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Geoscience Research
GSI
Suirbhéireacht Gheolaíochta Éireann
Geological Survey of Ireland

Geological Survey of Ireland Research Programme
- Short Call 2015, Final Report -

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Organisation name	Trinity College		
Organisation type:	☒HEI	☐Public Sector (other)	☒Private Sector
Department/section	Geology		

Project Title	Assessing marine and anthropogenic influences on the terrestrial biosphere strontium isotope budget
Contract No.	2015-sc-061

INFOMAR
Integrated Mapping for the Sustainable Development of Ireland's Marine Resource

Tellus
Understanding Underground

Marine Institute
Foras na Mara

2. Project information:

Title of project	Assessing marine and anthropogenic influences on the terrestrial biosphere strontium isotope budget
Did you make any formal amendment to the project workplan / budget?	☒ yes ☐ no If yes, please specify: Subsequent to signing the research contract, it was noticed that the original budget had included a TCD charge related to indirect costs, which was incorrect. The budget was adjusted accordingly; this did not affect GSI's contribution. The final budget statement differs slightly from that which is in the signed contract. Aoife Braiden at GSI Research was notified of this change on March 8th 2016.

Project Report (*max 1500 words, excluding figures and headings*):

(i) Objectives and scientific/engineering targets beyond the state of the art

The use of Sr isotopes in biosphere studies is a novel research application and one which is becoming widely used as a provenance tool with wide ranging applications (e.g. animal migration, archaeology, food authentication and forensic science). Despite proliferation of the technique, Sr isotope maps (Sr "isoscapes") are frequently solely based on $^{87}Sr/^{86}Sr$ values measured or inferred from bedrock

composition, with little or no consideration given to deviations from bedrock values due to interaction or contributions from other reservoirs. Scientifically, the main objective of this project is to gain a better understanding of the extent to which the terrestrial Sr isotope budget is affected by additions from marine and anthropogenic reservoirs. Samples and sample sites were carefully selected based on geochemical variations evident from existing Tellus soil data. The high-spatial resolution and high sample density Tellus soil geochemistry datasets was integrated with high-precision $^{87}Sr/^{86}Sr$ measurement of bulk soil, soil cation extracts, vegetation, stream water and commonly used fertilisers.

Main scientific outcomes: Our research shows that the Sr terrestrial biosphere budget in Ireland is strongly affected by both marine-derived and anthropogenic sources reservoirs. Dispersion of marine-derived Sr is assisted by (i) prevailing south westerly Atlantic winds, (ii) areas of enhanced rainfall and (iii) the presence of blanket bogs. Up to 90% of plant Sr may by derived from marine sources and this affect is not limited to the west coast, as noted from sample transects along south and eastern Ireland. These sample transects demonstrate that plant $^{87}Sr/^{86}Sr$ trends towards marine values approaching coastlines and that this effect is measureable several km from coastal areas. In the case of anthropogenic Sr contributions, analysis of stream waters from Co. Antrim indicates that up to 75-80% of dissolved Sr has been derived from fertiliser. This is likely to be an extreme case, in that water samples were collected over the same time period as fertiliser application. Analysis of oak tree cores from Co. Antrim show that a significant shift in $^{87}Sr/^{86}Sr$ occurred between 1947 and 1965 for a tree grown on agricultural land, but not for a tree on non-agricultural land during the same time interval. This demonstrates, for the first time, that modern fertilisers have a significant and lasting effect on local Sr isotope signatures.

All project outcomes were met. There were no major difficulties in completing the project. In terms of advancing the state of the art, our results show that in addition to bedrock sources, Sr isotope of the terrestrial biosphere need to consider both marine-derived and anthropogenic sources as possible contributors to the overall Sr budget. Given that several Sr-isoscapes have been based on or inferred from bedrock composition, this research makes a fundamental contribution to our understanding of cycling of Sr through the terrestrial biosphere. This has particular relevance to archaeological research, as well as studies of animal migration (both modern and past), food authentication, forensic science and hydrogeology.

