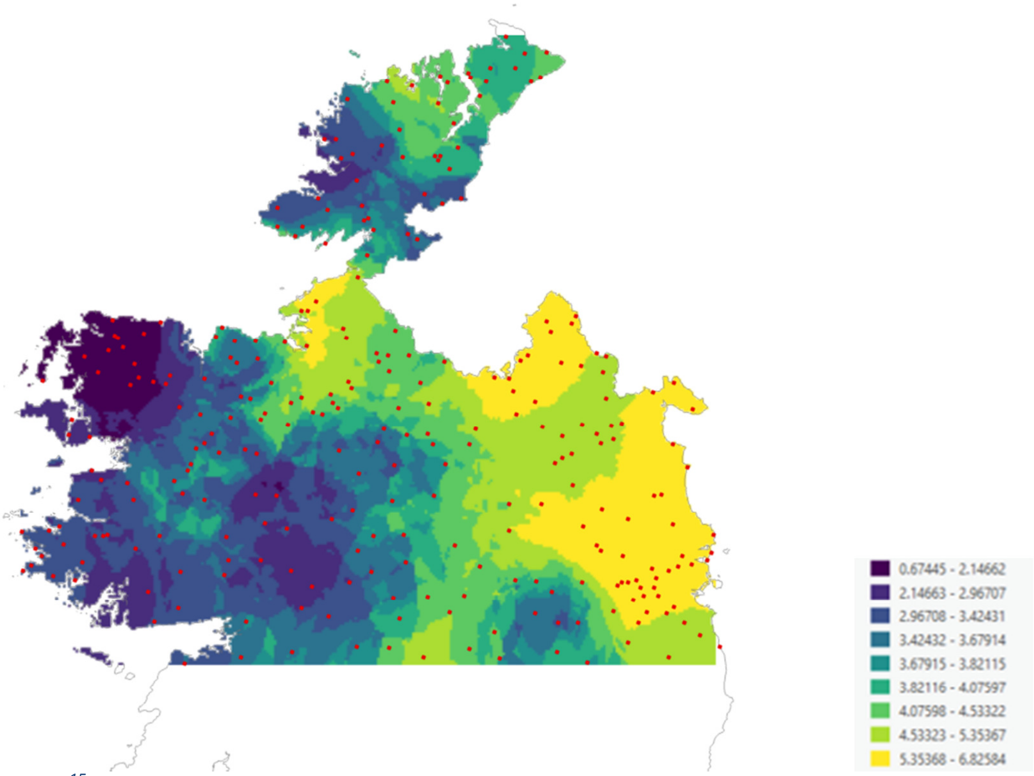

Figure 4 Bulk Soil δ^{15}N Isoscape. Red dots are sampling locations

Soil Carbonate δ^{13}C and δ^{18}O Analysis

245 Soil carbonate δ^{13}C and δ^{18}O values are listed in Section 3 and their isoscapes presented below in Figures 5 and 6. The caveat with soil carbonate analysis is that unlike bulk soil carbon and nitrogen analysis where no more than a milligram or two is required for analysis, this project found that on average, 300-350mg was required to obtain a measurable signal. Indeed, in some cases 500mg was not enough for a signal due to the lack of carbonate in the sample. Figures 5 and 6 again show the east-west gradation in isotope values for both.

Carbon values are reflective of the isotopic value of the soil gas, which in turn is determined by the isotopic value of the overlying vegetation. Such an isoscape can now serve as a baseline to possibly investigate future shifts in vegetation over. Other factors at play though include the degradation rate of organic matter and shifts in atmospheric CO_2, the former perhaps playing its part in the signal derived for the peatlands of Donegal, the West and Cavan/Monaghan as opposed to soils collected around Dublin.

The carbonate oxygen isotope value within soil is more a reflection of the oxygen isotopic value of the soil water at the point of collection and its source - meteoric or runoff for example. A visual comparison of Figure 6 with the oxygen values of surficial water (Figure 9) demonstrates a close correlation.

