Roinn Cumarsáide, Fuinnimh & Acmhainní Nádúrtha
Department of Communications, Energy & Natural Resources

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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| *For official use only* | | |
| *Date received:* | *Ref. No.:* | |
| ☐ **GSI Geoscience** | ☐ **INFOMAR** | ☐ **Tellus** |



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|---|---|
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|---|---|---|---|
| Organisation name | Queen's University of Belfast | | |
| Organisation type: | ☒HEI | ☐Public Sector (other) | ☐Private Sector |
| Department/section | School of Natural and Built Environment | | |
| Address | Elmwood Building<br>Queen's University of Belfast<br>Belfast<br>Northern Ireland<br>BT7 1NN | | |



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|---|---|
| Project Title | Development of integrated protocols for the rapid mappping and assessment of metal contamination in intertidal sediments |
| Contract No. | 2015-sc-074 |
| Total financial support requested from GSI (as per proposal) | €24,930 |

The details presented in this report are a true and accurate reflection of the work undertaken and the associated financial expenditure. All work was carried out within the GSI Terms and Conditions and as per the Contract (unless formally amended).

Signed: Helen M Roe
Lead Investigator

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

Tellus Understanding Underground

Marine Institute Foras na Mara

1. **NEW Partner information** – (in addition to those named in project proposal)
*please copy table as needed*:

| | |
|---|---|
| Co-applicant name | Dr Robin Edwards |
| Role in the project | Assisted with the foraminiferal analyses |
| Organisation name | Trinity College Dublin |
| Organisation type: | ☒HEI ☐Public Sector (other) ☐Private Sector |
| Company Registration No. (if applicable) | |
| Department/section | Department of Geology |
| Address | Museum Building<br>Trinity College Dublin<br>Dublin 2, Ireland |

| | |
|---|---|
| Co-applicant name | Professor Tim Patterson |
| Organisation name | Carleton University, Ottawa, Canada |
| Organisation type: | ☒HEI ☐Public Sector (other) ☐Private Sector |
| Company Registration No. (if applicable) | |
| Department/section | Department of Earth Sciences |
| Address | Herzberg Building<br>Carleton University,<br>Ottawa, Ontario,<br>K16 5B6, Canada |

**Staff funded by the GSI Short Call Project** (add lines if required)

| **Name** | **Male/female** | **Position** | **Expertise** |
|---|---|---|---|
| **Stephen Prentice** | M | Part time Research Assistant. | Foraminiferal analysis; assisted with geochemistry, core sub-sampling and fieldwork |
| **Chloe Floyd** | F | Part time Research Assistant. | Spatial data analysis; geostatistics; preparation of figures. |
| **Rachel Patterson** | F | Part time Research Assistant. | Part time Research Assistant. assisted with LOI and Particle Size analysis; core subsampling; preparation of figures for publication |
| **Rory Flood** | M | Part time Research Assistant | Geostatistics; ITRAX-ICP calibration model development |

2. **Project information**:

| | |
|---|---|
| Title of project | Development of integrated protocols for the rapid mappping and assessment of metal contamination in intertidal sediments |
| Did you make any formal amendment to the project workplan / budget? | ☒ yes ☐ no<br>If yes, please specify:<br><br>Some minor amendments were requested and approved in October 2016. |

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

## (i) OBJECTIVES AND SCIENTIFIC/ENGINEERING TARGETS BEYOND THE STATE OF THE ART

The project had seven objectives:

***Objective 1:* To develop new calibration models and sampling procedures for the measurement of metals in intertidal and supratidal sediments using *ITRAX-XRF core scanning* cross-validated with ICPMS.**

Twenty seven sediment cores were collected; 19 from mudflat and 8 from saltmarsh settings in an estuarine study site in County Down, Northern Ireland.

*Model Development and Evaluation:* Twenty cores were analysed on the ITRAX scanner and 70 core subsamples were used to build calibration models.

**The log-ratio calibration equation (LRCE) method developed by Weltje and Talllingii (2008) was applied to high resolution (0.5 mm) ITRAX-core scans; this is the first time this method has been utilised for analysis of ITRAX-data from mudflat and saltmarsh sediments.** With the exception of cores that showed marked lithological change, raw XRF element profiles show low amplitude elemental variability in sediments across the site. For this reason it was important to optimize discrete sub-sampling for the LRCE. Sub-sample intervals (10mm) for ICP analysis were selected from centred log ratio (clr), sub-compositional datasets using Ward's (1968) method (cf. Wieltje et al., 2015). Sub-samples were analysed for an assay of elements by ICP-OES and used for calibration. The results of the LRCE model show that Mn is the optimal log-ratio denominator as defined by the Euclidian distance (Table 1) with good predictions for several elements. This will improve with the further integration of particle size and loss-on-ignition (organic matter) datasets.

The results are promising given the relatively small calibration dataset (n=70) and the low variability in concentrations of the majority of elements found in the core sediments (Fig. 2) and, with the aforementioned refinement, are expected to allow relative concentrations of the sub-compositional dataset to be determined.


