Roinn Cumarsáide, Gníomhaithe ar son na hAeráide & Comhshaoil
Department of Communications, Climate Action & Environment

Geological Survey
Suirbhéireacht Gheolaíochta
Ireland | Éireann

Research Programme
- Short Call 2022 –
- Final Report -

Lead Applicant Name	Dr John Weatherill
Host Organisation name	University College Cork
Project Title	CONceptualising SubsurfacE hydRogeochemical enVironmEnts of alluvial aquifer-hyporheic zone systems in headwater agricultural stream catchments (CONSERVE)
Contract Number	2022-sc-025

This report covers the period 1st December 2022 to project end date 31st December 2023

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2. (a) Project information:

Executive summary

Groundwater supplies just under one in four people in Ireland with clean drinking water and provides a vital supply of baseflow to streams and rivers during dry weather periods and in drought conditions. The groundwater-surface water interface (known as the hyporheic zone) and alluvial aquifer systems along stream networks mediates baseflow discharge and may serve as a natural bioreactor for diffuse pollutant transformation as well as a source of geogenic potentially toxic elements (PTEs) to surface water ecosystems. The CONSERVE project aims to develop an integrated conceptual understanding of the hydrostratigraphy and chemostratigraphy of groundwater-surface water interfaces in extreme vulnerability fractured bedrock environments in Ireland. The demonstration project has developed an integrated multi-scale 'toolkit' of shallow, non-invasive hydrogeophysical techniques including electrical resistivity tomography (ERT) and ground-penetrating radar (GPR). These non-invasive approaches could successfully delineate bedrock structural controls on baseflow discharge pathways which could be validated by streambed temperature profiling as an independent surrogate for groundwater flow. The project also demonstrates cost-effective percussion drilling methods for rapid and highly accessible monitoring well installation, hydraulic testing and intact core sampling where drilling programmes can be informed and optimised by hydrogeophysical techniques as part of a wider toolkit for integrated conceptual model development at aquifer-stream interfaces. The project included the geochemical analysis of homogenised sediment and heavily weathered bedrock samples (n = 132) for a range of PTEs using portable x-ray fluorescence (pXRF) which had good sensitivity to Pb, Se, As, Hg, Zn, Cu, Ni and Co. The geochemical findings from high-resolution hyporheic zone profiles revealed elevated As hotspots (up to 50 mg/kg) which may pose hazard to ecosystem health. The research has provided critical new empirical data on mechanisms of groundwater baseflow discharge and geochemical processes which will be of value for integrated catchment management and water resource protection in Ireland and further afield.

(i) Results

The CONSERVE project aimed to develop an integrated conceptual understanding of the hydrostratigraphy and chemostratigraphy of shallow alluvial aquifer-hyporheic zone systems at reach scale (Figure 1) where potentially toxic elements (PTEs) may pose risks to surface water ecosystems and human health. The research has demonstrated the application of cost-effective intrusive and non-intrusive site characterisation technologies for developing integrated, multi-scale conceptual site models at groundwater-surface water interfaces in extreme vulnerability fractured bedrock environments.

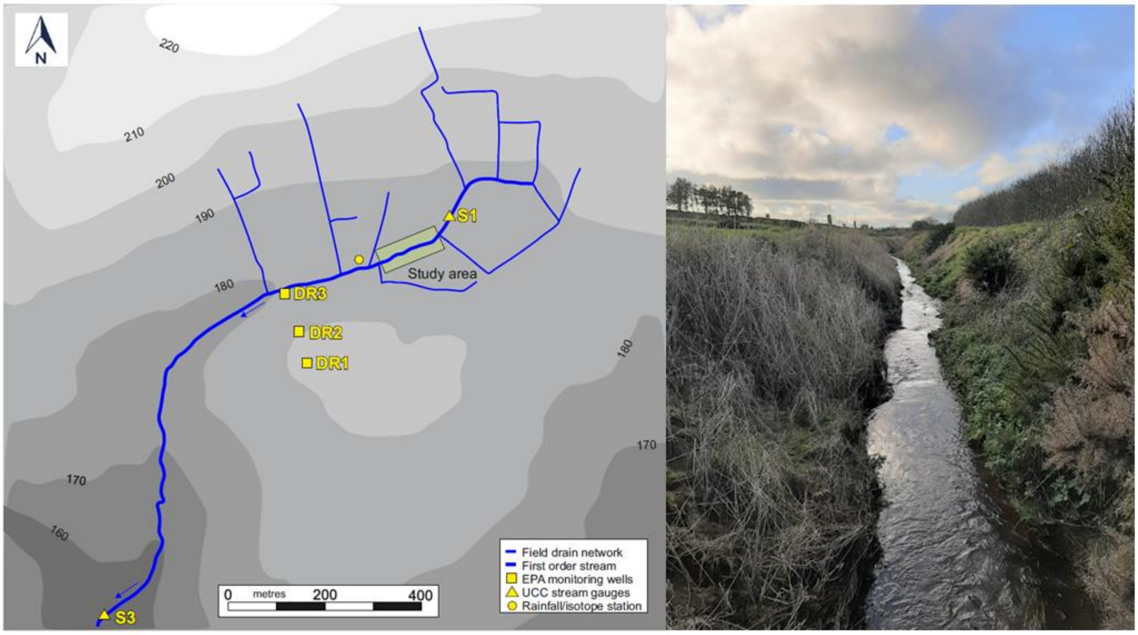

Figure 1: *Study area and first order stream in the Dripsey catchment in Co. Cork with the location of the exiting EPA groundwater level and quality monitoring network and ongoing UCC hydrological monitoring (stream flow, rainfall and stable isotope sampling)*.