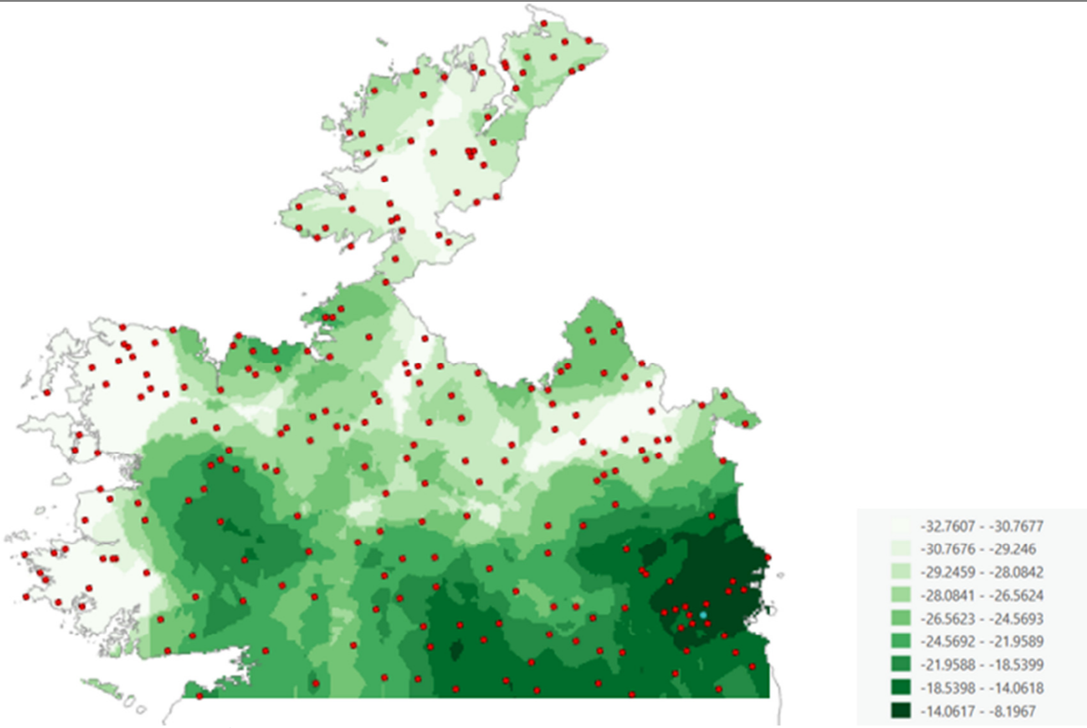

Figure 5 Soil carbonate δ^{13}C Isoscape. Red dots are sampling locations

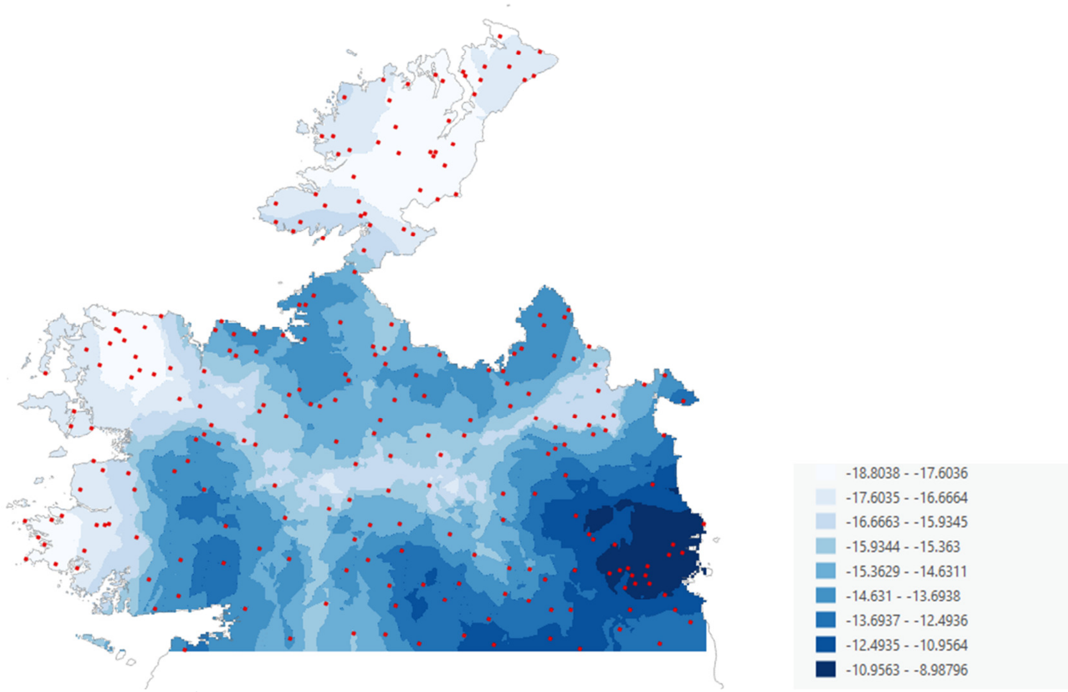

Figure 6 Soil carbonate δ^{18}O Isoscape. Red dots are sampling locations

Bulk Soil $\delta^{34}S$

In total, 294 bulk soil samples were analysed for their $\delta^{34}S$ values and results are tabulated in Section 3. Samples ranged from the most enriched, +16.00‰ (583330), west of Sligo to the most depleted -5.22‰ (650533) northwest Dublin. The latter may be an outlier within the dataset, however the next most depleted value is -2.44‰ (615315), outside of Trim in Meath. The overall isoscape for the dataset is presented in Figure 7.

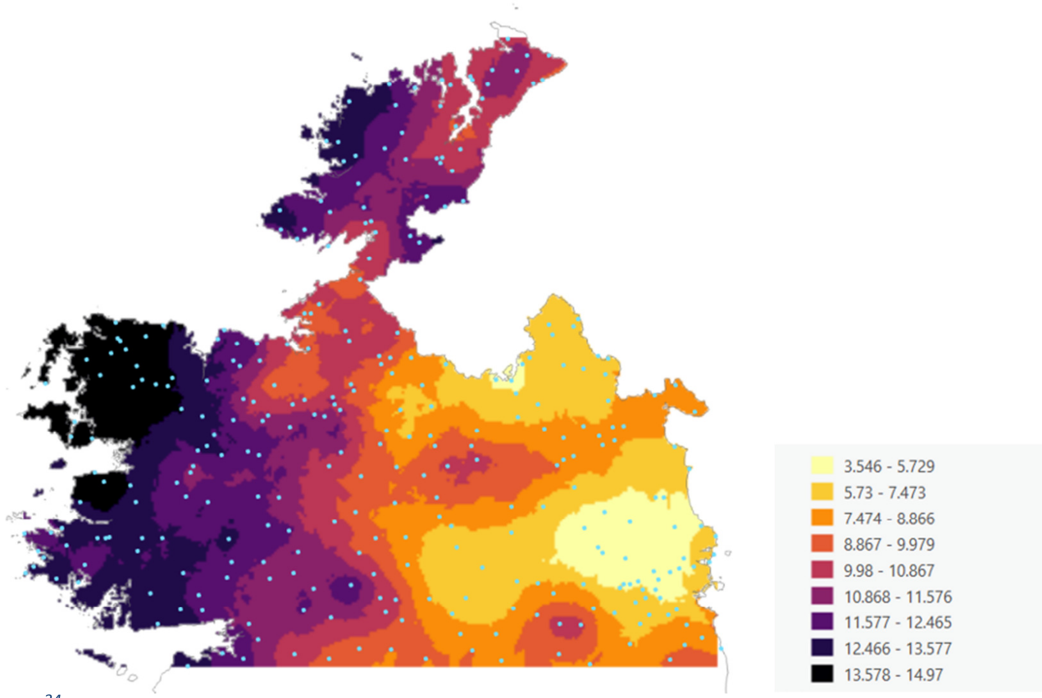

Figure 7 Bulk soil $\delta^{34}S$ Isoscape. Light blue dots are sampling locations

Sulphur isotopes in soil is a complex mix of factors including local lithology, provenance of rainfall, soil oxygen concentration, microbial processes within certain soil types etc. but the data here suggests that there is a predominant west east split in modelled values. Such a gradation has already been suggested from results of the Tellus Border project with samples also measured at QUB (Rock and Stack, 2011) with most positive values in the west and depleting the further one goes east. They suggest that gleying or organic matter content is the most controlling factor. The predominance of peat in the west and central midlands may reinforce this theory.

Fortunately, in addition to the sulphur isotopic values of the soil, sulphur content was also recorded and a modelled map of its distribution is shown in Figure 8. In general, peat has a sulphur content in the range 0.1-0.4% and Figure 8 suggests that indeed, it is the western counties that exist within this range.

