



Research Programme
- Short Calls, Final Report -

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Host Organisation name	National University of Ireland Galway
Project Title	Building on Tellus: Preliminary Investigations into Geochemical Processes occurring in Connemara Blanket Bogs.
Contract Number	2017-sc-012

Date: 13/11/2018

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

During the 1st 4 months of this project we have made good progress with regard to site selection and establishing sampling protocols, we had intended to use the Tellus geochemical stream and sediment data for Connemara as an input to our site selection criteria and though the samples for this were collected in 2016 that data is still at time of writing (Nov, 2018) not available to the public, thus we chose to focus on a single test site initially. Bad weather during the winter and early spring limited sampling opportunities but we were able to carry out a site survey for locating our test site in Connemara National Park along with some field work collecting stream samples as part of a wider project into chemical weathering initiated by Prof Lyons as part of his Fulbright scholarship in Ireland. Other sites in Connemara, but outside CNP, which had been sampled in previous scientific studies (as identified by our literature search) were also considered, but the opportunity to work with the conservation rangers within a public site were considered advantages for this preliminary study.

Ireland 2018:
Sampling Locations Projected on Stream Bodies



During the 2nd 4 months of the project we made good progress with regard to establishing sampling protocols both in the field and in the laboratory. Unfortunately, the weather still had a significant impact on our site sampling within Connemara National Park, as the bad weather during the winter and early spring limited sampling, the hot dry summer complicated sampling the peat for porewater as the peat become unusually very dry. Rhizon sampling was only able to extract 0.5-1 mL from peat cores due to the low water content. Due to the dry conditions the DGT samplers were not deployed as they require sufficient water to fully cover/wet the samplers. Radon efflux measurements at CNP were complicated by the dry vegetation making a good seal over the soil for the gas flux measurements and repeated sampling for an hour or more found no detectable ²²²Rn flux. More samples were collected around Ireland as part of the stream sampling aspect of the project (Figure 1).

Figure 1: Sampling Locations for stream water study.



Over the last 4 months of the project we concentrated on analysis of the stream water samples that had been collected and analysis of porewater samples collected at our CNP site and from one visit in collaboration with QUB to a pristine bog at their Letterrunshin site in Co. Sligo.

Laboratory work: We have gained considerable experience now with using the Rhizon and DGT samplers in a peatbog and with their subsequent analysis in the laboratory. The hot dry summer experienced in 2018 meant we could not deploy the DGT samplers in the field as there was insufficient water in the peat bog to ensure good recoveries. The Rhizon samplers were able to extract some water from the dry peat bogs but this low recovery has limited the number of analytes we could measure so far. Standard operating protocols (SOPs) have been developed for use in the field and laboratory for analysis of the different analytes considered in this study and will be finalized and made available as meta data accompanying the data products.

Stream water samples were analysed for CDOM/FDOM at NUI Galway on an Aqualog (Horiba) fluorometer and for major cations/anions (IC and ICP-MS) and O/H isotopes (Cavity Ring Down – Picarro Instruments) at Ohio State. The FDOM data for the porewater and stream water was fitted using standard PARAFAC protocols and identified 3 independent components that were related to humic-like fluorophores, not protein-like fluorophores were detected. It was found however that the Rhizon samplers did give a strong protein-like signal if they were not rinsed with ultrapure water prior to sampling the peatbog porewater, this is presumably a preservative used in the manufacture of the Rhizon's. Thus care was taken to rinse the Rhizon's with ultrapure water prior to use.

A considerable amount of laboratory time was devoted to developing a protocol for Iodine speciation of the peatbog porewaters and the stream waters. In the bog porewater, the iodine was apparently mostly present as organic iodine species, as expected, though the inorganic species, iodide and iodate were difficult to detect due to the interference of CDOM with the usual methods of analysis for this species. In particular for the determination of iodide by voltammetry, it appeared that humic material was adsorbing to the Hg drop and blocked iodide deposition resulting in high background currents and no observable iodide signal. For iodate measured by spectrophotometry after addition of iodide and reduction of the iodate to iodine, the usual analytical peak at 350 nm (I_3^- peak) was superimposed on the CDOM signal, small signals were observed using a 10 cm pathlength, but with a 100 cm pathlength cell the CDOM absorption is too great to determine iodate reliably. It was noted that for some samples the iodate peak increases with time when left in the cuvette, this suggests that either the sulfamic acid added was insufficient to react with any nitrite formed or that there is another photo produced oxidant in these samples. Total iodine was measured using voltammetry after UV irradiation of samples in Teflon vials for 2-4 hours with a Hg lamp (Pen Ray: UVP now Analytik Jena) until the CDOM signal was almost back to baseline (cf Ultrapure water). This process removed the interfering humic signal and converted the organic iodine into iodide and iodate, allowing determination of the iodide content and the total iodine after addition of ascorbic acid to reduce any iodate that had formed during photo-oxidation. It was noted that longer irradiations resulted in more iodate than iodide in the sample and preliminary data suggests that no iodine is being lost during the irradiation. Preliminary work was also started using AG 1-X8 columns in order to extract iodide from the samples prior to irradiation and investigation on this is ongoing.

At the time of writing this report, stream water samples are still planned to be run on an ICP-MS at OSU for selected trace metals. Once this dataset is collected it will be integrated with the other data collected on the same samples and be made available via the GSI website.



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

Gantt chart from original proposal:

		2017		2018											
Geochemistry of Connemara Blanket Bogs		N	D	J	F	M	A	M	J	J	A	S	O		
Data Acquisition	1.1 Acquisition of Rainfall Collection Equipment														
	1.2 Collection of rainwater data														
	2.1 Acquisition of Rhizon and DGT samplers														
	2.2 Site selection visits														
	2.3 Peat core sampling - Rhizon porewater														
	2.4 Peat core sampling - DGT probes														
	2.5 Peat core sampling - Radium Quartet														
	3.1 Testing and calibration of RAD7														
	3.2 Radon Efflux from bogs														
	3.3 Stream sampling														
MILESTONES															
Milestones	1.1 First rainwater samples collected														
	2.1 First peat core sampling														
	2.2 Rhizon sampling														
	2.3 DGT sampling														
	3.1 Radon efflux measurements														
	4.1 1st Stakeholder Meeting														
DELIVERABLES (AT THE BEGINNING OF THE MONTH INDICATED)															
Deliverables	1.1 Rainwater database														
	2.1 Porewater CDOM/FDOM database														
	2.2 Porewater trace metal database														
	3.1 Radon efflux database														
	4.1 Stakeholder Meeting - Progress Report														
	4.2 National/International Conference Presentation														
	4.3 Peer reviewed journal article														

There were some deviations from the original project plan, as the Tellus geochemical stream and sediment data for the Connemara region did not become available during the lifetime of this project, it was intended to use this dataset as a criterion for identifying other potential sampling sites. The Tellus aerial radiometry data for Connemara was available though and used for this purpose. In place of the Tellus data we expanded our stream sampling coverage to include all of Ireland and this become a major focus of the project work as it still allowed us to address our original questions but also over a wider geographical range. Sampling of the peatbog study site was also less than originally anticipated due to the extremely dry conditions experienced across Ireland in the summer of 2018, which resulted in a very low water content of the peat bog limiting our ability to sample porewaters as in many cases there was effectively no porewater or only trace amounts. Radon and rain sampling was also impacted by the weather during the year but as noted above, some progress was made in these areas.

Acknowledgments: Prof Berry Lyons was supported by a Fulbright-GSI scholarship during his time in Ireland. Special thanks to Prof. Anne Carey (OSU) for her efforts and expertise for the Irish river sampling and to Chris Gardner, Susan Welch and Dermot Smith at OSU for their help with the isotopic and elemental analysis of those samples. Prof. Raymond Flynn at QUB was a gracious host for us during a snowy visit to Belfast and helped us immensely by sharing his experience and data on Irish peatbogs, and from this sprung a very fruitful tripartite north-south-USA collaboration.



Analytical work on CDOM/FDOM at NUI Galway was also supported by related activities in the Irish Centre for Research in Applied Geochemistry (iCRAG). Thanks to Kiera Henn and Cathal Faherty, both 4th year EOS students for their help with peatbog sampling. The help and support of the National Parks and Wildlife Service, and in particular Dermot Breen and Cameron Clotworthy, is much appreciated in allowing us to sample in Connemara National Park.

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

1.1 Rainwater chemical analysis database - The dry summer also impacted our ability to collect rain samples, which coming after the snow and ice of the winter resulted in us being unable to obtain good trace metal clean rainwater samples as the current manual sampling system employed needs to be deployed during a rain event with low to moderate winds. Unfortunately, when the rains returned in the Autumn so did the wind, for future work we are looking into a clean automated rain sampling system that can be fixed to the ground to withstand typical Irish weather conditions.

We were able however to obtain chemical data for precipitation in Ireland that will help us interpret our peatbog and stream data thanks to the help of Margaret Ryan at Met Éireann who runs the sampling program for precipitation data collected at Valentia and other sites in Ireland. We are extremely grateful to Margaret for pointing us towards the European Monitoring and Evaluation Programme (EMEP) website and the chemistry database (<http://ebas.nilu.no/>).

Additionally, we were also made aware by Professor Thomas Church (University of Delaware), of archived frozen Mace Head rainwater samples that were collected during the AEROCE program (1990-1994) but have yet to be analyzed. These samples will now be analyzed at some point in the future by Dr Simon Ussher (University of Plymouth) who has previously made rain measurements at Mace Head and is involved in the Penlee Point Atmospheric Observatory in the UK.

2.1 Porewater CDOM/FDOM database – Porewater data was collected from the two peatbog sampling sites and combined with the Irish stream data we collected to form an initial database for CDOM/FDOM of 80 samples. We will continue to grow this data set with new work being conducted over the course of our newly funded EPA program Nuts&Bolts (see below).

2.2 Porewater trace metal/iodine speciation database – As mentioned in 2.1 the porewater dataset was combined with the Irish stream data we collected, and this will be extended as part of the work in Nuts&Bolts. As noted above the iodine speciation work on the stream samples is still ongoing.

3.1 Radon efflux database – ²²²Rn efflux measurements were attempted in the summer of 2018 in Connemara National Park but no quantifiable efflux was observed (i.e. we had no counts at all after an hour of accumulating radon). A number of factors may have caused this, as we did not remove the vegetation cover, and this may have caused a poor seal with radon leaking out or the dew on the plants resulted in radon existing mostly in the aqueous phase, we are adjusting our protocols to do more tests for this in the summer of 2019.

4.1 Stakeholder Meetings – Our initial stakeholder visit was to develop a cross border collaboration with Professor Ray Flynn at Queens University Belfast. Unfortunately, due to heavy snow at the time in January, we were unable to visit QUB's Garron Plateau field site, it did however prove to be an extremely fruitful meeting as Prof. Flynn gave us a good introduction into the different peatbog sites, they were sampling as part of their program.



Our peatbog sampling site in Connemara National Park (CNP) was set up in consultation with the rangers at CNP and we meet with Dermot Breen on Feb 6, 2018 to choose a test site that was representative of a contemporary Connemara peat bog and that was accessible by foot but not so far from road access, and also not likely to be frequented by the public. The sites in CNP are not pristine and have been strongly influenced by recent human activity but the peatbogs there still behave as ombrotrophic mountain bogs. We intend to develop an information kit for CNP over the next months, explaining what we are doing there and its relevance to the Park and to the public.

4.2 National/International Conference Presentation – Preliminary results from this project were presented in two talks at the Geological Society of America's Annual Meeting, held in Indianapolis in Nov this year, and in a poster presented at Geoscience Ireland 2018 in Dublin Castle on Nov 6, 2018.

4.3 Peer reviewed article – A manuscript arising from the stream data is currently in preparation and is expected to be ready for submission in the 1st or 2nd quarter of 2019. Once the Tellus geochemical stream and sediment data for Connemara is available we still intend to use this as a basis for a further paper as was originally intended on weathering processes in Connemara and the role of the peat bogs.

Note: During the course of this project, the lead PI, Prof. Croot was also successful in securing additional funding related to aspects of this project. Initially via two Marine Institute 2017 infrastructure projects which have allowed us to purchase a seaFAST analysis system for trace metals and a Membrane Inlet Mass Spectrometry for use with climate relevant gases (e.g. O₂, Ar, N₂, CO₂, CH₄). Aspects of the current project will also be extended to the marine transitional zone in a newly funded EPA project entitled NUTS&BOLTS which examine the fluxes of elements to the coastal zone via riverine flow and its impact on the primary productivity and biogeochemistry in those zones.

Task No.	Deliverable description	Planned delivery (as per proposal)	Date of delivery
1.1	Rainwater chemical analysis database	Every 6 months	End of Dec 2018
2.1	Porewater CDOM/FDOM database	Every 6 months	End of Dec 2018
2.2	Porewater trace metal/iodine speciation database	Every 6 months	End of Dec 2018
3.1	Radon efflux database	Every 6 months	End of Dec 2018
4.1	Stakeholder Meeting – Progress Report	Every 4 months	End of Dec 2018
4.2	National/International Conference Presentation	See Gantt chart	GSA 4-7 Nov, 2018
4.3	1 peer reviewed article in an international journal, national and an international conference contribution	Draft manuscript ready for submission at conclusion of the project	Mid 2019



Publications to date:

[Conference Publication] Lyons, W.B., Croot P., Carey, A.E., Henry, T., Welch, S., Gardner, C. and Flynn, R. (2018) The Geochemistry of Rivers in Ireland: A Snapshot. *Geological Society of America 130th Annual Meeting* – Indianapolis, Indiana, USA, Abstract 133-12 5-Nov-18

<https://gsa.confex.com/gsa/2018AM/meetingapp.cgi/Paper/319340>

[Conference Publication] Carey, A.E., Henry, T., Smith D.F., Croot P. and Lyons, W.B. (2018) Are climate dynamics reflected in the stable isotope hydrology of Irish river water during 2018? *Geological Society of America 130th Annual Meeting* – Indianapolis, Indiana, USA, Abstract 230-11 7-Nov-18

(<https://gsa.confex.com/gsa/2018AM/meetingapp.cgi/Paper/317052>)



- c. Preliminary Data 2017-sc-012 contained in an excel file. Please note other data sets are still in analysis and will be incorporated into this database within the next 6 months.

SUPPLEMENTARY MATERIAL

(This section will be included in your published report unless otherwise instructed. If you have a published report, publication, etc. you may include it here).