A total of 1,452 m of 2D electrical resistivity tomography (ERT) lines were acquired within the study area using a gridded approach to allow development of a 3D representation of bulk subsurface geoelectrical properties at constant depth (Figure 2) as a surrogate for water-filled (secondary) porosity of bedrock and subsoil as well as clay content. Findings show a discrete zone of low resistivity (<80-150 Ω m) from 1.58 to 5.51 m depth with the lowest area (≤80 Ω m) centred around the streambed to the north and south between 2.16 and 3.4 m depth. This zone and surrounding areas of higher resistivity (200-400 Ω m) exhibit a well-defined NNW-SSE linear orientation suggesting a major structural feature in the Old Red Sandstone bedrock. By overlaying data from a high-resolution streambed temperature survey from summer 2018 (Jeggo and Weatherill, 2019) (Figure 3), it was possible to demonstrate that the low resistivity feature is spatially associated with preferential groundwater discharge through the streambed porewater where temperature serves as an independent surrogate for groundwater baseflow discharge.

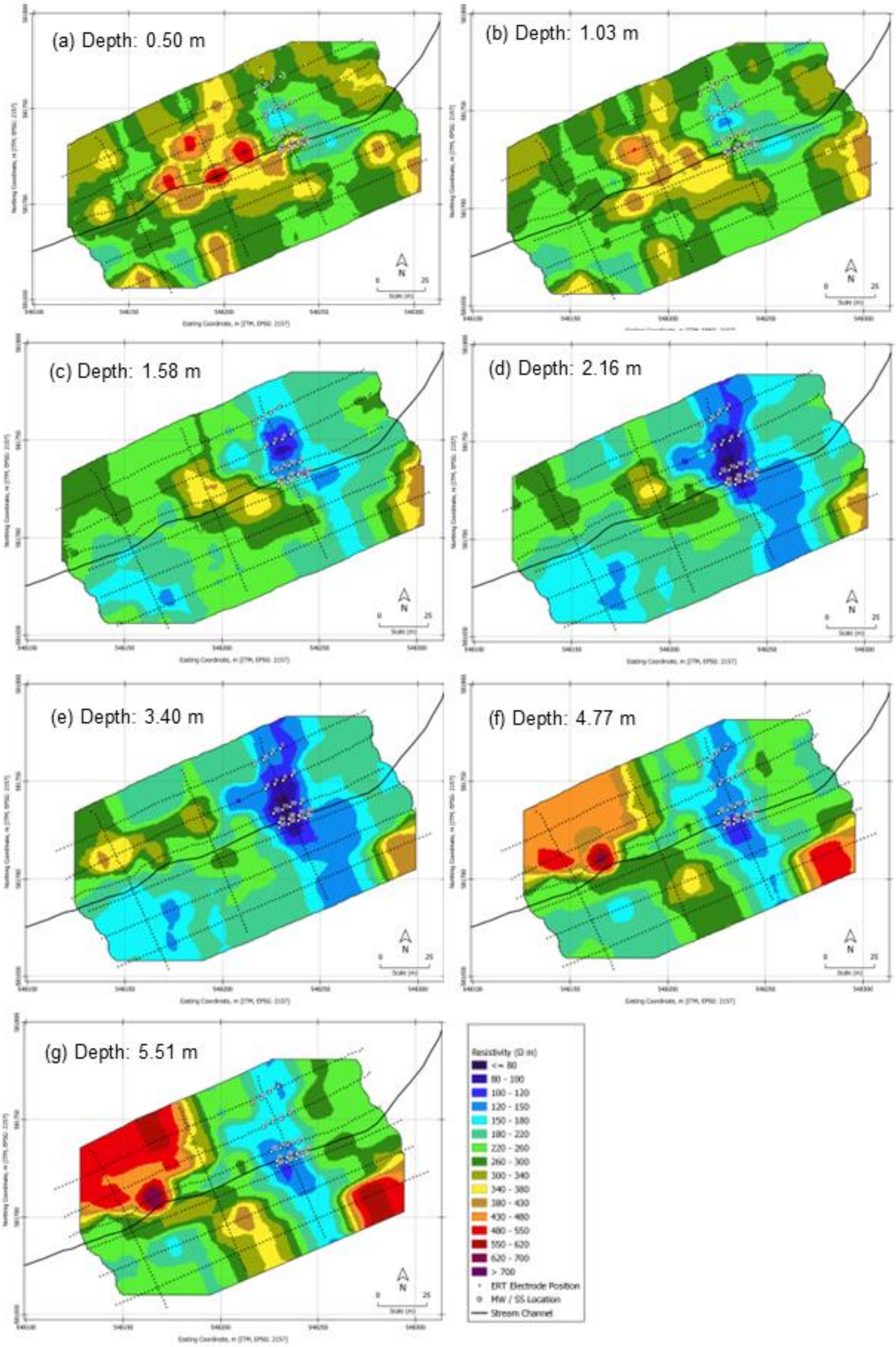

Figure 2: *Interpolated 3D representation of modelled geoelectrical properties at constant depth (a-g) from a parallel grid of 2D profiles collected using rollover techniques in the study area with a maximum depth of 6 m. The effects of the stream channel were not considered for the shallowest depths (a-b).*