**Fig 1. a) Core collection. Three replicate cores were collected from each station and dug out in vertical position; b) split cores collected from the mudflat stations.**

| Al | As | Ba | Bi | Ca | Cd | Ce | Co | Cr | Cu | Fe | Ga | K | La | Mg | Mn | Ni | P | Pb | Rb | S | Se | Sn | Sr | Ti | U | V | W | Y | Zn | Zr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2.73 | 0.64 | 6.97 | 0.97 | 0.70 | 8.48 | 0.76 | 3.24 | 10.94 | 0.94 | 1.59 | 114.73 | 8.69 | 2.01 | 2.21 | 0.60 | 8.52 | 1.30 | 1.03 | 0.92 | 0.95 | 2.97 | 7.06 | 1.33 | 1.84 | 1.50 | 1.33 | 1.57 | 119.24 | 0.75 | 0.70 |

**Table 1. Euclidian distances for elements used in the log-ratio calibration equation (LRCE). The lower the values the better the model fit for that element.**

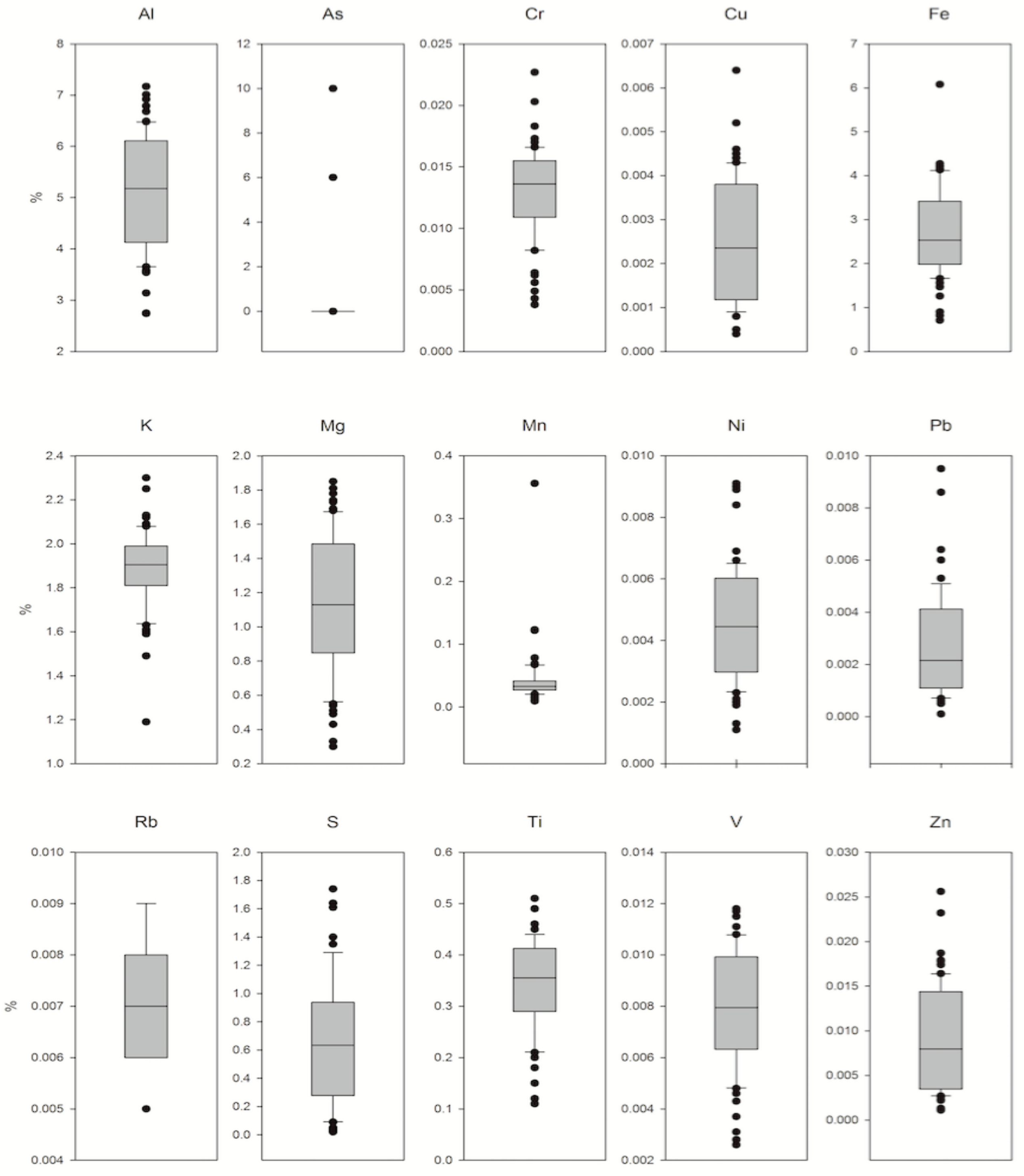


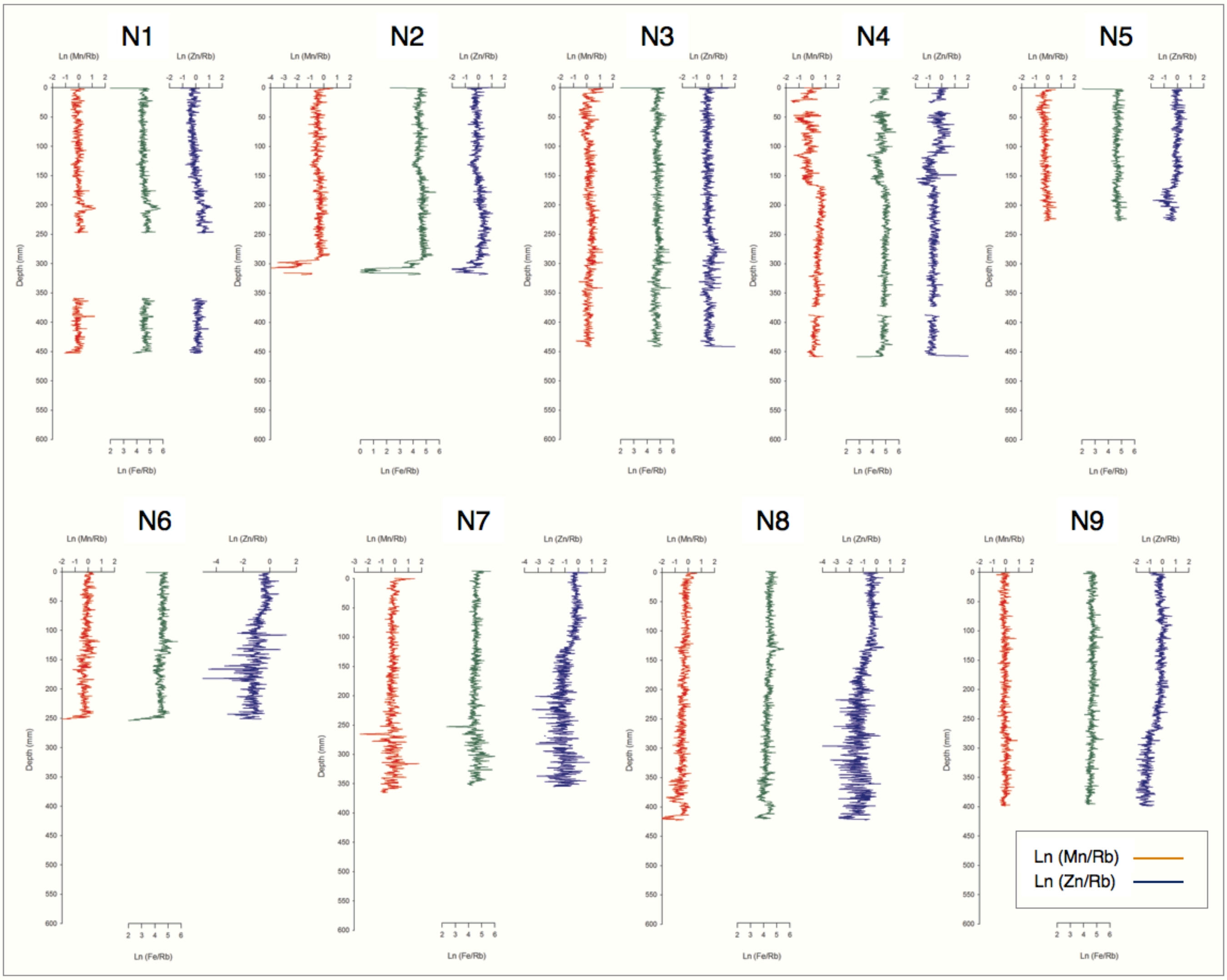

**Fig 2. Boxplots of element concentrations in the 70 samples analysed using ICP-OES showing relatively low variability within the sampled intertidal sediment cores.**

***<u>Objective 2:</u> To examine the distribution and pathways of metal contaminants through a gradient of sedimentary environments and tidal settings and to examine associated sediment matrix-related effects.***

To examine the spatial distribution of metal contaminants, surface sediment samples were collected from the study site and subject to subject to ICP-MS, PSA and LOI analysis. <u>The results of this work are currently being written up for publication in a peer-reviewed journal and will be made available once the work is published in late 2017/early 2018.</u>

***Objective 3:*** ***To (i) use ITRAX-based XRF analysis to examine the vertical distribution of leachate-derived metals in the sediments from short (50 cm) sediment cores (n = 10) collected at varying distances from a contaminated site; and (ii) to inform the development of protocols for measuring metal concentrations in intertidal sediments, including saltmarsh sediments.***