(ii) Implementation

One deviation from implementation of the project plan was that some of the Sr isotope measurements were conducted (by Saskia Ryan) at Cambridge University (UK), this allowed the project milestones to be completed on-time, which would not have been the case if all the Sr isotope analyses had been conducted at the University of Belgium as planned. The following is an outline of how the scientific and management objectives were implemented.

Marine Sr Reservoir

Integrating existing Tellus data

The Chemical Index of Alternation (CIA) (Nesbitt & Young, 1982) was applied to Tellus topsoil geochemistry. The CIA illustrates relative changes in concentrations of calcium (Ca), potassium (K), sodium (Na) and and aluminium (Al) and hence the degree of weathering. Because Sr readily substitutes for Ca, the CIA data are also indicative of potential Sr reservoirs. Na, K and Ca are largely supplied by the weathering of feldspar and due to the fact that Sr is also highly concentrated in feldspar, the breakdown of feldspar minerals is as a major source of mineral-derived Sr to the biosphere. Thus, the CIA of local topsoils can give an indication as to how much Sr is liberated in different soil types and the relative importance of soil Sr contribution relative to other possible sources (e.g. marine, fertiliser).

CIA values, which were categorized in five groups (0 – 19.99, 20 – 39.99, 40 – 59.99, 60 – 79.99 and 80 - 100) and plotted onto the 1:120,000 superficial geology map (Fig. 1). The categorized map reveals that

the portion of topsoils with CIA <20 (9% (n = 10341)) strongly correlates with areas of blanket peat and proximity to the western coastline. In these cases, the low CIA values indicate enrichment in Na and Ca and relatively depletion in Al. We suggest a geographic correspondence between a CIA<20 and western coastal areas and/or peat bogs indicates a considerable geochemical contribution from the marine environment to these regions and that peat is acting as a long-term capture of these elements, thus providing a time-integrated signature. Soil and vegetation samples were subsequently selected from areas with and without secondary enrichment of Na and Ca in order asses the degree to which marine-derived Sr has affected the terrestrial biosphere Sr budget.