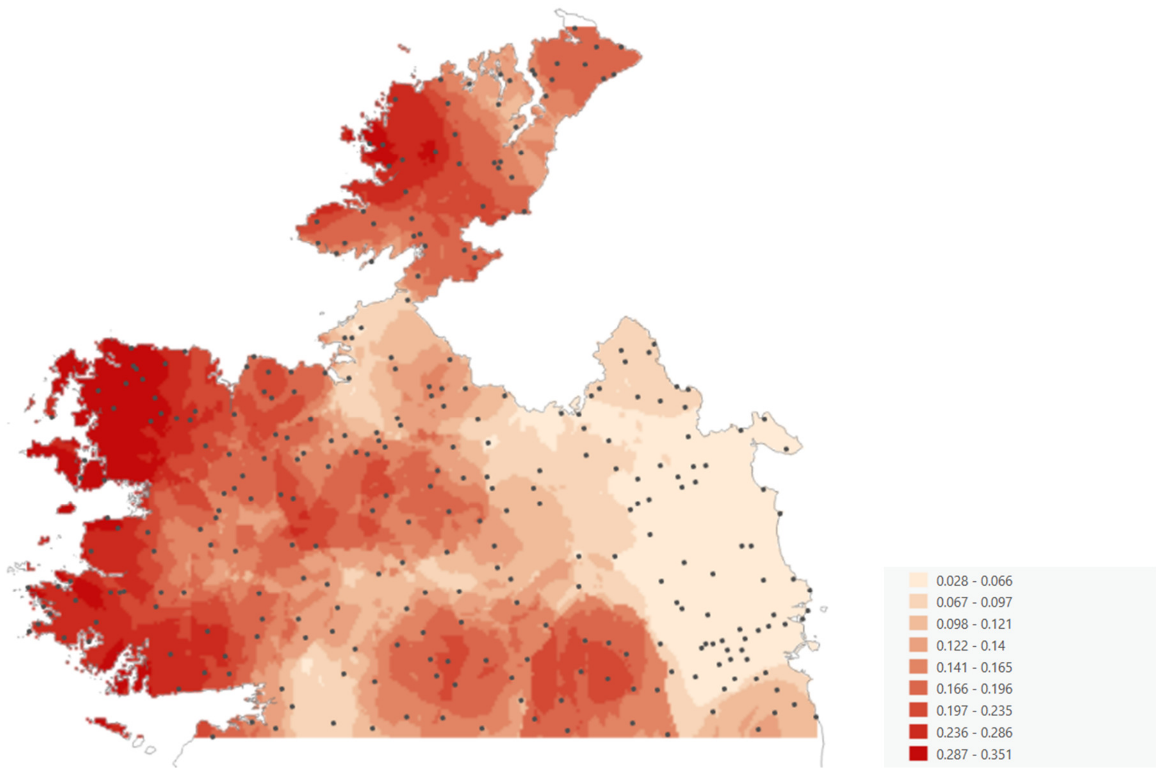

Figure 8 Modelled percentage sulphur content of soil samples. Black dots are sampling locations

Surficial Water δ^{18}O and δ^{2}H

337 water samples from the G1, G3 and G4 survey areas were analysed for their δ^{18}O and δ^{2}H signature. Results are displayed in Section 3 and their isoscapes presented in Figures 9 and 10, respectively. Values for both isotopes covered a wide range with hydrogen values ranging from +0.27‰ to -54.59‰ and oxygen from -0.9‰ to -7.99‰. The most positive sample for both isotopes was from outside Clifden in County Galway and the most negative from Kinnagoe Bay, County Donegal. There is a strong relationship between δ^{18}O and δ^{2}H as shown Figure 11 and how it compares to the Global Meteoric Water Line is also shown. This local relationship allows the d-excess to be calculated which can be used to identify source regions of rainfall and chart the evaporative behaviour of the freshwater system.

Result interpretation is constrained because samples were collected at different times of the year as well as over a number of years. Also, they represent only a snapshot of the prevailing conditions at the time of collection. However, the results would appear to adhere to predictive behaviour. For example, prevailing wind conditions and air masses bring rainfall predominantly from the Atlantic and isotopic dynamics dictate that the most enriched isotopes rainout first and get progressively more depleted as rainfall events passes over the land (continentality effect). To have such an effect feedthrough to surficial waters is to be expected, however this would be to ignore other contributory inputs to a complex system such as the lithography and the soil type over which the water is flowing. Again, the isoscapes suggest that the predominance of peatlands to the west and northwest may have a role to play.

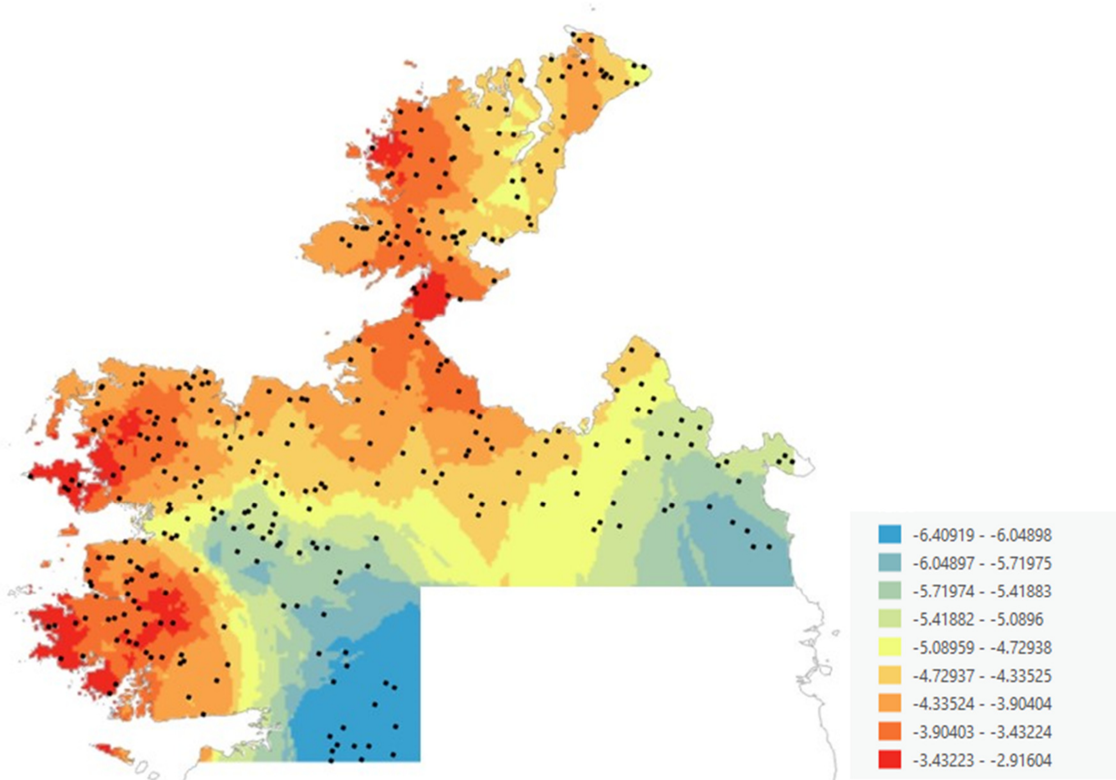

Figure 9 Surficial Water $\delta^{18}O$ Isoscape. Black dots are sampling locations