**Evaluation: The large ITRAX core dataset (n=20) collected in the study provided an important framework to examine down-core elemental distributions rapidly at very high-resolution; no study has hitherto achieved this in such detail for an estuarine site.** Although, statistically, Mn represents the optimal divisor in the LRCE model, the ITRAX data showed variable Mn distribution in the cores that could be related to REDOX conditions and/or contamination. As these Mn data would potentially skew or mask patterns of relative contamination, the element Rb was used an alternative divisor, because it shows strong relationships to targeted elements and is relatively uniformly distributed in sediments across the site (Supplementary Fig. 1). Fig. 7 shows selected scaled log-ratio profiles (Fe, Mn, Zn) for mudflat cores on the north and south banks of the study site from W to E. In cores N1 to N3 elevated Zn is recorded below 200 mm with the peak at 270 mm corresponding to c. 260 ppm (about 10 times higher than Zn concentrations at the base of reference core S8). Cores taken from the east of the site and along the south bank all showed elevated Zn concentrations in the top 300-100 mm. Fe and Mn trends are less consistent, with some evidence of Fe and especially Mn accumulation at depth. However, Mn does show marked increases in log-ratios (corresponding to increased concentrations) in the upper mm of cores N2-N4 around the contaminated site. Interpretation of the patterns in the saltmarsh cores is more difficult because of inherent variability associated with organic matter and noise in the Itrax profiles. **Further comments on the wider application of the protocols and approach are given in Section (iii) 'Impacts' below.**



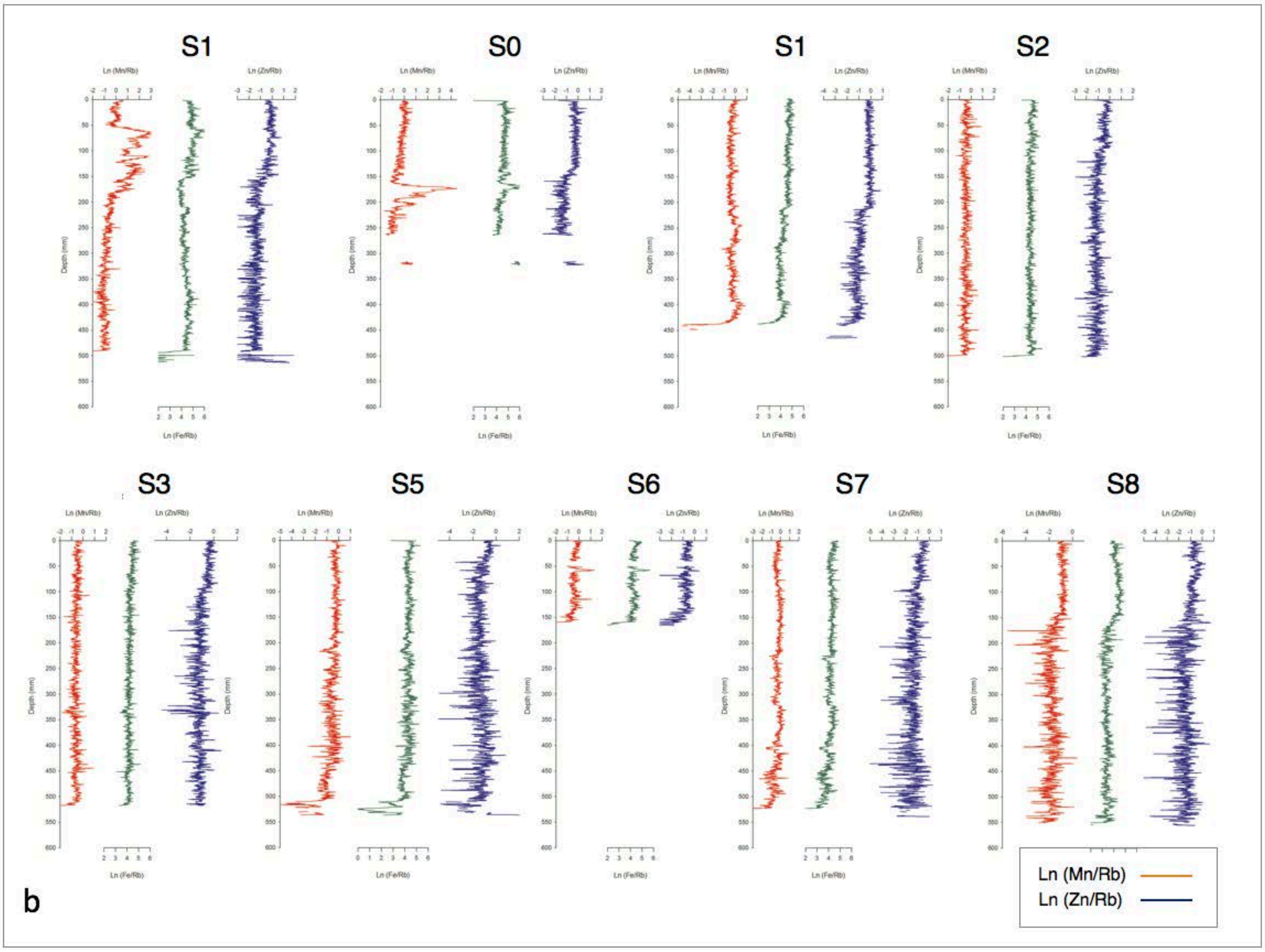



**Fig. 7 High resolution (0.5 mm) ITRAX-XRF plots for the sampled mudflat cores for Mn (red); Fe (green) and Zn (blue); from (a) the north side of the study site and (b) the south side. A gradual increase in the three elements in the top few mm of Cores N2, N3, N4 and N5 may reflect leaching from the landfill site. The lack of significant change in these elements in the other profiles suggests that vertical leaching of metals down core has been minimal. It may also reflect high clay content in the upper mudflat sediments, which could have prevented significant down-core mobilisation of most metals.**