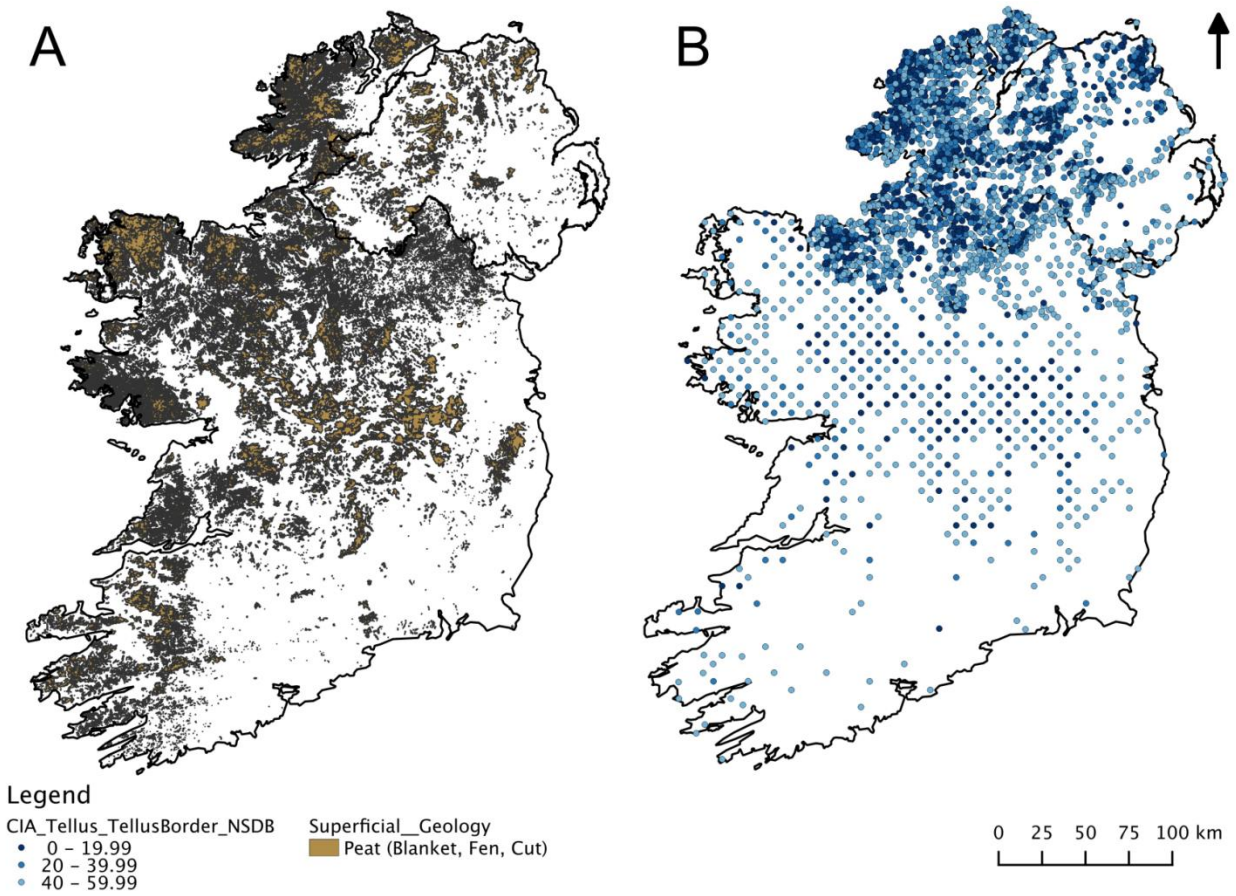

Figure 1. **A** Surficial geology map of Tellus and Tellus Border sampling areas and **B** Categorised top soil Chemical Index of Alteration (CIA) values. Note that there is a strong correlation of anomalously low CIA values (<20) with areas underlain by peat and western coastal areas. These low CIA values highlight that peat is ombrotrophic, receiving nutrients from the atmosphere and may also be receiving marine-derived aerosols, thus producing a time-integrated geochemical reservoir which is isotopically and hydrologically isolated from the underlying bedrock. EPA soil data (lower density sampling) has also been utilised.

In early Spring 2016, five separate transects of plant and soil samples were taken from different coastal areas with distinctive lithologies (Waterford, Galway x 2, Clare, Kerry). Sr isotope analyses of 28 samples were carried out in Brussels and trace element analysis was undertaken in TCD Spring-Summer 2016. Results demonstrate highly significant trends (R^2 up to 0.96), showing that marine-derived Sr strongly influences the Irish biosphere. The contribution of marine-derived Sr can be quantified for individual sample localities and with respect to distance from the coast (Fig. 2). Up to 93% of plant Sr has been marine-derived in some costal localities.