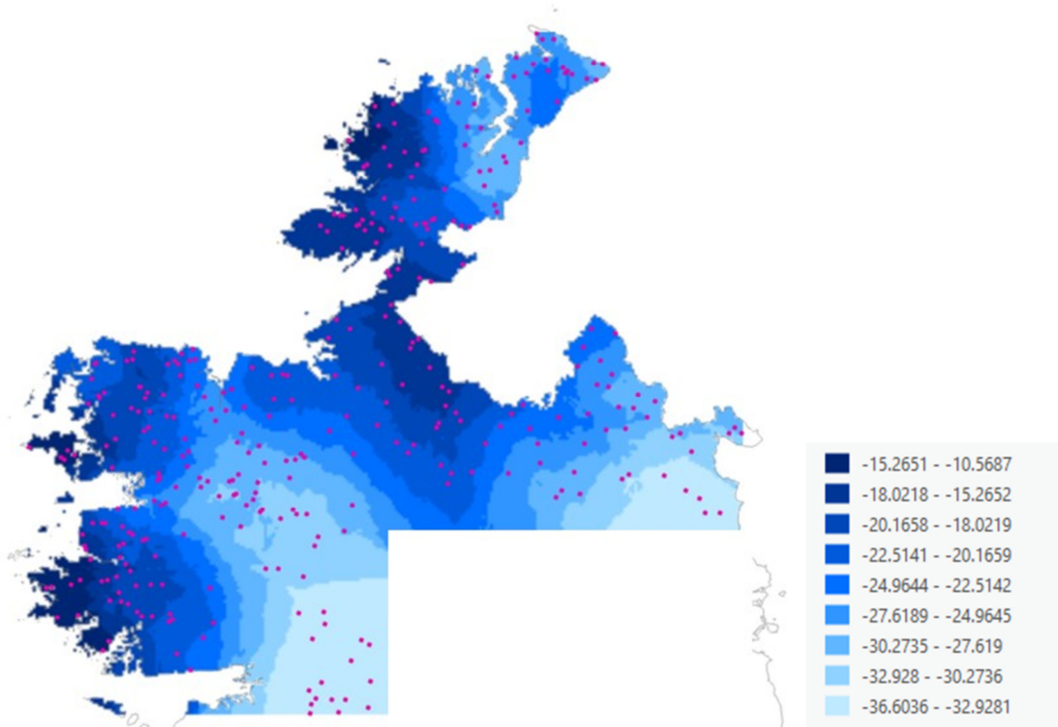

Figure 10 Surficial Water $\delta^{2}H$ Isoscape. Purple dots are sampling locations

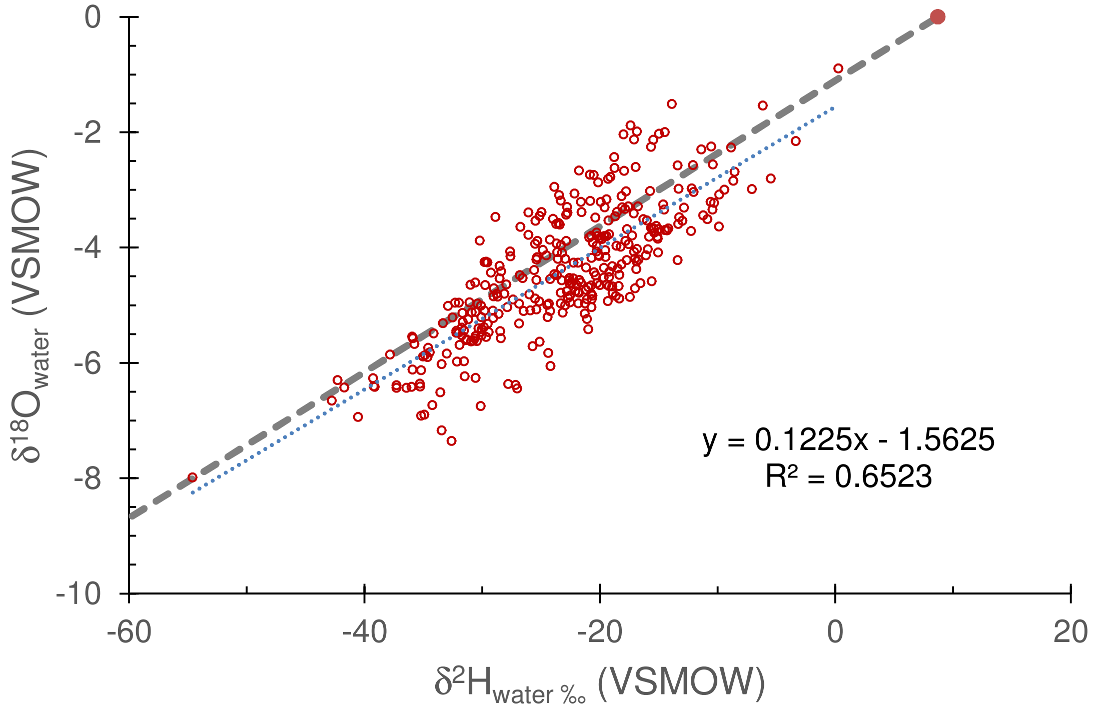

Figure 11 Relationship between δ^2H and δ^{18}O of 337 water samples. Grey dashed line is the Global Meteoric Water line. Blue dotted line is the freshwater line for this study. VSMOW (Vienna Standard Mean Ocean Water) is the international isotopic standard for water.

Surficial Water δ^{13}C DIC

Surficial water $\delta^{13}C_{DIC}$ can be both an indication of DIC source (or sink) as well as provide an insight into water purity. From the 217 samples analysed (not all samples contained enough carbon for analysis), values ranged from -12.65‰ (604039W) near Clough in County Galway to -2.67‰ (585080W) near Gleneely in County Donegal. As before, the predominance of the most enriched samples was to be found in the west (Donegal, western Mayo and Galway). Interestingly, there is an axis of depleted values stretching southeast from Ballina in County Mayo into Galway to the extremity of the sampling area. As Figure 13 shows there is a predominance of raised, deeper bogs in this locale so perhaps with a better developed sphagnum layer when compared to the blanket bogs to the west this can affect the water isotope chemistry of water bodies as they course through the area.