***<u>Objective 4:</u> To examine foraminiferal distribution in a subset of the samples to appraise the utility of the group for biomonitoring and habitat assessment in contaminated intertidal environments.***

*<u>The results of this work are currently being written up for publication in a peer-reviewed journal and will be made available once the work is published.</u>*

***<u>Objective 5:</u> To run additional ICPMS analyses on existing Tellus geochemical samples and new sediment samples using a range of different pre-treatment protocols to examine the effects of differing extraction techniques on metal speciation.***

To address this, 15 Tellus Soil-A samples were selected from the hinterland around the estuarine study site for analysis using a four-acid digest method. The results were compared with existing ICP Aqua Regia and XRF datasets for the same samples. Cluster dendrograms were generated for each dataset based on isometric log-ratio transformation (ILR) values, which were used as part of the data exploration discovery process (Fig. 10). **A compositional approach is important for avoiding spurious results due to the inherently multivariate relative information conveyed in geochemical data** (McKinley et al. 2016).

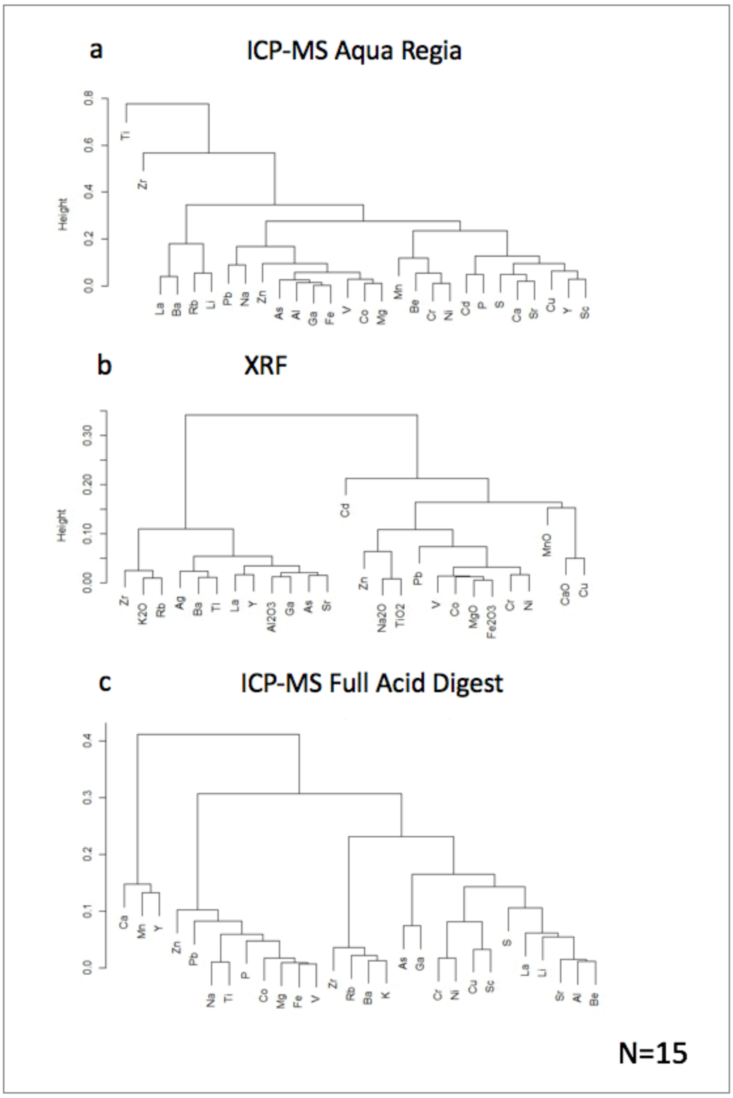



**Fig. 10 Cluster dendrograms showing the results of different pre-treatments on 15 Tellus Soil A samples collected from the hinterland around the study site. (a) ICP-MS Aqua regia (source: Tellus NI Database); (b) XRF (source: Tellus NI Database) and (c) ICP-MS Full Acid Digest (this study). Note: Plot C does not include values for Cd which was below detection limits. *Interpretations:* whilst similarities exist in the three dendrograms, different associations are shown. In particular, the patterns for Zr and Mn differ. Two distinct partitions are observed in the XRF dendrogram. In the ICP-MS Aqua regia plot Ag, Ti and Zr show different associations from the other elements, whilst the Full Acid dataset shows three distinct partitions.**

__Evaluation:__ The dendrograms show some consistency between the XRF and 4-acid digest approaches (e.g. Ca/Mn; Na/Ti; Zr/Rb.K; Fe/Mn/V/Co), but much greater variation with the aqua regia outputs. Whilst these finding are not unexpected, they emphasise the importance of replicating analytical methods in regional studies integrating Tellus outputs. **This finding also has important implications for other researchers who plan to use the Tellus geochemistry datasets to understand spatial metal loadings around contaminated sites and for other biomonitoring studies where the availability of soluble, bio-available metals is key.** Further work is required to assess this.

Comparisons were also drawn between the estuarine surface sample dataset and Tellus Soil A Aqua regia data and the Tellus stream datasets to provide a fuller understanding of baseline metal distributions in the regional sediments and to examine the provenance of the metals in the intertidal area. For the comparative soil study, 125 Tellus Soil A samples were selected from the hinterland. Evaluation: The results of this analysis are important and confirm that many key metals of interest in the study (with the exception of Mn) occur in greater concentrations in the mudflat and saltmarsh sediments than in the surficial layers of the regional soils (Fig 12). **This indicates that metals have either been concentrated in the fine mudflat sediment and/or have been derived from contaminant inputs within the estuary hinterland. These findings re-affirm the importance of using the Tellus geochemistry data to evaluate regional metal distribution patterns both in terrestrial and high intertidal/saltmarsh settings.**

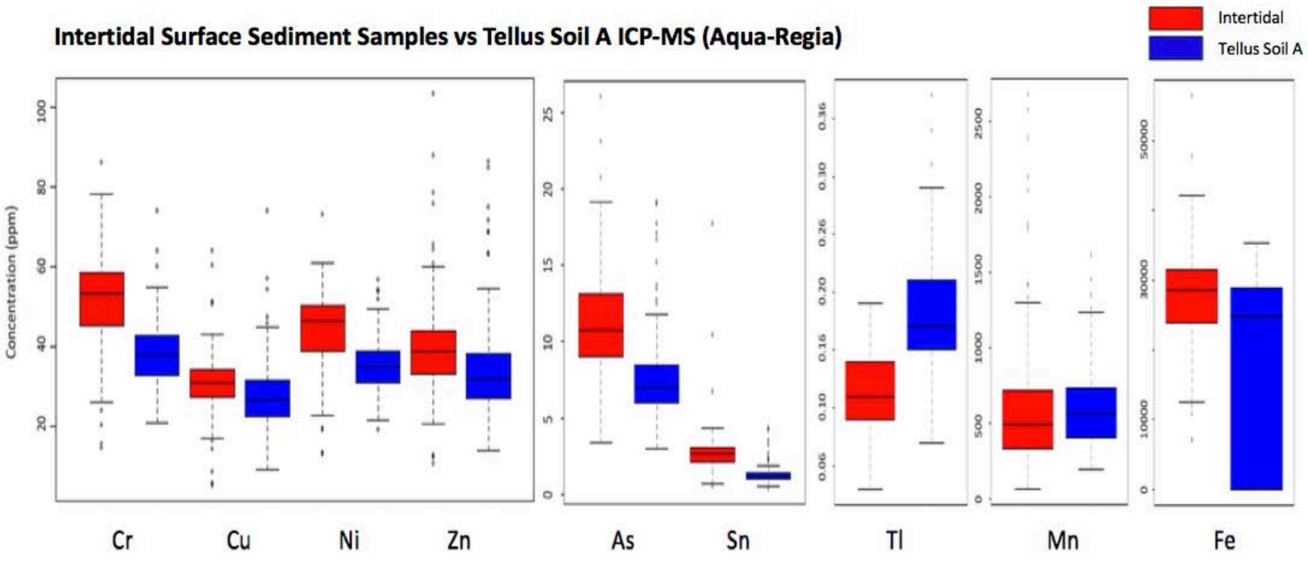



**Fig. 11 Box and whisker plots showing selected metal ICP-MS results from the Tellus Soil A samples in the hinterland (n=125) and the intertidal surface sediment dataset (n=178). All samples were prepared using consistent extraction procedures (Aqua regia digest).**

***Objective 6:*** ***To use GIS and spatial statistical approaches to map and interpret patterns of metal concentration in intertidal and supralittoral areas, thus aiding in understanding the impacts and pathways of contaminants in coastal regions.***

As noted above (Objective 2), several statistical techniques were used to interpret the mudlflat ICP-MS and ITRAX-XRF data. In addition to sample density plots, Kernel Density plots were generated. We opted not to run other spatial analytical approaches (e.g. kriging) on the surface sample data because of the compositional nature of the data (see above) and access issues and the unstable nature of the mudflats meant that it was not possible to collect sufficient surface samples across the site.

***Objective 7:*** ***To develop new analytical procedures that will have wide applicability for the rapid monitoring and assessment of other metal-contaminated coastal sites in Ireland and further afield.***

Please see points above and further comments on this in Section (iii) 'Impacts' below.

## (ii) Implementation (including reference to timelines, milestones, management)

All seven project objectives were achieved and many of the project goals were exceeded (e.g., we scanned 20 ITRAX cores instead of a planned 10, we extended the ICP-MS analyses for the cores and surface samples to improve the calibration models and gain a better understanding of metal fluxes). For **Workpackage 4: ICP Extraction protocols**, more emphasis was placed on examining existing Tellus data from the hinterland to allow fuller consideration of baseline metals in the regional sediments. Some of the Tellus Soil A samples from the hinterland also had no sediment available at the GSNI core repository for further primary analysis so only 15 samples were analysed.