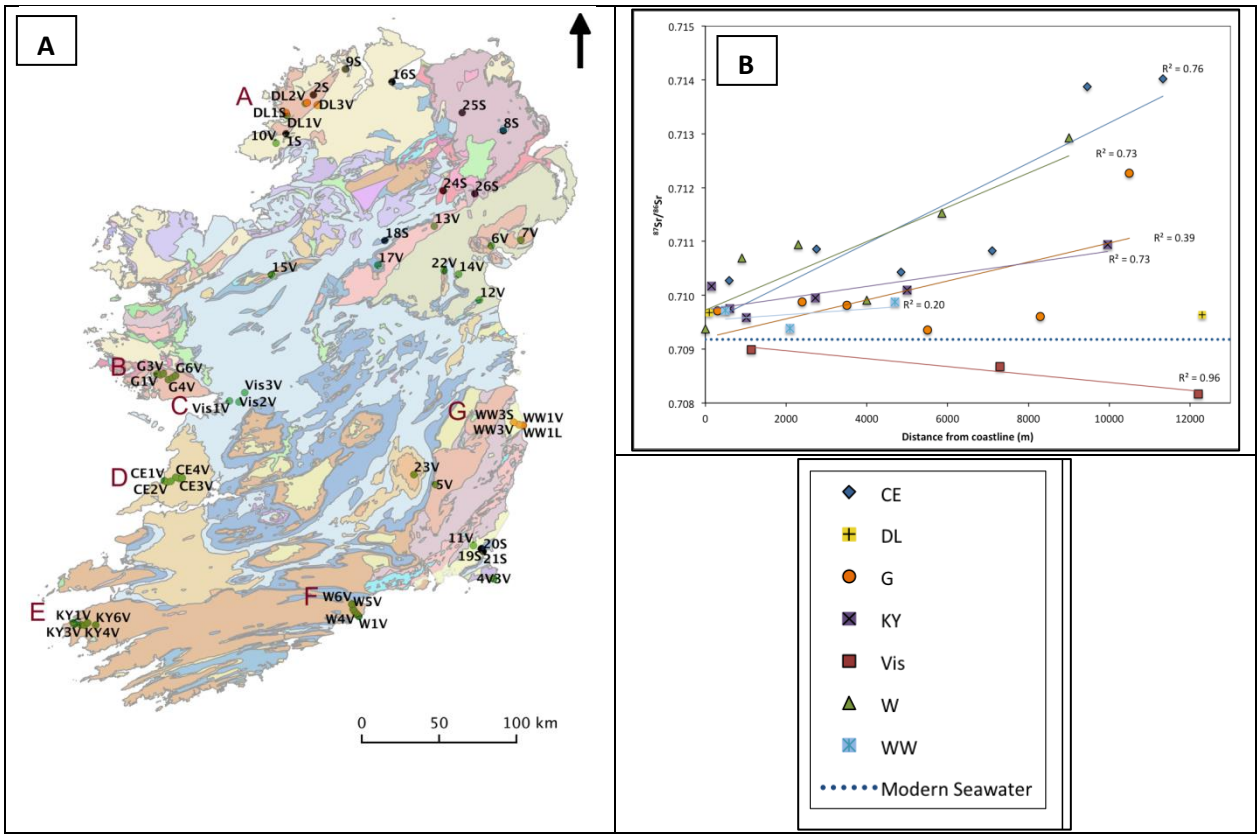

Fig. 2. A Simplified geological map of Ireland showing eight individual sample transects and additional samples used to investigate the influence of marine-derived Sr in the terrestrial biosphere (V: vegetation, S: soil). **B** $^{87}Sr/^{86}Sr$ of collected samples; note that $^{87}Sr/^{86}Sr$ values converge towards a marine value of 0.7092 towards the coast, regardless of bedrock type.

The relative contributions from seawater and bedrock/soil sources (mineral weathering) were quantified and vary significantly between sample sites. Vegetation samples from sites closest to the coast in almost every transect have $^{87}Sr/^{86}Sr$ values which closely resemble that of seawater. Contrastingly, these values progressively diverge from seawater compositions landward, with the samples furthest inland generally displaying the most radiogenic $^{87}Sr/^{86}Sr$ values.