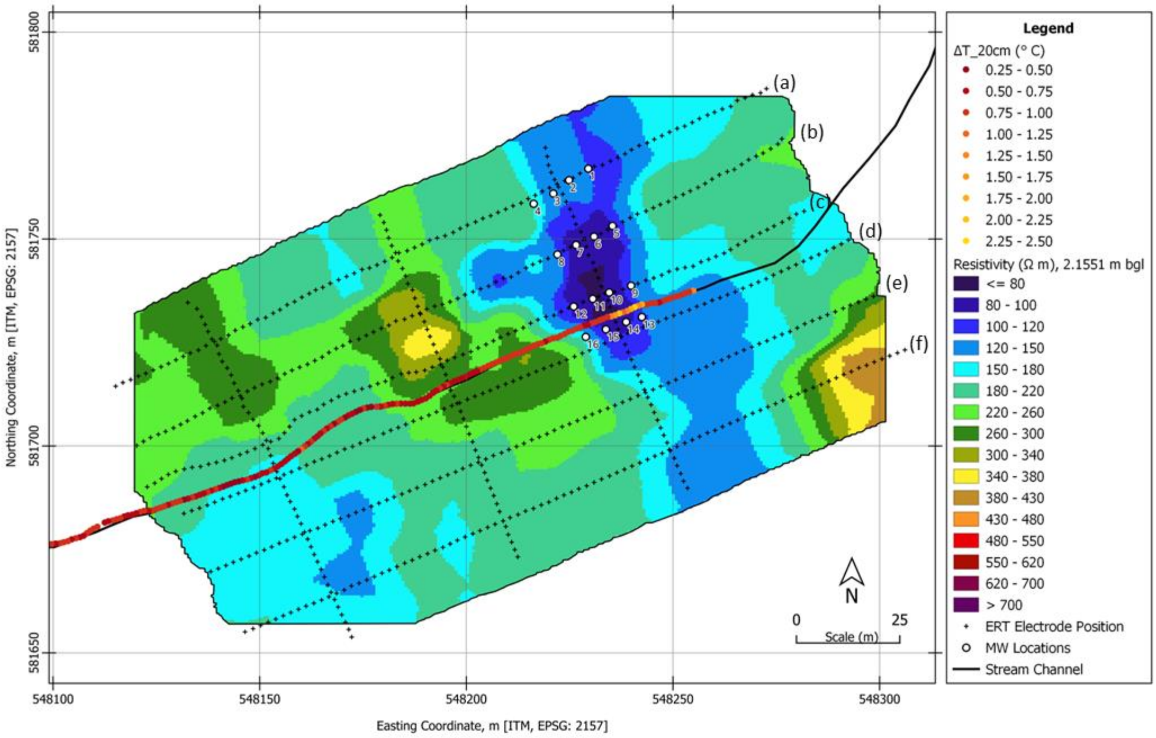

Figure 3: *Interpolated 3D representation of modelled electrical resistivity at 2.51 m depth overlaid with mapped streambed temperature profiles at 1 m longitudinal resolution. ΔT is calculated as the difference between the mean daily surface water temperature and streambed sediment porewater temperature measured in-situ at 20 cm depth. Location of monitoring wells (MW01-MW16) installed during the intrusive investigation are shown. GPR lines (a-f) collected later in the project are given (not all survey lines shown for clarity).*

Streambed porewater temperature profiling in summer and winter (where temperature contrasts with stream water and near-constant temperature groundwater are greatest) enable areas of active, preferential groundwater flow to be delineated with a high spatial resolution possible using roaming surveys (Figure 3). A total of 1,376 m of ground-penetrating radar (GPR) lines at 200 and 100 MHz frequencies were acquired alongside ERT profile lines to provide independent geophysical evidence of subsurface architecture along the investigated reach (Figure 4). GPR findings indicate a potential bedrock topographic feature located 50-60 m along the profiles, particularly for lines (c), (d) and (e) close to the streambank which are associated with the low resistivity zone and associated streambed temperature features. These hydrogeophysical insights suggest groundwater baseflow is concentrated through discrete structural features in stream catchments fed by shallow fractured bedrock aquifer systems.