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## (iii) Outputs

- [Conference Presentation] Roe, H.M., Patterson, R.T., Nasser, N., Edwards, R.J., Graham, C. (2016). Development of integrated protocols to track the deposition and impacts of metal contaminants in tidal riverine environments. *Geophysical Research Abstracts Vol. 18, EGU General Assembly 2016, EGU2016-15439, 2016, Vienna, Austria, 21 April 2016.*

- [Conference Presentation] Roe, H.M., Patterson, R.T., Nasser, N., Edwards, R.J., Ruffell, A.J., Graham, C. (2016). Integrated protocols for monitoring the impacts of landfill-derived leachates in intertidal environments. *35th International Geological Congress, Cape Town, 27 Aug - 4 Sept 2016.*

- [Workshop Presentation] Roe, H.M., Turner, J., McKinley, J.M., Graham, C., Prentice, S.V. (2016). Applications of Tellus data for the assessment of metal contamination in intertidal environments. *Tellus Stakeholder Meeting and launch of 'Unearthed: impacts of the Tellus surveys of the north of Ireland', Royal Irish Academy, Dublin, 5 October 2016.*

- [Conference Presentation] Turner J., Roe, H.M., McKinley J.M., Amirnezhad Mozhdehi, S., Graham C., Prentice, S.V. (2016). Rapid assessment of metal contamination in intertidal environments: a case study from County Down, Northern Ireland. *Irish Geomorphology Group Fourth Annual Scientific Workshop, University College Cork, Cork, 25 Nov 2016.*

  Other: Journal manuscripts are in preparation and planned.

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

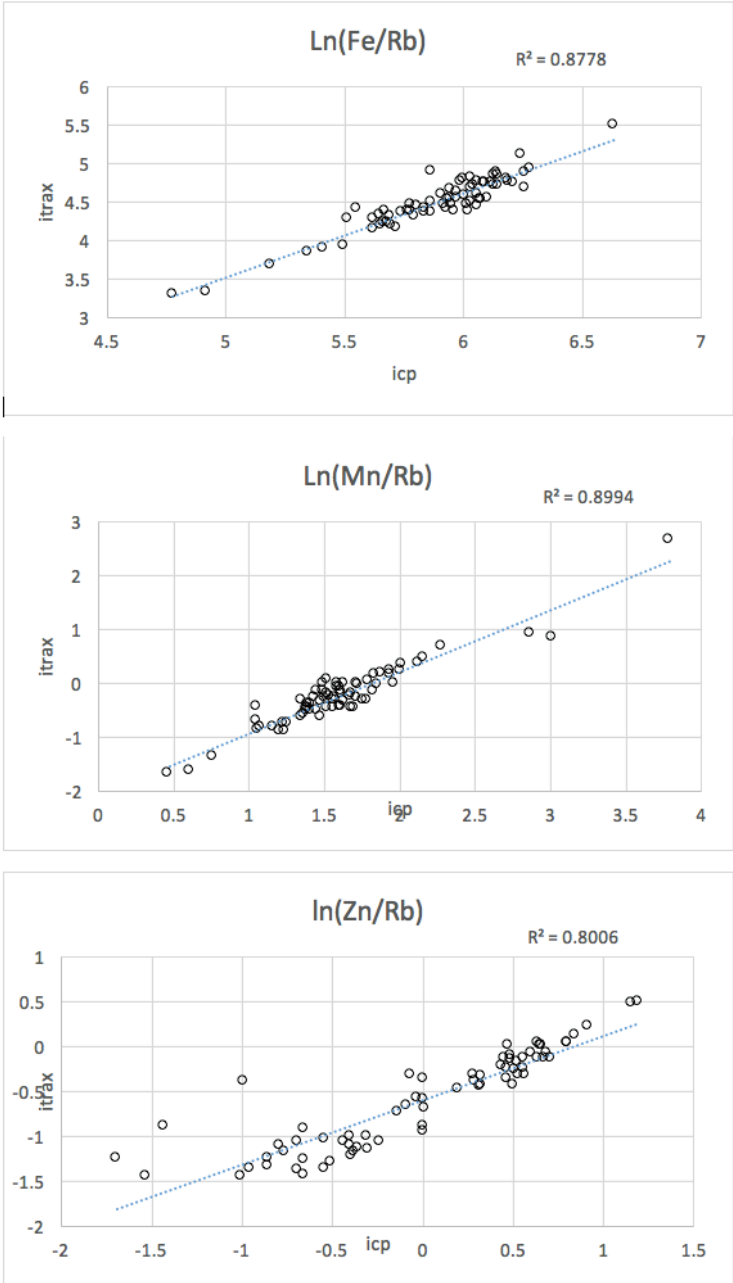
This study has highlighted the utility of **integrated biogeochemical approaches** for the analysis of metal contamination in intertidal sediments. The ITRAX core scanning allows ultra high resolution, rapid assessment of elemental distributions spatially and at depth. The preliminary model that has been developed demonstrates that calibrated relative concentrations based on the LRCE (log ratio calibration equation) approach can be achieved even in sediments which show relatively small variations in element concentrations. **This method therefore has potential for investigating subtle levels of contamination with precision in sensitive settings, where thresholds for impact may be relatively low (for example, in comparison to other settings like mining sites), but where absolute element concentrations are nevertheless having an impact on the biota.** This approach could be beneficial in many other coastal regions, for example, estuaries impacted by industry but with no clear visual signs of pollution, or to assess distal as well as proximal leachate impacts around other landfill sites. In the case of the study site, the ITRAX-scanning technique was successful in permitting rapid and wide ranging spatial assessment of the sedimentary fill of the estuary in a short time-frame (ca. 4 months). Equivalent ICP-MS analysis of the same number of cores would have much slower and significantly more costly.