Fertiliser as an anthropogenic Sr Reservoir

The addition of fertiliser to agricultural land is a possible non-local source of Sr, although the degree to which fertiliser can affect the terrestrial Sr isotope budget is still somewhat undefined in the literature. We targeted surface waters from an agricultural and relatively geologically homogeneous area of Co. Antrim to assess the possible effect of modern fertilisers on the terrestrial Sr budget. Significantly this area is predominantly underlain by basalt bedrock and does not feature any Carboniferous limestones, which may overlap with the modern marine $^{87}Sr/^{86}Sr$ value. Quantifying an anthropogenic contribution is especially important for Sr isotopes applied to archaeology, as it is generally assumed that local $^{87}Sr/^{86}Sr$ signatures have not changed through time. To this effect, modern biosphere samples are analysed to determine if archaeological remains are local or non-local, but little or no consideration is given to the possibility that at a local level $^{87}Sr/^{86}Sr$ values may differ significantly to that of the archaeological past. Samples were collected along a gradient of highland with no till cover to lower land till-covered areas.

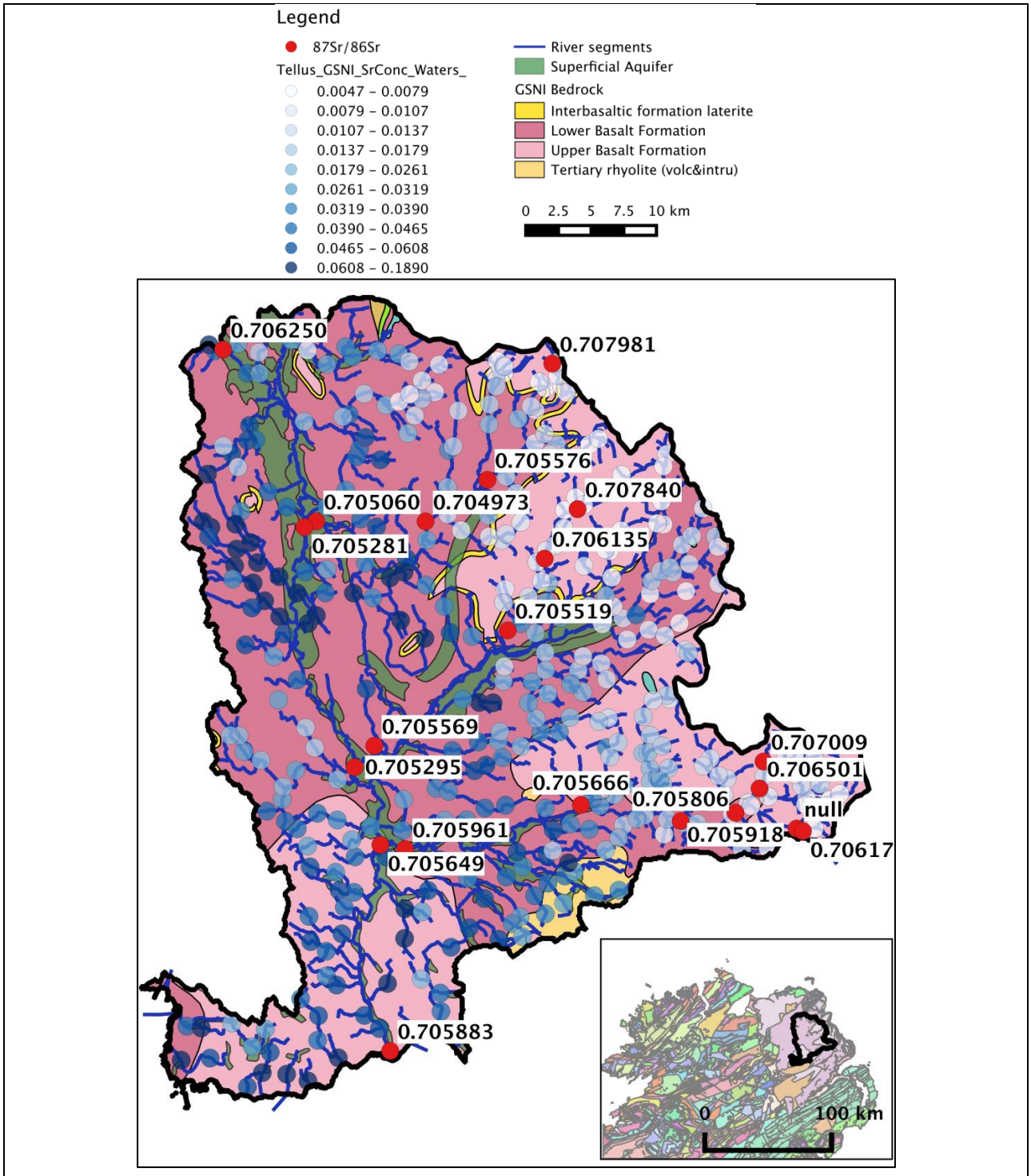

Fig. 3. Stream water Sr ppm (shown as blue circles, with darker shades corresponding to higher Sr concentrations; Tellus data source) and $^{87}Sr/^{86}Sr$ values collected from an area of Co. Antrim.

Mass balance calculations indicate that, in some instances, up to 75-80% of stream water Sr has been derived from fertiliser (Fig. 4).