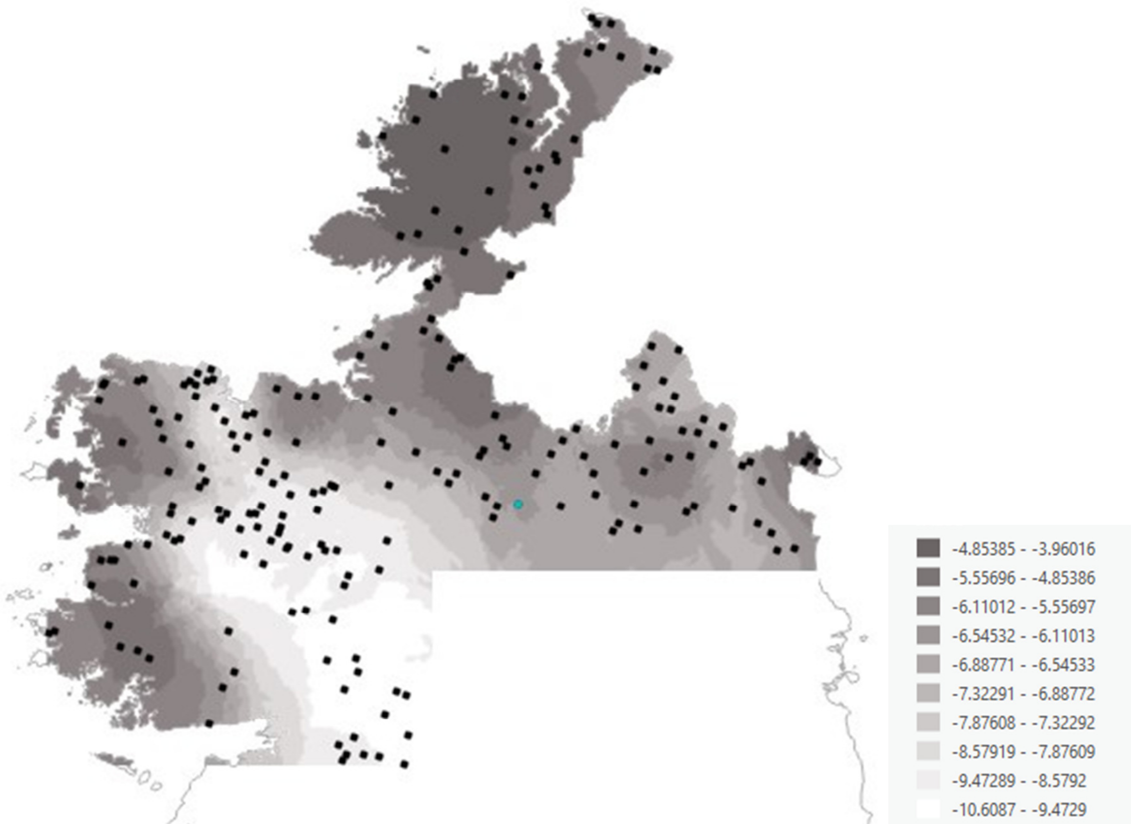

Figure 12 Surficial Water $\delta^{13}C_{DIC}$ Isoscape. Black dots are sampling locations

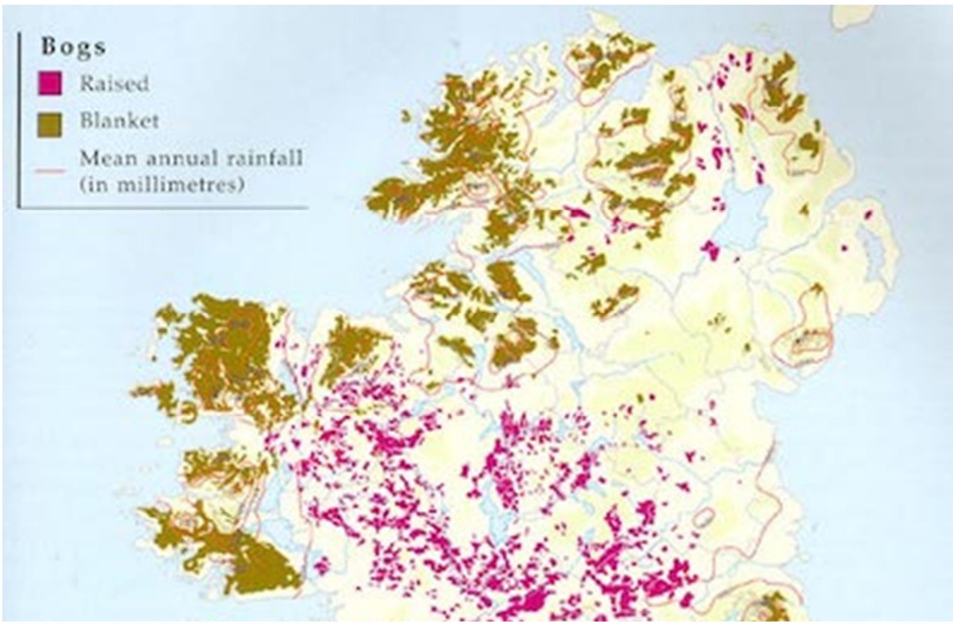

Figure 13 Raised and Blanket Bogs of Ireland. Source: www.askaboutireland.ie

(iv) Impact

- Relevance/application to GSI programmes, where applicable

All data collected in this project supplements other geochemical analysis carried out as part of the TELLUS program. The project can also be seen to compliment other past Tellus projects such as 2017-SC-004 "Iso-Mech (Development of a national groundwater isoscape for mechanistic recharge estimation and bacterial fingerprinting) especially as this project deals with surface waters as opposed to groundwater.

- Other impacts

In addition to adding to the body of knowledge of past isotopic analysis not only on Tellus samples (e.g. Rock and Stack, 2011) but within relevant previous PhD projects carried out in QUB, data gathered as part of this project should serve to inform a range of interested parties: particularly peatland ecologists in the first instance but others should find the data informative: climate modellers (especially the water isotopes), participants within the agri-food industry, policy makers etc.

Publications:

The author and colleagues are currently subjecting the initial data to further analysis such as PCA and R-Stats with the goal of being published in a high-impact journal in 2022. Also planned is delivery of said data at a major national/international conference TBD in summer/autumn 2022

3. *Supplemental information/datasets*

Bulk Soil δ^{13}C and δ^{15}N values

Sample Number	Easting	Northing	δ^{13}C	δ^{15}N
580032	252773	446597	**-28.63**	**3.19**
580062	245128	453112	**-29.30**	**5.11**
580107	248809	440751	**-27.96**	**1.96**
580136	238904	440861	**-28.69**	**1.51**
580143	237379	435261	**-27.88**	**0.26**
580178	261324	446711	**-29.23**	**5.37**
580190	234958	429514	**-28.49**	**4.54**
580233	230480	438536	**-29.37**	**6.03**
580289	255143	435511	**-30.24**	**5.91**
580298	258718	437119	**-29.62**	**5.43**
580300	231214	437164	**-30.11**	**4.81**
580335	219450	437247	**-27.60**	**6.72**
580342	224778	418802	**-29.21**	**4.95**
580349	222419	435074	**-29.96**	**3.17**
580425	217375	406370	**-28.71**	**1.62**
580437	218659	404579	**-28.66**	**1.58**
580452	219408	406440	**-29.69**	**4.57**
580458	223160	401056	**-27.96**	**4.95**
580463	218636	426648	**-29.55**	**5.65**
580510	227531	389423	**-28.17**	**1.44**
580533	220293	387205	**-28.44**	**2.10**
580609	198416	435456	**-28.93**	**5.06**
580636	208532	433699	**-29.15**	**4.69**
580680	200931	426963	**-27.86**	**1.48**
580701	213157	391070	**-29.14**	**5.96**
580707	204826	405707	**-28.66**	**4.75**
580796	226482	409683	**-29.98**	**5.07**
580849	203455	416443	**-27.77**	**5.51**
580900	182888	428582	**-28.15**	**4.59**
580907	185165	407194	**-27.80**	**2.38**
580926	173750	412969	**-27.47**	**2.31**
580931	178574	412799	**-27.14**	**0.95**