The foraminiferal study has similarly highlighted the **potential of biomonitoring approaches for assessing metal contamination in intertidal environments.** Through this approach it has been possible to highlight some of the complex sedimentary and geomorphic controls on metal accumulation in estuarine settings. The results of this work are being written up for publication in a peer-reviewed journal and will be made available once published.

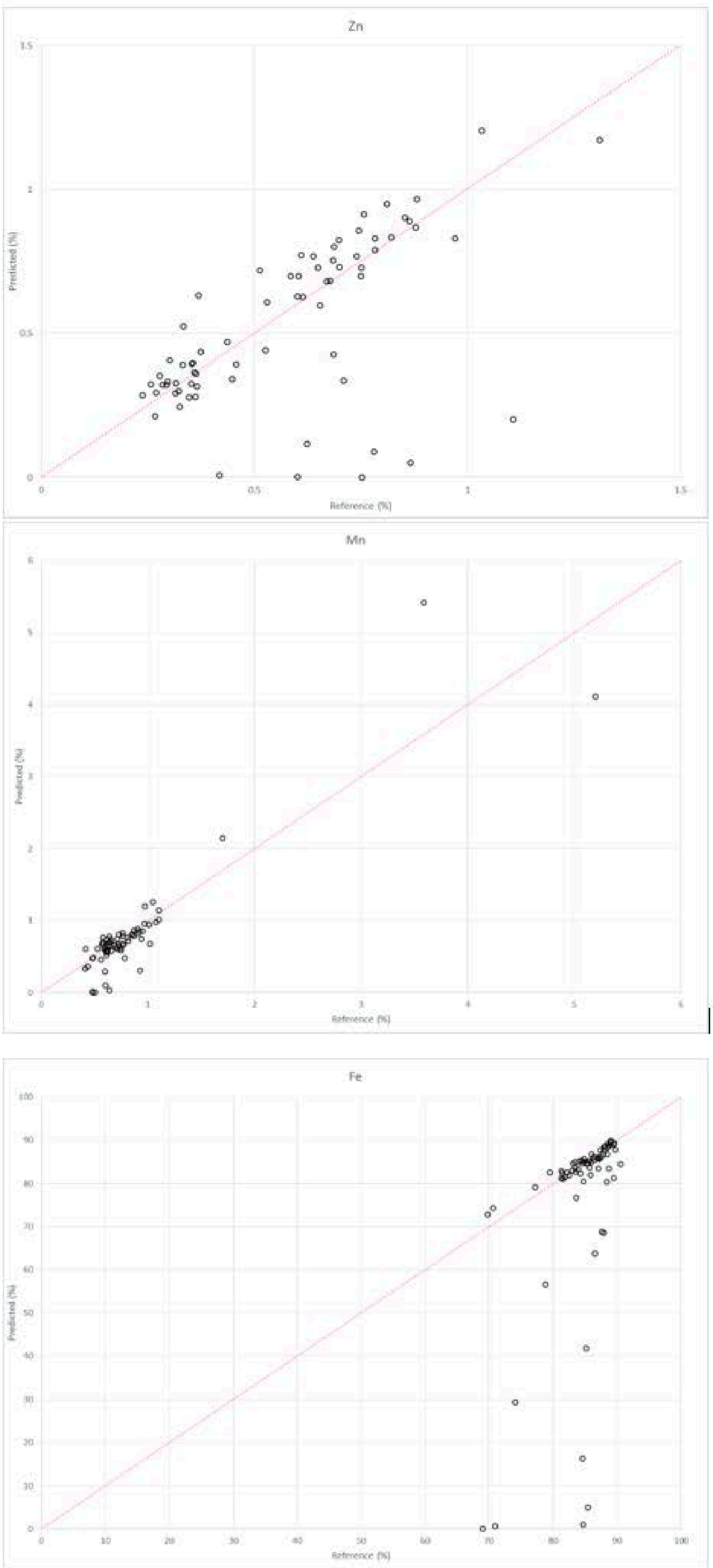
The analysis of the Tellus geochemical data from the hinterland soil samples and Tellus Steam data samples provided critical context for interepreting the metal concentration data from the estuarine samples; as noted above, these findings **re-affirm the importance of using the Tellus geochemistry data to evaluate regional metal distribution patterns both in terrestrial and high intertidal/saltmarsh settings**.

**Additional figures and data cited in the text in relation to the Project Objectives:**

*Objective 1: ITRAX model development*




**Supplementary Fig. 1. Log ratio plots showing goodness of fit using Ln(Rb) as the devisor.**




**Supplementary Fig. 2. Validation plots used for the LRCE model.**