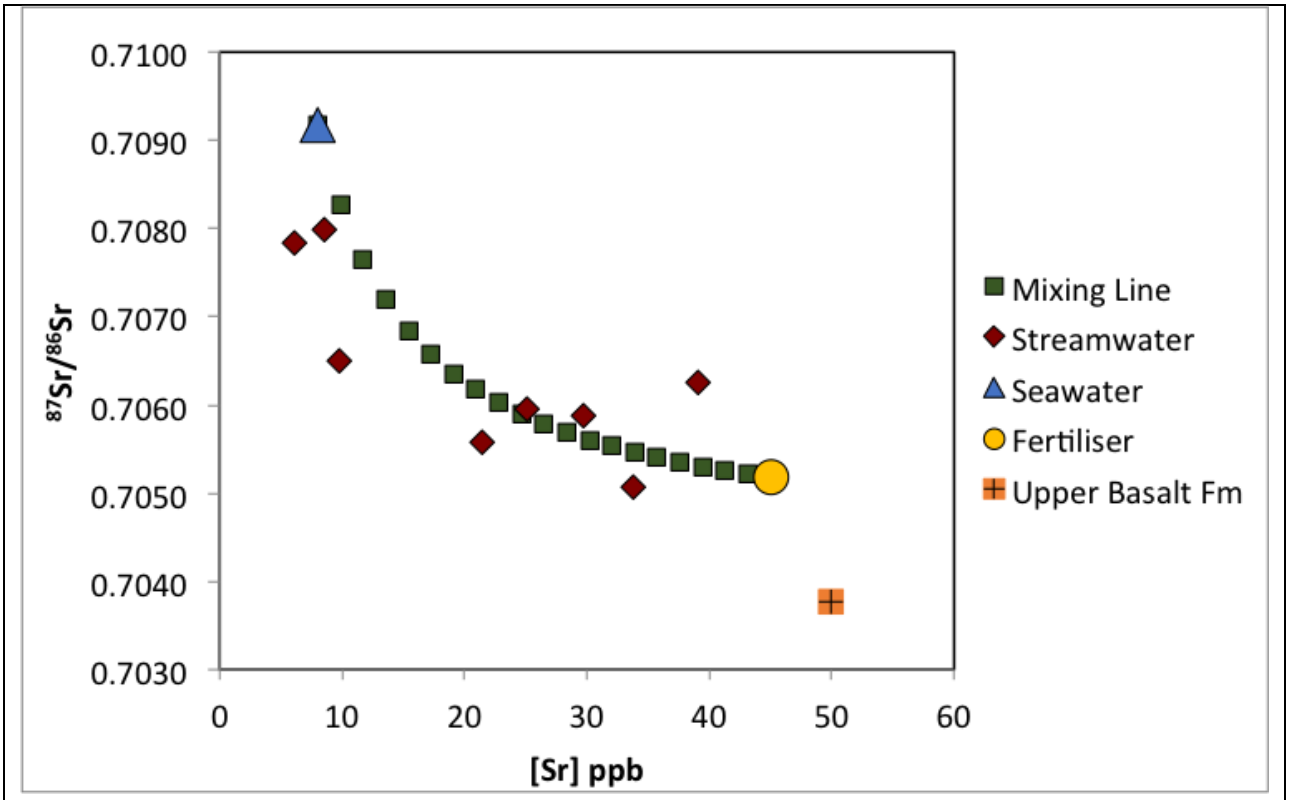

Fig. 4. $^{87}Sr/^{86}Sr$ vs Sr ppm for selected stream water samples collected in Co Antrim (samples are from the SE of the studied area). Sample analyses show a clear mixing relationship between seawater and sampled fertiliser values, and lie of the expected trend expected if the Upper Basalt Formation were acting as a dominant Sr source.

Concentrations of trace elements, in particular the Rare Earth Elements (REE) and yttrium (Y) were also measured from stream waters, as Y/Ho ratios are highly informative on fertilizer contributions. Generally, higher Y/Ho signifies more carbonate-sourced dissolved element load, which can be correlated with $^{87}Sr/^{86}Sr$. Fertilisers have Y/Ho in the range of 48.6 – 70.3 (Martin and McCulloch 1999) whilst values between 24.7 and 27.2 are expected for upper continental crust. Stream water samples collected here have Y/Ho values between 28 and 33, also indicating end-member mixing relationship between bedrock and fertiliser.

Two tree cores were taken from mature oak trees in Co. Antrim in Summer 2016. One of the cores was taken from a tree on agricultural land and the other from a control site on non-agricultural land. Dendrochronology was conducted by Saskia Ryan at Queen's University Belfast indicating that the trees covered a time period between 1913 and present day (Fig. 5). Sub-samples representing a ten year growth period were analysed for Sr isotopes at the Cambridge University (by Saskia Ryan) in Summer 2016. Data indicate a substantial shift in $^{87}Sr/^{86}Sr$ for the tree on agricultural farm land post 1947 (towards fertiliser values), but no such isotopic shift was detected for the tree on non-agricultural land.