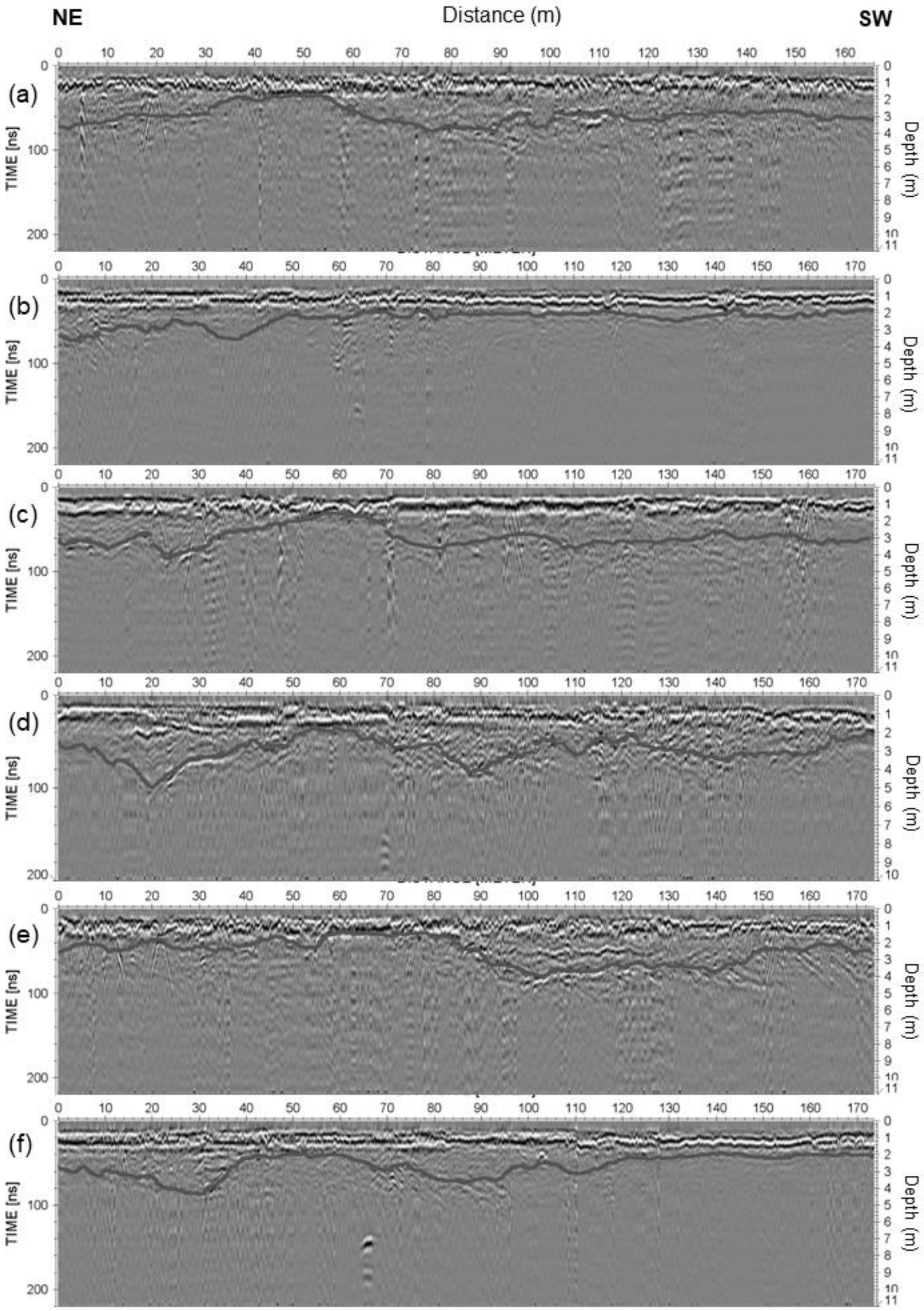

Figure 4: *Ground penetrating radar profiles (a-f) collected at 100 MHz corresponding to bank parallel ERT lines a to f (Figure 3) with tentative depth-to-bedrock depths delineated for each profile showing changes in topography associated with the low resistivity feature noted in Figures 2 and 3.*

The hydrogeophysical investigation provided targets for an intrusive site investigation campaign using lightweight percussion drilling (petrol-operated Cobra TT hammer drill) and intact sampling techniques in order to develop a shallow groundwater monitoring network (Table 1) to validate geophysical data, characterise subsurface hydraulic properties, collect intact samples for geochemical analysis and develop an integrated conceptual model. The drilling results confirmed shallow heavily weathered bedrock comprising semi-friable purple-grey mudstone/shale overlain by silt subsoils with occasional sand and gravel horizons. Saturated hydraulic conductivity (K_{sat}) for the shallow bedrock and subsoils was low to moderate with a geometric mean of 0.15 m/d, comparable to shallow bedrock and transition zone pathways of the EPA monitoring wells (CDM/OCM, 2010) with the observed K_{sat} distribution with depth (Figure 5) following a distinct (e.g., R^2 = 0.7) power law relationship.

Table 1: *Details of hydrogeological monitoring network developed using lightweight percussion drilling techniques with K_{sat} determined from in-situ variable head tests.*

Well ID	Easting	Northing	Z	Depth	Response Zone	Aquifer Lithology	K_{sat}
	m	m	m AOD	m bgl	m bgl		m/d
MW01	548230	581767	182.76	2.25	1.25-2.25	Mudstone	0.175
MW02	548225	581764	182.76	2.1	1.1-2.1	SAND/SILT	1.572
MW03	548221	581761	182.4	2.6	1.6-2.6	Mudstone	0.277
MW04	548216	581759	182.67	1.6	0.6-1.6	Mudstone	-
MW05	548235	581753	182.78	2.3	1.3-2.3	Mudstone	0.133
MW06	548231	581751	182.4	2.4	1.4-2.4	Mudstone	0.023
MW07	548227	581749	182.56	2.2	1.2-2.2	GRAVEL/Mudstone	0.580
MW08	548222	581746	182.57	2.3	1.3-2.3	Mudstone	0.081
MW09	548240	581739	182.51	2.15	1.15-2.15	SILT/silty SAND	0.013
MW10	548235	581737	182.54	2.05	1.05-2.05	Mudstone	0.018
MW11	548231	581736	182.38	2.35	1.35-2.35	Mudstone	0.490
MW12	548226	581734	182.33	2.2	1.2-2.2	Mudstone/GRAVEL	0.251
MW13	548242	581731	182.27	2.05	1.05-2.05	SILT/SAND	0.790
MW14	548239	581730	182.21	2.2	1.2-2.2	SILT/GRAVEL	0.262
MW15	548234	581728	182.13	2.3	1.3-2.3	SILT/GRAVEL	0.398
MW16	548229	581726	182.1	2.2	1.2-2.2	silty SAND/GRAVEL	0.026

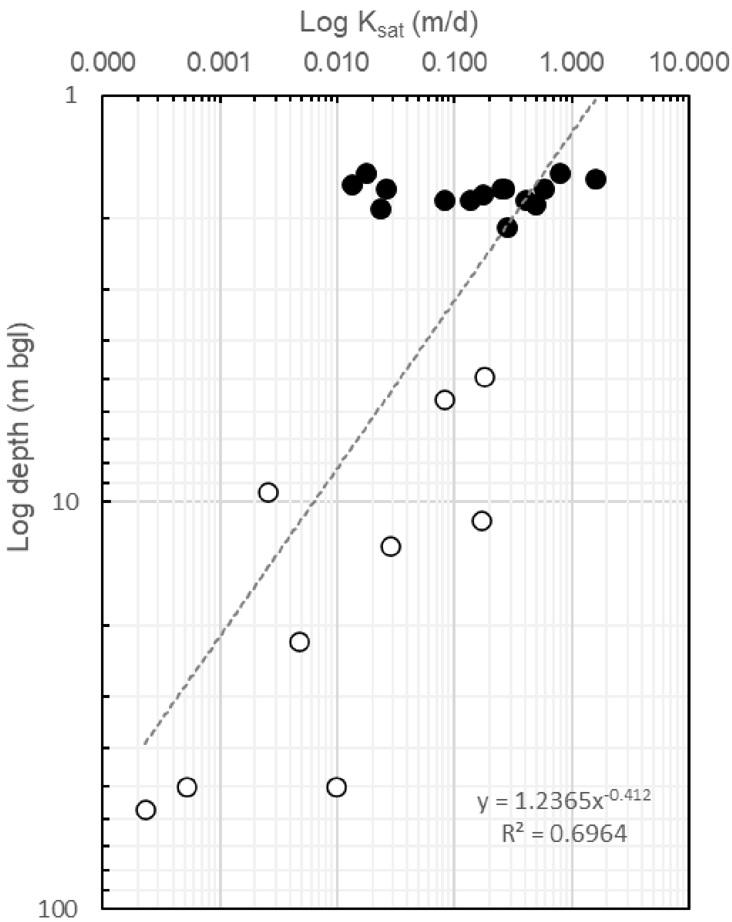

Figure 5: *Log-log scatter plot of K_{sat} with depth of response zone mid-point for the present study (filled circles) and data for the EPA monitoring wells (open circles) (Figure 1) acquired during their original installation (CDM/OCM, 2010.*

With the benefit of an extensive monitoring network, it was possible to develop a 3D conceptual understanding of groundwater surface water interactions within the study area, building on the insights provided by the hydrogeophysical results. Lateral groundwater flow paths with resistivity and temperature observations are presented in Figure 6 with head notably higher on the northern side of the stream channel than on the southern side where land use is intensively managed grassland and deep field drainage is a common feature. Both lateral and vertical groundwater flow paths are visualised in Figure 7 with integration of heads measured in PW2 streambed piezometer cluster. These insights demonstrate that groundwater baseflow from the shallow heavily weathered mudstone on the northern side of the stream with potential for lateral flow to the stream and hyporheic exchange on the southern banks where groundwater discharge pressures are weaker. Overall, the intrusive and non-intrusive characterisation approaches demonstrated here offer a promising toolkit for investigating groundwater-surface water interactions where multiple, overlapping measurements at nested spatial scales are often required to characterise heterogeneity and pathways of groundwater flow at reach scale, in headwater streams fed by extreme vulnerability fractured bedrock aquifers.

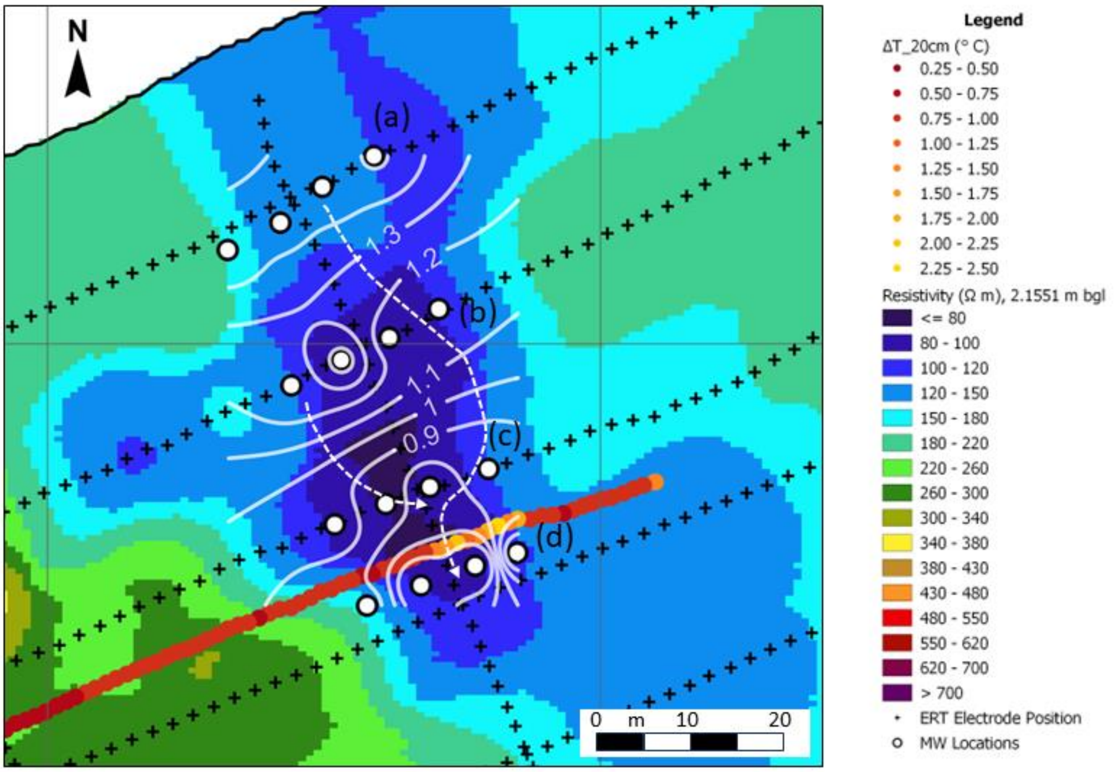

Figure 6: *Groundwater flow directions under average flow conditions in December 2023 expressed as water table elevation in m above stream channel invert level. Monitoring wells IDs are as follows (right to left): transect (a) MW01-04, (b) MW05-08, (c) MW09-12 and (d) MW13-16. The stream channel location is indicated by the temperature data.*

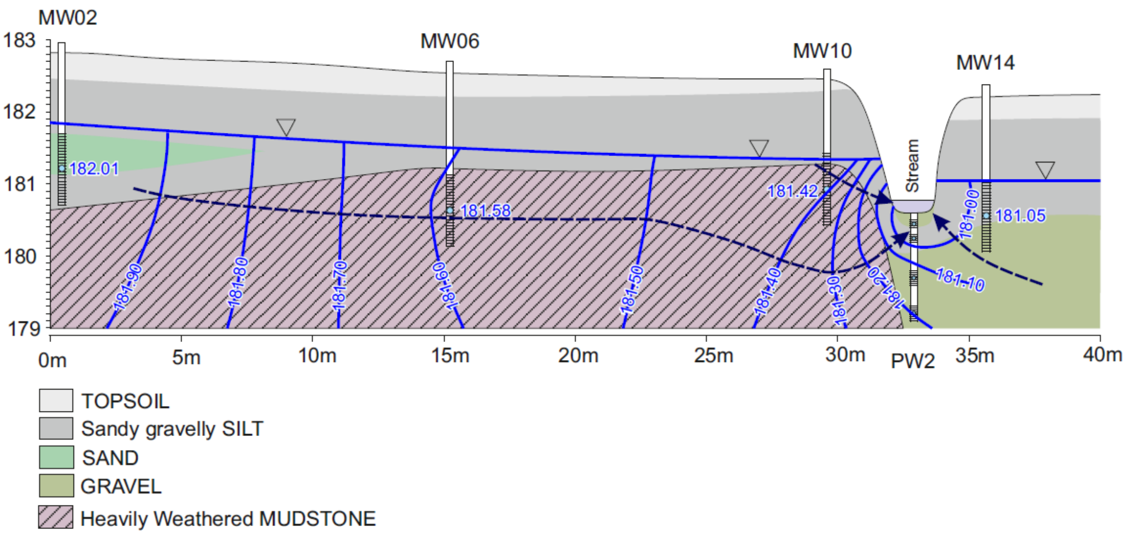

Figure 7: *Conceptual model and cross-section from north to south (MW02-MW14) integrating intrusive investigation data illustrating lateral and vertical groundwater baseflow pathways towards the first order stream channel and hyporheic zone.*

Approximately 40 m of intact cores were retrieved during the intrusive investigation (Table 1) which included four cores directly from the streambed sediments and hyporheic zone (Figure 8). Each core was logged and sub-sampled by lithology to collect homogenised (<2 mm) samples (n = 132) for geochemical analysis including pH, moisture content, organic matter (OM) content (from loss-on-ignition at 550 ^{o}C) and elemental analysis using a factory-calibrated Niton XL2 portable x-ray fluorescence (pXRF) analyser (Figure 8) used in a fixed position in the laboratory (Figure 8).

Figure 8: *Details of intact core retrieval from the streambed and sample processing for geochemical and pXRF analysis. CONSERVE project team members Emilia Palenius and Sophie Lilburn are shown using the core extraction system in the streambed.*

A statistical summary of the geochemical results are presented in Table 2. The pXRF method provided good sensitivity for a range of PTEs including Pb, Se, As, Hg, Zn, Cu, Ni and Co with method detection limits (MDL) of 2 to <30 mg/kg, of which As and Ni are of particular interest in the present study. The method was less sensitive for Ba, Sb, Cd and Cr with few if any samples above MDLs.

Table 2: *Non-parametric statistical summary of homogenised subsoil and heavily weathered bedrock samples (<2 mm fraction, n = 132) analysed in triplicate with MDL calculated from replicate analysis of blanks (pure silica sand) (n = 50).*

Parameter	units	**MDL**	**Min**	**Median**	**Max**	**Range**	**Occurrence**
pH	pH units		3.06	4.43	7.51	4.45	100%
OM	%	<0.01	1.37	2.71	7.19	5.82	100%
Moisture	%	<0.1	5.53	11.08	37.29	31.76	100%
Ca	%	<0.42	0.62	1.76	7.60	6.98	100%
K	%	<0.40	1.24	2.46	4.24	3.00	100%
Fe	%	<0.16	1.28	3.37	9.58	8.29	100%
Mn	mg/kg	<85	179	486	1597	1418	100%
Ba	mg/kg	<450	454	467	481	28	2%
Sb	mg/kg	<77	<77	<77	<77	-	0%
Cd	mg/kg	<34	<34	<34	<34	-	0%
Pb	mg/kg	<9	9.3	12	22	13	70%
Se	mg/kg	<2	2.2	2.8	5.3	3.0	19%
As	mg/kg	<5	5.3	7.8	50	44	48%
Hg	mg/kg	<8	<8	<8	12	-	0.8%
Zn	mg/kg	<18	21	47	137	116	100%
Cu	mg/kg	<22	22	34	1287	1265	42%
Cr	mg/kg	<82	<82	<82	111	-	0.8%
Ni	mg/kg	<29	30	43	92	62	80%
Co	mg/kg	<17	20	93	256	236	98%
V	mg/kg	<49	50	73	114	64	79%

Samples were grouped by lithology to compare potential solid-phase sources of As and Ni with samples from the hyporheic zone (Figure 9), dissolved concentrations of which are known to be elevated in groundwater and streambed pore water in the study area. Redox indicators Fe, Mn and OM are shown for comparison. As was detected in 48% of samples and was generally low across all lithologies apart from discrete hyporheic zone samples. The heavily weathered mudstone bedrock was a potential source of Ni with both the hyporheic zone and weathered mudstone bedrock samples having comparable Fe content (Figure 9). Fe known to be an important control on redox conditions and PTE mobilisation to the aqueous phase in reducing geochemical environments.

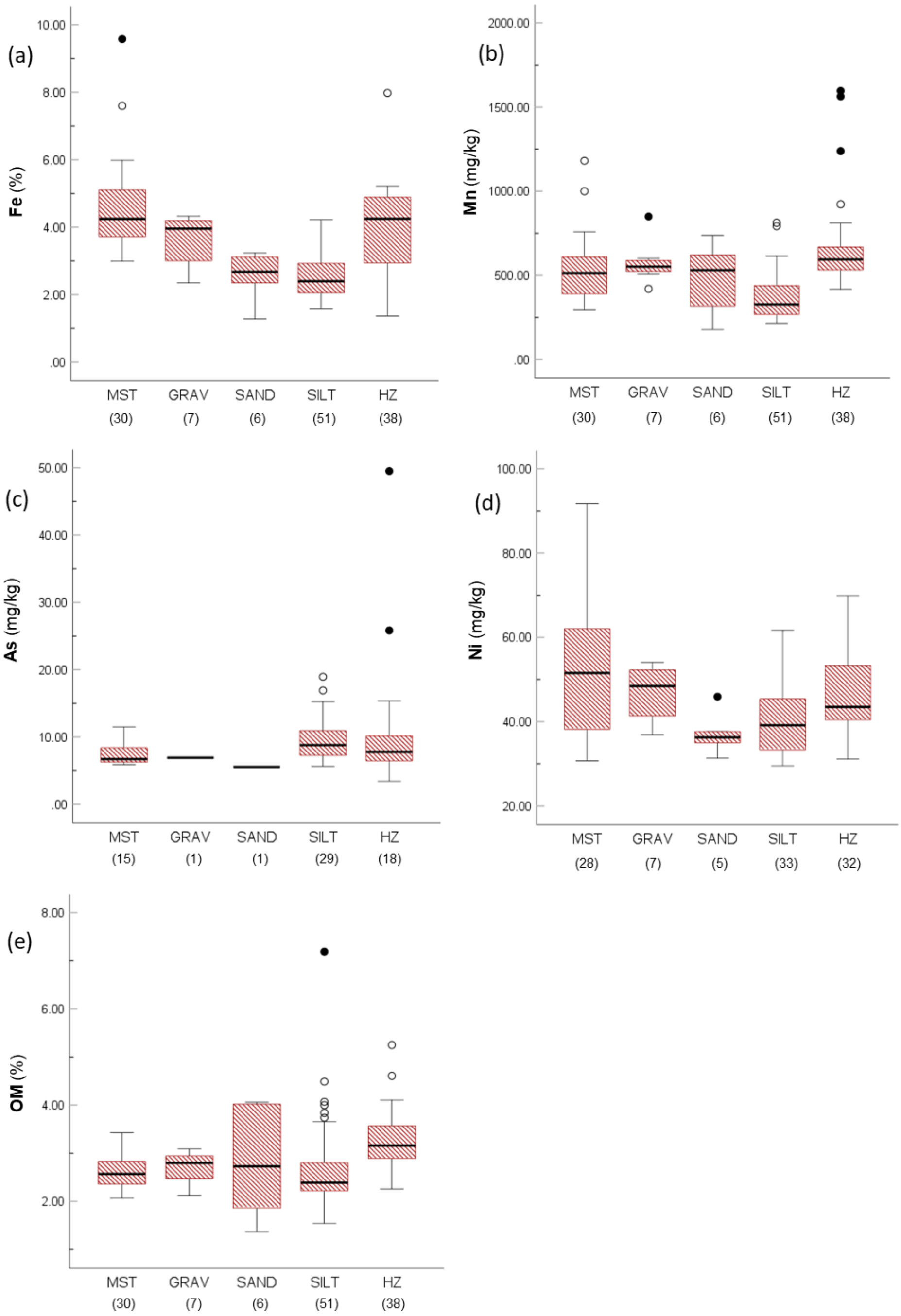

Figure 9: *Boxplots illustrating sample lithology group relationships for geochemical parameters of interest (a-e) with sample size (n) given in parentheses. 'MST' indicates heavily weathered purple mudstone bedrock (Table 1) and 'GRAV' denotes gravel lithology.*

Streambed sediment cores (SS1-4) taken directly from the hyporheic zone (Figure 8) were sub-sampled at 10 cm vertical resolution to provide high-resolution chemostratigraphy (Figure 10). At this resolution, hotspots of As were noted in the shallow samples (<20 below bed level) with concentrations up to 50 mg/kg. This finding is noteworthy as As is an important risk driver for ecosystem function and human health. Solid phase As may originate from fine stream sediment downwelling during hyporheic exchange or from coprecipitation as a result of oxygenation during hyporheic exchange. Overall, the application of pXRF enables the rapid and cost-effective identification of hotspots of PTEs (which may be environmentally hazardous) when combined with lightweight drilling and intact core sampling. Such approaches may be particularly suitable for contaminated land investigation and risk assessment; however, PTE mobility and bioavailability cannot be assessed from total element concentrations measured by pXRF alone.

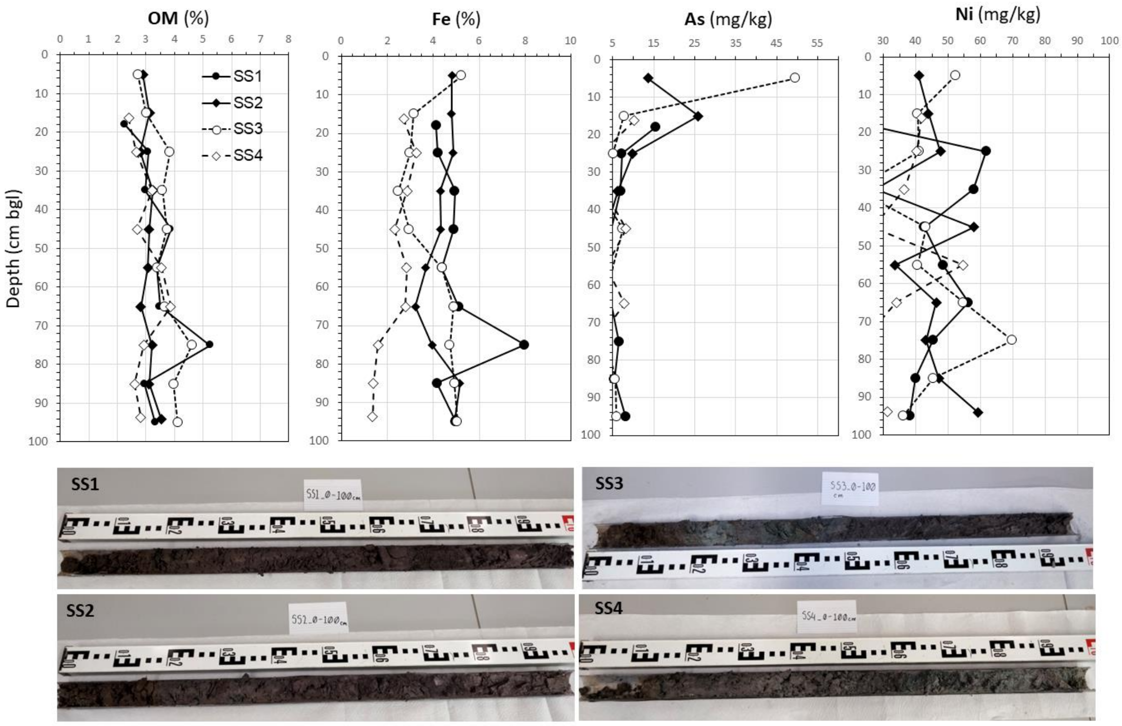

Figure 10: *High-resolution chemostratigraphy profiles from streambed sediment cores in the hyporheic with notable hotspots of As in shallow samples measured by pXRF.*

(ii) Project Implementation

The project implementation was centred around key sequential field data collection campaigns in spring and summer of 2023, including initial geophysical investigations followed by the drilling programme and monitoring well installation in late June 2023 which was a key milestone for the project. It was not possible to include monitoring well transects on the southern side of the stream due to landowner concerns for grassland management. Core sample logging (BS5930:1999/Eurocode 7), processing and geochemical analysis which was complete by the end of August 2023 was another key milestone for project implementation. Processing of samples from intact cores to fine fractions for geochemical analysis (<2 mm) took longer than anticipated due to the presence of heavily weathered bedrock in many cores requiring extensive crushing to provide a <2 mm fractions which were further crushed to a <0.2 mm fine powder for pXRF analysis. Hydraulic testing and analysis of monitoring wells was completed between September and December 2023 which required development of bespoke testing equipment and generated a large volume of transducer time series data with six individual rising/falling tests per well (n = 96). The final phase of GPR data collection (100 MHz) was delayed until December 2023 due to the availability of the geophysical consultant (Andrew Trafford).

(iii) Outputs to date

- Lilburn, S., Palenius, E., Weatherill, J. 2023. *Delineating groundwater pathways and chemostratigraphy of hyporheic zones in headwater agricultural catchments*. GSI Geoscience 2023 Conference, Dublin Castle, 7th of November 2023.
- Lilburn, S., Palenius, E., Jeggo, S., Trafford, A., Weatherill, J. *In preparation*. Uncovering Shallow Groundwater Baseflow Pathways in Fractured Bedrock Agricultural Environments. Submission to AGU journal *Geophysical Research Letters* (impact factor 5.57) with gold open access expected.
- A second manuscript is in preparation featuring pXRF data in combination with existing UCC groundwater, pore water and surface water ICP-MS data for PTEs (As and Ni) and will be submitted to the Q1 journal *Environmental Pollution* (impact factor 0.98) with gold open access expected.
- National and international conference presentations will be prepared with data from the two aforementioned manuscripts.
- Datasets acquired during the project including georeferenced geophysical data, georeferenced borehole logs, georeferenced geochemical data, hydraulic test analysis reports and GIS models are stored on a secure dedicated OneDrive folder managed by UCC. It envisaged that these full datasets will be published as open access supplementary information with the above associated manuscripts.

(iv) Impact

The CONSERVE project has provided valuable new empirical data which sheds light on mechanisms of baseflow discharge processes in extreme vulnerability fractured bedrock environments where the dominant pathway is the bedrock-subsoil transition zone. Of particular interest to the GSI groundwater programme is the additional characterisation of poorly productive bedrock aquifer flow regimes which are the least understood in Ireland but play an important role in baseflow to rivers and drinking water sources. As such, the outputs of the CONSERVE project will feed into and compliment ongoing GSI research projects on climate adaptation (GWClimate) and groundwater resource assessment (GW3D).

The project has demonstrated the application of cost-effective and improved accessibility percussion drilling and intact core sampling techniques for shallow hydrogeological investigations of floodplains, riparian zones and directly in stream and riverbed deposits (not accessible with conventional drilling rigs) where non-invasive hydrogeophysical techniques (ERT, GPR and temperature profiling) can provide drilling targets to conceptualise shallow subsurface heterogeneity and hotspots of geogenic PTE accumulation using pXRF approaches. Integrated methods developed in the project represent an optimised ‘toolkit’ for the development of conceptual and numerical models of groundwater-surface water interfaces which currently presents a significant monitoring gap in many contaminated land field investigations. This is particularly relevant for risk-based management of legacy groundwater contaminant plumes, diffuse pollution and emerging micropollutants where baseflow discharge pathways may form potential pollutant linkages to vulnerable receptors.

The project has produced a valuable, high quality XRF geochemical dataset (132 field samples) which provides an important baseline for comparison with the Tellus soil and streambed geochemical surveys which in time will cover the entire country as well as ongoing European and international geochemical surveys. The project geochemical results will also complement the GSI-funded iCRAG environmental geoscience urban soil PhD project (Hannah Binner) which used the same pXRF methodology. Monitoring networks, hydraulic test data and hydrogeophysical models developed during the project will feed into the iCRAG-funded HYPOFLUX PhD project as well as the large-scale GSI/EPA-funded GRADS & SMARTS project in TCD for stable isotope sampling of which the Dripsey catchment is one of the key project study areas. Isotopic sampling of rainfall and surface water at the field site has been ongoing since June 2023 as part of this collaboration. Finally, the field site and data acquired in the project will be used to develop a proposal re-submission to future Horizon Europe calls with an existing consortium "*Enhancing the natural bioreactor - Protecting the pollutant transformation capacity of the hyporheic zone in the context of global and climate change – HyporEnhance*" of which UCC is a key partner.

References

Jeggo, S., Weatherill, J. 2019. *Revealing shallow groundwater pathways to headwater stream networks in fractured bedrock environments*. Proceedings of the International Association of Hydrogeologists Irish Group, 39th Annual Groundwater Conference, 30th April-1st May. Tullamore, Ireland.

CDM/OCM, 2010. *Well Completion Report, Dripsey Catchment, County Cork*. Prepared for Carlow County Council and the Environmental Protection Agency. July 2010.

Publications:

Lilburn, S., Palenius, E., Weatherill, J. 2023. *Delineating groundwater pathways and chemostratigraphy of hyporheic zones in headwater agricultural catchments*. GSI Geoscience 2023 Conference, Dublin Castle, 7th of November 2023.

3. Supplemental information/datasets *(please clearly mark any sensitive or confidential information that should not be published and include a justification for the request)*