580962	180600	405300	**-27.35**	**2.00**
581063	186446	396267	**-28.56**	**2.78**
581120	171568	389480	**-28.89**	**5.01**
581133	175071	384973	**-28.81**	**0.88**
581143	196588	410225	**-29.16**	**5.06**
581174	189314	380710	**-28.86**	**3.47**
581220	174490	371723	**-28.68**	**5.70**
581242	165202	378296	**-28.25**	**2.41**
581297	162285	374673	**-26.98**	**5.55**
581304	191221	381640	**-27.99**	**1.66**
581340	155402	385744	**-28.66**	**3.50**
581351	190542	366820	**-28.83**	**6.17**
581383	193144	377056	**-29.15**	**6.79**
581394	187240	358480	**-29.36**	**4.45**
581397	155697	378279	**-28.02**	**2.11**
581448	210462	373363	**-28.39**	**2.05**
581475	206729	375717	**-28.21**	**2.21**
581513	249238	304505	**-29.82**	**3.40**
581518	188556	386743	**-28.30**	**2.62**
581539	246610	318750	**-28.67**	**6.64**
581592	240605	319136	**-28.57**	**3.95**
581596	248295	313565	**-29.55**	**6.12**
581620	270839	340393	**-28.48**	**3.57**
581643	261328	340967	**-29.62**	**4.70**
581660	272810	343114	**-28.34**	**7.23**
581733	230801	292806	**-29.60**	**4.11**
581761	233139	298945	**-29.21**	**6.94**
581813	259654	299694	**-28.83**	**5.45**
581818	256873	309360	**-28.74**	**6.07**
581904	201693	337606	**-27.88**	**2.59**
581914	199033	327721	**-27.17**	**3.88**
582048	284567	310988	**-29.36**	**4.86**
582077	220946	325121	**-29.27**	**3.93**
582144	262845	336869	**-28.31**	**6.19**
582197	207124	327634	**-28.49**	**4.75**
582204	267140	324750	**-29.33**	**4.42**
582225	253646	327533	**-28.58**	**7.55**
582255	280762	328347	**-28.55**	**4.40**

582265	211489	316964	**-29.18**	**4.40**
582271	284682	327221	**-24.82**	**5.70**
582331	274865	323387	**-29.14**	**5.30**
582481	290737	300832	**-28.16**	**3.00**
582504	264596	285310	**-29.26**	**4.48**
582506	267153	287576	**-28.99**	**4.02**
582563	267194	295957	**-29.14**	**4.46**
582583	275009	300682	**-29.57**	**4.32**
582624	286448	300259	**-28.93**	**5.89**
582633	287232	294998	**-27.13**	**7.46**
582637	306444	272885	**-26.79**	**6.69**
582649	281061	296951	**-29.22**	**5.03**
582655	302805	313090	**-28.87**	**5.84**
582772	316690	283739	**-28.15**	**7.44**
582782	310784	292603	**-29.23**	**7.79**
582792	311046	316748	**-27.90**	**5.44**
582803	216598	292729	**-28.89**	**3.94**
582820	199497	321467	**-28.28**	**4.66**
582832	318725	306652	**-27.75**	**6.21**
582842	283521	321128	**-28.56**	**5.97**
582844	214640	296900	**-29.48**	**4.53**
582872	195188	325060	**-29.38**	**4.31**
582902	206353	296454	**-21.53**	**4.70**
582923	215105	308802	**-28.84**	**5.32**
582926	251070	325345	**-27.34**	**8.60**
582974	194516	328502	**-27.90**	**1.29**
583056	202832	307091	**-29.93**	**4.99**
583058	197292	298899	**-29.08**	**5.00**
583142	166789	331189	**-28.77**	**5.28**
583221	169288	305283	**-28.82**	**5.85**
583229	177009	309247	**-28.83**	**5.12**
583237	150708	305062	**-27.94**	**1.59**
583239	179272	307174	**-28.87**	**2.24**
583252	148837	302791	**-28.80**	**4.53**
583255	165034	311076	**-29.18**	**5.69**
583283	172972	304809	**-28.86**	**4.87**
583330	138622	333406	**-27.28**	**-0.29**
583365	131142	335043	**-29.07**	**4.49**

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583366	160660	309210	**-28.83**	**5.99**
583375	133613	338784	**-28.38**	**6.73**
583388	176338	312254	**-29.30**	**4.53**
583434	139582	324532	**-28.16**	**0.82**
583453	141074	311541	**-29.11**	**6.32**
583456	137162	326737	**-27.19**	**0.23**
583483	144920	310611	**-29.24**	**4.47**
583509	158396	332913	**-29.56**	**4.56**
583515	183342	317260	**-28.55**	**8.49**
583583	184559	314811	**-28.34**	**3.32**
583635	165070	345338	**-29.50**	**6.54**
583661	182723	334519	**-28.39**	**6.46**
583733	153191	316986	**-17.27**	**4.20**
583748	167552	345244	**-28.36**	**7.47**
583777	181227	338336	**-28.82**	**5.54**
583797	170801	348701	**-28.31**	**5.41**
583891	146700	333413	**-28.83**	**6.49**
583985	147553	326436	**-27.70**	**1.38**
610044	82760	282573	**-29.10**	**4.41**
610075	86370	278812	**-28.29**	**2.40**
610168	96493	277547	**-27.45**	**0.51**
610211	63414	317590	**-28.47**	**4.64**
610243	94737	330986	**-27.39**	**0.11**
610248	89158	329523	**-27.24**	**1.22**
610442	73508	296605	**-28.17**	**3.33**
610446	83670	256822	**-28.12**	**2.41**
610455	60603	251621	**-28.68**	**3.98**
610466	81626	295591	**-27.73**	**3.71**
610501	55589	243143	**-28.54**	**5.48**
610539	69697	260557	**-27.69**	**4.24**
610540	62729	249023	**-27.92**	**2.31**
610563	58648	245360	-4.72	**2.05**
610564	55011	258332	**-28.32**	**2.49**
610596	65565	258952	**-29.18**	**3.40**
610621	88526	257079	**-27.92**	**4.03**
610638	76152	239342	**-28.43**	**1.90**
610656	67533	241021	**-28.38**	**2.04**
610669	71595	253618	**-27.71**	**3.30**

610683	78709	246260	**-28.09**	**4.77**
610700	77113	271041	**-27.67**	**1.65**
610852	74832	302396	**-27.04**	**1.91**
610854	87158	256714	**-28.06**	**2.62**
610868	114832	278464	**-27.66**	**4.52**
610905	102906	336350	**-26.92**	**0.02**
610936	92880	334658	**-27.01**	**1.08**
610944	91516	335554	**-27.13**	**0.13**
610953	90767	341659	**-27.96**	**0.84**
610975	109517	340646	**-28.69**	**5.11**
611009	84957	321037	**-27.18**	**0.83**
611040	113233	319685	**-29.19**	**5.31**
611041	79526	327066	**-27.72**	**0.87**
611137	120418	282636	**-29.57**	**4.38**
611142	194821	293620	**-27.30**	**0.23**
611146	97599	316283	**-27.00**	**0.78**
611209	106576	317237	**-27.01**	**0.23**
611212	126925	318750	**-28.97**	**4.98**
611215	101165	319180	**-27.22**	**0.74**
611283	142924	290695	**-29.03**	**5.21**
611296	111492	316620	**-29.51**	**5.28**
611300	99361	324288	**-27.76**	**1.34**
611332	125094	304829	**-28.12**	**1.16**
611335	137118	303342	**-29.48**	**5.53**
611350	118399	273300	**-29.12**	**4.84**
611382	116810	307638	**-28.72**	**1.19**
611452	132650	289474	**-26.68**	**-1.20**
611495	126823	292983	**-28.73**	**1.57**
611547	129715	297016	**-29.40**	**3.96**
611550	123355	291242	**-26.43**	**5.04**
611675	121547	285150	**-30.48**	**5.75**
615798	282581	251018	**-26.71**	**5.91**
616027	136373	247157	**-28.27**	**5.82**
650017	299163	233286	**-28.27**	**5.82**
650039	293318	238557	**-28.48**	**4.95**
650062	295280	231706	**-28.98**	**6.34**
650069	296598	239641	**-29.06**	**5.61**
650089	290762	238801	**-29.45**	**5.83**

650096	298187	236450	**-29.01**	**5.25**
650226	315401	222673	**-28.68**	**5.27**
650252	305188	233429	**-24.85**	**5.92**
650324	300652	226653	**-29.13**	**4.83**
650339	311376	228662	**-27.11**	**6.32**
650384	324284	247171	**-19.24**	
650400	308273	226357	**-24.29**	**3.67**
650431	314294	248791	**-28.44**	**6.42**
650435	318254	245697	**-25.98**	**4.36**
650499	326131	250267	**-27.48**	**6.35**
650533	309128	243335	**-21.25**	**6.35**
650576	304392	240506	**-28.29**	**5.37**
650585	312735	244859	**-27.10**	**6.70**
650641	302426	243807	**-29.39**	**4.61**
650676	303325	236539	**-27.30**	**6.36**
611794	98858	271059	**-28.63**	**3.97**
611859	99608	251700	**-28.80**	**2.10**
611920	119151	206560	**-28.34**	**3.83**
611960	117463	242918	**-28.78**	**4.67**
612002	107255	222986	**-27.57**	**2.58**
612014	116551	228593	**-27.38**	**0.94**
612040	104708	235003	**-27.27**	**1.78**
612135	141230	209251	**-23.90**	**4.24**
612190	143386	223058	**-29.79**	**4.64**
612199	109084	256779	**-29.65**	**3.76**
612311	134762	241361	**-28.01**	**3.95**
612330	135485	256464	**-27.23**	**-1.35**
612385	126987	270848	**-28.14**	**5.33**
612505	159555	300513	**-28.48**	**2.59**
612538	147302	289265	**-28.08**	**2.23**
612635	155112	272620	**-29.08**	**3.69**
612793	164834	228480	**-26.69**	**-0.66**
612812	321580	217600	**-28.72**	**4.13**
612977	149083	247301	**-29.56**	**5.28**
613000	161343	211080	**-29.10**	**3.65**
613021	160924	243101	**-28.62**	**4.01**
613045	159078	259638	**-27.26**	**-0.91**
613215	179634	290446	**-26.16**	**-1.48**

613271	175419	225323	**-29.61**	**5.46**
613272	217048	272852	**-27.32**	**2.36**
613302	168872	237023	**-20.22**	**2.75**
613303	186693	213095	**-28.94**	**5.78**
613484	199150	213001	**-29.27**	**5.25**
613592	176919	263187	**-28.94**	**4.05**
613618	200941	232509	**-27.85**	**3.01**
613647	183613	238492	**-26.58**	**-1.92**
613648	201486	284699	**-29.43**	**3.38**
613761	186872	250809	**-29.12**	**4.15**
613764	193276	256679	**-29.47**	**4.16**
613898	192403	242726	**-26.45**	**3.50**
613928	203414	224355	**-28.48**	**4.73**
613937	225103	253108	**-28.90**	**4.88**
613986	185113	266924	**-29.24**	**5.64**
614094	205688	246422	**-28.23**	**4.40**
614095	200757	270696	**-28.63**	**3.61**
614197	187303	281158	**-28.88**	**5.86**
614212	212804	209254	**-27.73**	**5.94**
614222	205021	257136	**-28.54**	**4.90**
614291	282579	293177	**-28.86**	**5.36**
614356	221374	284969	**-27.89**	**2.00**
614517	228832	233416	**-29.50**	**5.51**
614574	214477	233013	**-27.93**	**2.54**
614599	223179	226928	**-28.10**	**2.21**
614773	246517	258951	**-28.50**	**6.85**
614840	235000	245000	**-28.97**	**5.31**
615089	240608	218998	**-28.19**	**5.80**
615102	271054	289025	**-28.94**	**3.50**
615128	259186	269207	**-27.37**	**5.91**
615166	248749	239656	**-27.49**	**1.74**
615202	256916	239250	**-29.16**	**6.56**
615297	150686	261604	**-25.79**	**2.22**
615315	275375	260590	**-28.80**	**7.31**
615316	275006	238724	**-22.10**	**5.59**
615388	263053	235179	**-29.11**	**4.94**
615435	277367	207010	**-28.84**	**5.47**
615439	289192	237237	**-29.86**	**5.48**

615574	283124	267217	**-27.93**	**5.72**
615577	242748	208749	**-28.66**	**5.54**
615664	293257	214953	**-28.77**	**5.79**
615677	326792	257226	**-27.41**	**7.32**
615687	303285	272861	**-29.69**	**6.19**
615691	246620	269225	**-28.66**	**5.13**
615732	310908	261059	**-27.10**	**7.45**
615734	280856	252916	**-29.58**	**6.38**
615867	293108	263188	**-28.45**	**5.67**
615987	231033	212496	**-27.95**	**5.12**
615989	291290	248810	**-28.17**	**5.91**
616004	297117	222809	**-29.92**	**5.70**
616089	308995	209022	**-27.78**	**2.73**
616170	287301	227095	**-27.27**	**5.89**
616217	273694	222540	**-26.46**	**-1.79**
616226	265127	211136	**-27.86**	**5.10**
616231	271278	276769	**-28.06**	**4.89**
616271	265520	222829	**-26.87**	**-1.32**
616475	256660	226583	**-27.98**	**0.86**

Soil Carbonate $\delta^{13}C$ and $\delta^{18}O$ values

Sample Number	Easting	Northing	$\delta^{13}C$	$\delta^{18}O$
580032	252773	446597	**-31.67**	**-18.52**
580062	245128	453112	**-30.51**	**-17.75**
580107	248809	440751	**-30.63**	**-14.35**
580136	238904	440861	**-32.14**	**-18.43**
580143	237379	435261	**-30.34**	**-18.56**
580178	261324	446711	**-32.18**	**-19.17**
580190	234958	429514	**-14.49**	**-14.60**
580233	230480	438536	**-32.40**	**-18.82**
580289	255143	435511	**-32.74**	**-19.21**
580298	258718	437119	**-12.90**	**-13.51**
580300	231214	437164	**-33.16**	**-19.40**
580335	219450	437247	**-25.63**	**-17.01**
580342	224778	418802	**-32.29**	**-18.81**
580349	222419	435074	**-26.51**	**-18.02**
580425	217375	406370	**-31.24**	**-17.73**
580437	218659	404579	**-31.80**	**-19.94**

580452	219408	406440	**-32.92**	**-19.97**
580458	223160	401056	**-8.17**	**-12.51**
580510	227531	389423	**-31.19**	**-18.56**
580533	220293	387205	**-31.64**	**-18.46**
580609	198416	435456	**-33.06**	**-18.90**
580636	208532	433699	**-33.26**	**-19.54**
580680	200931	426963	**-31.93**	**-19.72**
580701	213157	391070	**-33.04**	**-19.06**
580707	204826	405707	**-32.27**	**-18.51**
580796	226482	409683	**-32.22**	**-18.70**
580849	203455	416443	**-31.04**	**-18.04**
580900	182888	428582	**-2.32**	**-8.25**
580907	185165	407194	**-31.83**	**-18.99**
580926	173750	412969	**-30.32**	**-17.59**
580931	178574	412799	**-30.14**	**-18.13**
580962	180600	405300	**-31.43**	**-17.90**
581063	186446	396267	**-32.39**	**-18.09**
581120	171568	389480	**-32.98**	**-18.22**
581133	175071	384973	**-31.65**	**-18.16**
581143	196588	410225	**-31.40**	**-17.47**
581174	189314	380710	**-32.50**	**-17.48**
581220	174490	371723	**-0.94**	**-6.24**
581242	165202	378296	**-31.86**	**-17.56**
581297	162285	374673	**-32.03**	**-17.93**
581304	191221	381640	**-31.28**	**-18.35**
581340	155402	385744	**-31.66**	**-17.47**
581351	190542	366820	**-31.46**	**-17.04**
581383	193144	377056	**-33.22**	**-16.75**
581394	187240	358480	**-30.04**	**-15.11**
581397	155697	378279	**-29.99**	**-16.74**
581448	210462	373363	**-30.97**	**-17.58**
581475	206729	375717	**-31.48**	**-16.87**
581513	249238	304505	**-31.55**	**-15.21**
581518	188556	386743	**-31.43**	**-17.18**
581539	246610	318750	**-30.40**	**-14.03**
581592	240605	319136	**-31.04**	**-15.63**
581596	248295	313565	**-33.05**	**-15.16**
581620	270839	340393	**-23.21**	**-14.44**
581643	261328	340967	**-32.30**	**-16.56**
581660	272810	343114	**-28.20**	**-15.05**
581733	230801	292806	**-32.96**	**-16.19**

581761	233139	298945	**-32.72**	**-15.65**
581813	259654	299694	**-31.20**	**-16.63**
581818	256873	309360	**-32.90**	**-15.63**
581904	201693	337606	**-30.81**	**-16.65**
581914	199033	327721	**-31.91**	**-16.49**
582048	284567	310988	**-32.86**	**-16.29**
582077	220946	325121	**-33.44**	**-16.48**
582144	262845	336869	**-2.92**	**-9.51**
582197	207124	327634	**-26.43**	**-13.92**
582204	267140	324750	**-32.16**	**-15.17**
582225	253646	327533	**-26.56**	**-15.08**
582255	280762	328347	**-32.51**	**-17.44**
582265	211489	316964	**-30.68**	**-16.52**
582331	274865	323387	**-33.39**	**-15.19**
582481	290737	300832	**-31.95**	**-18.04**
582504	264596	285310	**-30.57**	**-16.27**
582506	267153	287576	**-30.07**	**-16.42**
582563	267194	295957	**-33.60**	**-16.78**
582583	275009	300682	**-33.69**	**-16.56**
582624	286448	300259	**-24.58**	**-15.12**
582633	287232	294998	**-20.82**	**-12.87**
582637	306444	272885	**-7.40**	**-9.27**
582649	281061	296951	**-32.66**	**-16.95**
582655	302805	313090	**-33.14**	**-16.94**
582782	310784	292603	**-31.49**	**-15.75**
582792	311046	316748	**-31.26**	**-15.26**
582803	216598	292729	**-32.31**	**-15.17**
582820	199497	321467	**-31.72**	**-13.46**
582832	318725	306652	**-5.62**	**-6.92**
582842	283521	321128	**-31.81**	**-15.30**
582872	195188	325060	**-32.32**	**-14.91**
582923	215105	308802	**0.60**	**-6.83**
582926	251070	325345	**-2.37**	**-8.11**
582974	194516	328502	**-30.41**	**-15.81**
583056	202832	307091	**-32.60**	**-16.08**
583058	197292	298899	**-28.73**	**-14.47**
583142	166789	331189	**-5.87**	**-10.04**
583221	169288	305283	**-3.25**	**-8.03**
583237	150708	305062	**-31.26**	**-17.01**
583239	179272	307174	**-31.29**	**-15.37**
583252	148837	302791	**-31.83**	**-16.12**