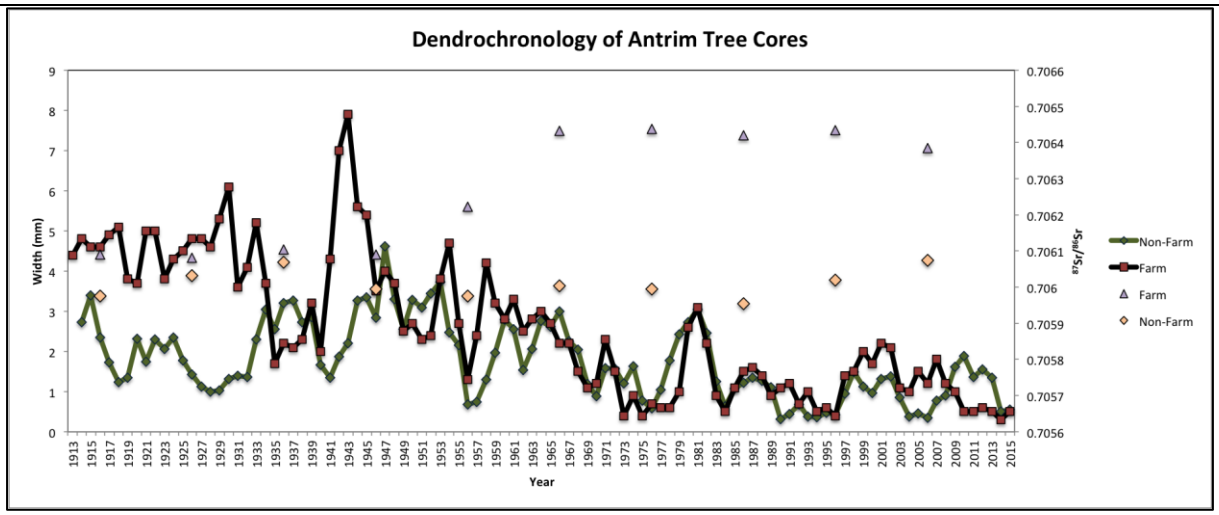

Fig. 5. Dendrochronology of two tree cores from Co. Antrim, one of which was taken from an oak tree grown on agricultural land and the other from an oak free from a control site on non-agricultural land. The width of annual bands is represented by solid lines, whereas the $^{87}Sr/^{86}Sr$ values (ten-year sample increments) are given by diamonds and triangles. The tree from agricultural land shows a distinct shift in $^{87}Sr/^{86}Sr$ between 1947 and 1965, compatible with commencement of application of modern fertiliser.

(iii) Outputs (please use bullet points)

- Final project report.
- Poster and short research talk at the GSI Tellus Impacts launch (RIA, October 2016).
- Manuscript submitted to the *Science of the Total Environment*.
- Preparation of a second manuscript for the *Journal Irish Archaeology*.
- Contribution to the PhD thesis of Saskia Ryan (at TCD).
- Feature written for the Irish Isotope Research Group (IIRG) website summarising main findings of research to the Irish and international archaeological and environmental sciences communities (yet to be published online).
- Contribution to a national Sr isotope biosphere map.
- Sr isotope baseline data used as a basis for an archaeological case study by Saskia Ryan, undertaken as a Geoscience Fulbright Fellow at Harvard University.

Impact/value of the project (M*ax 500 words*):

The funded research has added value to the Tellus geochemistry data sets and demonstrated their applicability to a wider research community. Apart from the Sr isotope data produced during this study, this research has highlighted the usefulness of regional geochemical mapping programmes, such as Tellus in elucidating complex geochemical interactions in the terrestrial environment. The use of the Tellus dataset in this regard constitutes development of a new methodology, in particular in assessing soils with likely marine signatures and agricultural soils which may display a greater propensity to be influences by anthropogenically derived Sr.

This project has enhanced our knowledge of the extent to which different isotope reservoirs affect the overall terrestrial biosphere $^{87}Sr/^{86}Sr$ signature. This is of relevance not only to those working in related research areas in Ireland, but is of benefit to similar studies globally. Data obtained as part of this project have contributed to an on-going compilation of an accurate biosphere $^{87}Sr/^{86}Sr$ map of Ireland.

The results from this study will form the basis of a Horizon2020 application. The Irish Isotope Research Group (IIRG) intends to submit an application to fund an ITN (specifically an ETN). This will involve Trinity College Dublin, Queen's University Belfast, Durham University, Ecole Normale Superieure de Lyon (France) and Vrije Universiteit Brussel (Belgium). The theme for the proposed ETN is Ancient Human

Population Dynamics in Europe.

A significant component of the project has dealt with training of a young PhD researcher. It is noteworthy that baseline data collected as part of this project will be utilised in a case study being performed by Saskia Ryan as a Geoscience Fulbright Fellow at Harvard University. In this manner, the project greatly assisted the career trajectory of a young researcher.

This project has also impacted on cultural heritage and geotourism in Ireland, as it provides a basis for better interpretation of archaeological sites in different regions.

Abstracts based on this work will be submitted to both EGU (Vienna) and Goldschmidt (Paris) conferences in 2017.

Appendix 1 – Publications & Presentations: Please use the following formats for your publications

[Journal Paper]

Ryan, S., Crowley, Q.G., Snoek, C., Babechuk, M. (*Submitted*). High Spatial Resolution Geochemical Mapping of Surface Processes: A Case Study in Ireland. *Science of the Total Environment.*

Appendix 2 – Any additional information not included above: