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Terra Soil Project:

Summary Geochemical Assessment

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Abstract

Terra Soil is a joint project between Geological Survey Ireland (GSI) and Teagasc, combining geological and geochemical with new agronomic analyses, with the aim of providing the agricultural sector with high quality, agri-environmental information about Ireland's soil to better inform the sector, support sustainable agriculture and protect Ireland's environment. The project has analysed almost 10,000 soil samples, originally collected as part of GSI's Tellus Programme, for available nutrients, metals, and trace elements, following digestion by both Mehlich's 3 (Al, Ca, Co, Cu, Fe, K, Mg, Mn, P, S, Zn) and Morgan's (K, P) reagents.

It has also analysed the samples spectroscopically to predict texture class and particle size. The resulting new Terra Soil datasets have been combined with existing Tellus geochemical data and mapped on a regional scale to produce derivative data products for the agricultural and wider community, giving greater insights into Ireland's soil fertility, crop and animal health, land drainage, nutrient management, and farm economics.

In general, Tellus ICP *aqua regia* (ICPar) data demonstrate a strong geogenic signature, at least in areas of mineral soil. Areas predominantly comprising peatland have a very attenuated geochemical signal, reflecting low absolute concentrations of elements in peat or soils with very high organic matter (OM) content. Thus, the geochemical maps generated from ICPar data typically display two contrasting signatures: higher element concentrations in the midlands, where mineral soils predominate, and low concentrations over blanket bogs in the uplands of Galway, Mayo, Donegal and Wicklow, and some raised bogs in the midlands. For the elements Al, Ca, Cu, Mn and S, Mehlich's 3 (M3) data, despite the much weaker digestion involved, display similar spatial distributions to ICPar data. In contrast, the elements Fe, K, Mg, Zn have spatial distributions that are essentially the opposite to those displayed by ICPar data, with areas of relatively high element concentrations on mineral soil, as measured by ICPar, appearing as areas of low M3 element concentration, while areas of peatland have relatively high M3 element concentrations. This phenomenon clearly reflects the selective nature of the M3 digestion. Estimated element extraction rates for elements in *aqua regia* are broadly similar for both mineral soils and OM-rich soils, including peat, with differences typically insufficient to affect the mapped distribution significantly. However, for M3 reagent, extraction rates for mineral soils and OM-rich soils can differ very significantly, with corresponding impact on the mapped distribution. For K, Fe, Mg and Zn, the extraction rates in OM-rich soils are substantially higher than for mineral soils, giving rise to measured M3 element concentrations that are higher in areas of peat than in areas of mineral soil. The resulting geochemical maps thus appear as inverses of the corresponding ICPar maps. The distribution of P is more complex. High P, as measured by ICPar, indicates both a significant geogenic signature, mainly linked to mineral soils, and an anthropogenic one apparently related to tillage farming, while low P is recorded over OM-rich soils. The M3 data are broadly similar but the higher extraction rate of P in OM-rich soils means that areas of peatland show some contrast to ICPar data. Morgan's data also display relatively high values over tillage areas and OM-rich soil but do not reflect the composition of mineral soils to the same degree as M3 data.

The ICPar, Mehlich's 3 and Morgan's data have been assessed in terms of soil attributes, including drainage class, texture, bedrock geology, Quaternary geology, land use, particle size and topography. In most cases, some of the observed variation in soil composition can be related, at least in part, to each attribute. This is especially true for bedrock geology, Quaternary geology and land use, for which distinctive categories of soil display specific compositions.

For other soil attributes, a relationship between the attribute and soil chemistry is less readily established or not observed at all. Topography falls within the latter category, with elevation, slope and slope direction exerting no clear influence on soil composition. Soil drainage and soil texture display some apparent correlation with soil chemistry, but both these attributes show considerable overlap with other features. Soil drainage reflects the OM content of soils, with the poor drainage class largely equivalent to peat soils. Soil texture classes partly reflect bedrock composition in addition to specific soil compositions, such as peat and marine sands.

1. Introduction

Terra Soil is a collaboration between Teagasc and Geological Survey Ireland (GSI). It aims to bring together GSI's geological data and knowledge and Teagasc's soils and agronomic expertise to provide the agricultural sector with high quality, agri-environmental information about Ireland's soil to better inform the sector, support sustainable agriculture and protect Ireland's environment. To do this, the project has analysed almost 10,000 soil samples, originally collected as part of GSI's Tellus Programme, for available nutrients, metals and trace elements. It has also analysed the samples spectroscopically to predict texture class and particle size. The resulting new Terra Soil datasets have been combined with existing Tellus geochemical data and mapped on a regional scale to produce derivative data products for the agricultural and wider community, giving greater insights into Ireland's soil fertility, crop and animal health, land drainage, nutrient management and farm economics.

As part of the project, geochemical assessments were carried out on the Terra Soil and Tellus data to provide an overview of the geochemistry of topsoil within the northern half of Ireland, providing a context for a wider understanding the new Terra Soil data. This summary document provides an overview of these assessments and summarizes their main findings.

Attributed geochemical data were assessed using exploratory data analysis (EDA), a process of "analysing data sets to summarize their main characteristics, often using statistical graphics and other data visualization methods", including spatial mapping. Much of the work was completed using iOGAS software. This visualization approach allows for identification of outliers and patterns in the data.

The results are expressed in various plots, notably Tukey boxplots, scatterplots, and 2-D maps. Boxplots, allow for rapid comparison of the data distributions of subsets of the data, including the various classifications of the data based on topsoil attributes.

1.1. Tellus survey areas and soil analyses

Tellus soil samples have been collected in Northern Ireland (2004-2006), the border counties of Ireland (2011-12), in the west of Ireland (2016) and in the north midlands and the peri-urban areas of Dublin and Galway (2017-2019).

Only samples collected in Ireland, i.e., excluding Northern Ireland (NI), have been employed for the Terra Soil project, yielding a total of 9911 ICP-OES analyses following Mehlich-3 extraction and slightly fewer following Morgan's extraction.

Available Tellus XRF data for NI, the border counties, west and periurban areas have been used to estimate extraction rates for soil samples digested with aqua regia (Tellus) and subsequently analysed by ICP. This approach assumes that an XRF analysis is a total analysis of a given sample and thus the equation (ICP/XRF)*100 is an estimate of the proportion of a given element that is digested or extracted by aqua regia. For Terra Soil samples, extraction rates for samples digested in Mehlich-3 solution were similarly estimated using Tellus XRF data, albeit excluding that for NI. Morgan's P and K data are reported in units (mg/L) that differ from those for XRF and ICP data (mg/kg or wt %) and for these no estimate of extraction rates is possible.

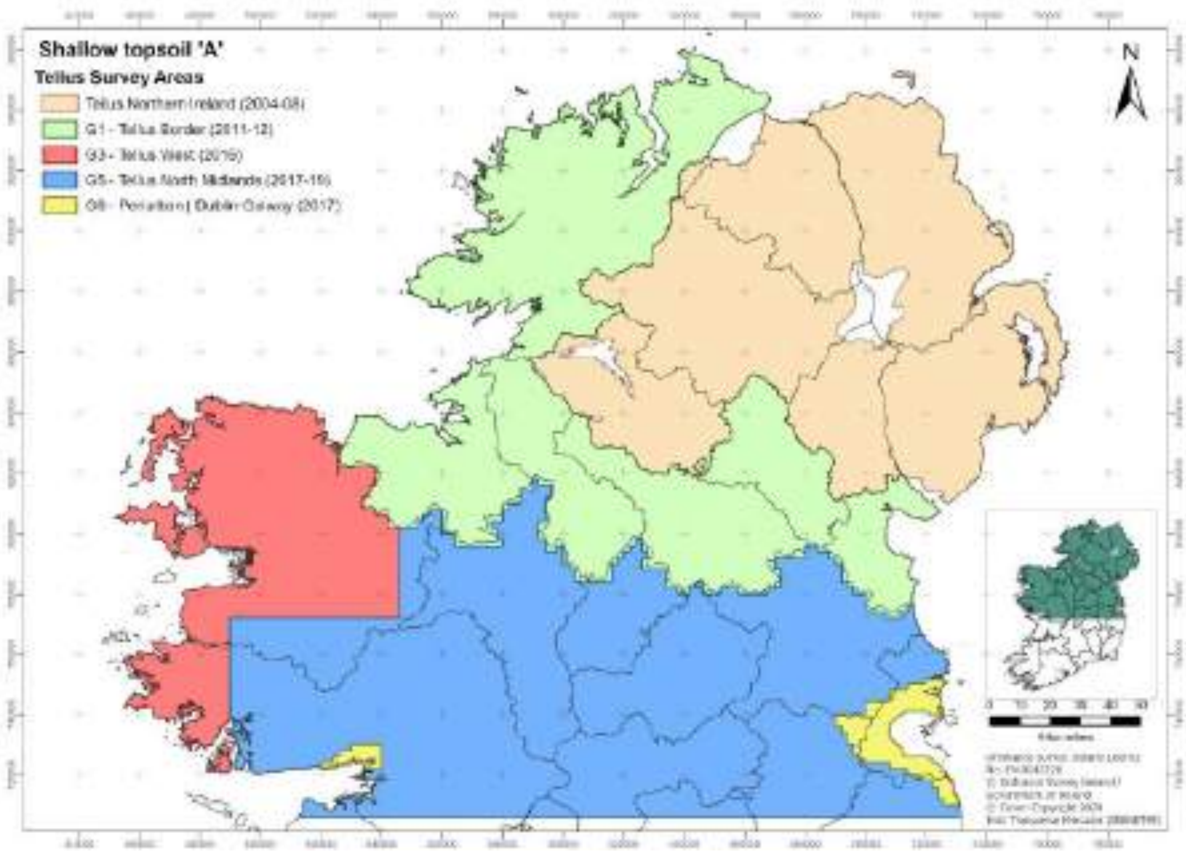


Figure 1: Tellus survey areas

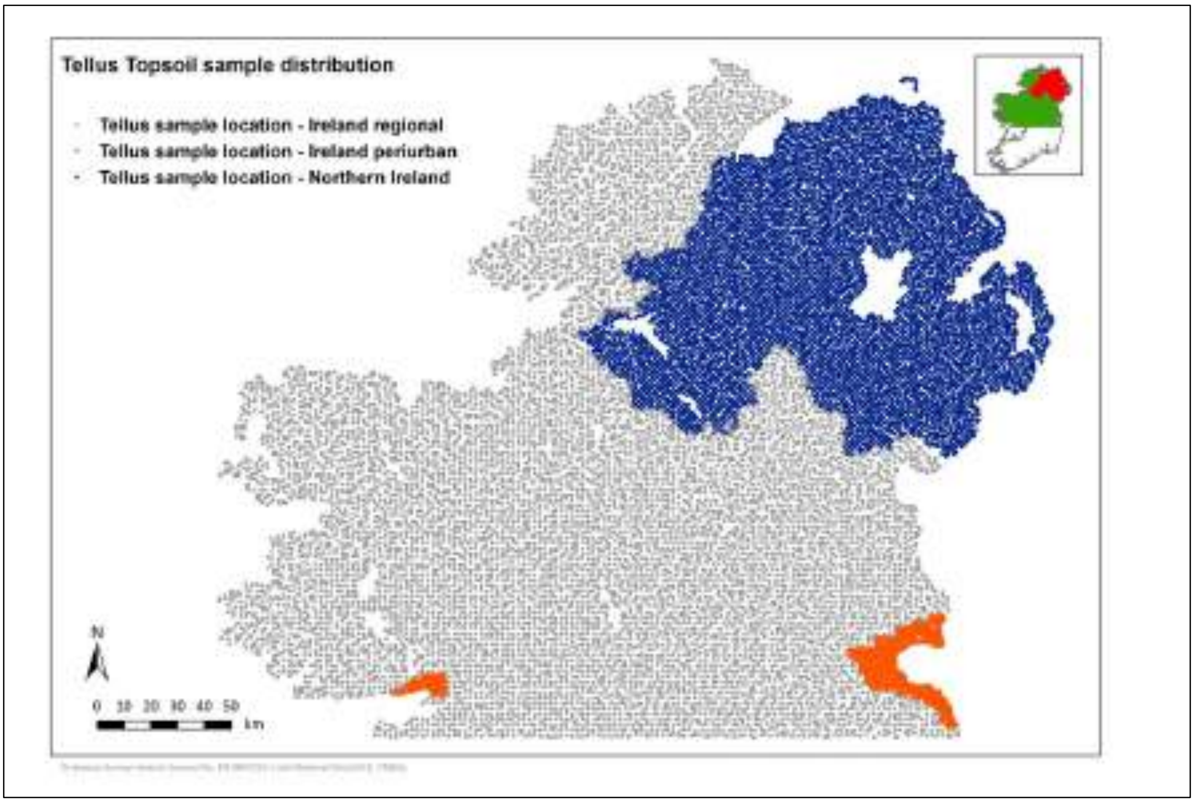


Figure 2: Tellus topsoil sample distribution

2. Scope and nature of geochemical assessment

The aim of the geochemical assessments is to provide an overview of the geochemistry of topsoil within the northern half of Ireland, providing a context for understanding the new Terra Soil data. This involves utilising spatial mapping and statistical techniques to examine possible controls on topsoil geochemistry across the region. Such controls potentially include (i) the characteristics of the topsoil itself, such as drainage, particle size distribution, OM content; (ii) the nature of the topsoil's source material, e.g., bedrock composition and Quaternary features, or (iii) land use, including anthropogenic influences.

Information regarding potential controls on topsoil chemistry was compiled from available sources and joined to the Tellus and Terra Soil geochemical data, so that each topsoil sample was assigned a value for each of the soil characteristics examined. Data sources for topsoil attributes were as follows:

Bedrock geology:	GSI Bedrock maps (1:100,000, 1:500,000 and 1:1M scale)
Quaternary geology:	GSI Quaternary sediments map (c. 1:50,000 scale)
Land use:	Corine data (2018)
Soil drainage:	Irish Soil Information System, EPA/Teagasc (1:250,000)
Soil texture:	Irish Soil Information System, EPA/Teagasc (1:250,000)
Particle size distribution:	Estimated using Terra Soil spectroscopy data
Geochemical Domain:	GSI SRF Domain compilation (1:40,000)
Organic matter/peat class:	Tellus LOI data
Pollutant Impact Potential (PIP):	EPA (Catchments) Critical Source Area maps
Slope / slope direction / elevation:	Modelling of DEM data using ArcMap
Soil indices (Cu, Mg, Mn, Zn only):	Terra Soil derivatives, based on Mehlich-3 data

3. Tellus data and Terra Soil data

3.1. Tellus data

Topsoil was analysed for Tellus by XRF (total analyses) and by ICP following *aqua regia* digestion (ICPar), on samples milled to < 32 µm. ICPar yields near-total analyses for some elements but more typically only partial analyses, with extraction rates for some elements less than 20 %. ICPar analyses were completed on 9921 shallow topsoil (“A”) samples from the entire study area in Ireland, i.e., Tellus Border, Tellus West, Tellus North Midlands and Peri-urban areas. A further 6874 samples were analysed from A samples collected in Northern Ireland. XRF data are not yet available for Tellus North Midlands. In addition, all Tellus soil samples were analysed for pH and LOI. Full details of Tellus sample collection, preparation and analytical methods, including detection limits, can be found in QA/QC reports and data files at https://www.gsi.ie/en-ie/data-and-maps/Pages/Geochemistry.aspx.

XRF data have been consulted as part of the geochemical assessments, where relevant, but have mainly been used to calculated extraction rates for elements analysed by ICP following incomplete digestion, i.e., by *aqua regia* and Mehlich’s 3 reagent. These calculations have employed not only shallow “A” topsoil samples but also deeper “S” topsoil samples where available.

Tellus samples were analysed by ICPar for 56 elements but not all elements were included in analyses of all samples in the entire study area. For others the detection limit was too high for useful data to be obtained, leaving 45 elements for which useful regional data are available:

Ag	Al	As	Ba	Be	Bi	Ca	Cd	Ce	Co	Cr	Cs	Cu	Fe	Ga
Hf	Hg	In	K	La	Li	Mg	Mn	Mo	Na	Nb	Ni	P	Pb	Rb
S	Sb	Sc	Se	Sn	Sr	Th	Ti	Tl	U	V	W	Y	Zn	Zr

3.2. Terra Soil data

Shallow topsoil “A” samples collected as part of the Tellus project were reanalysed for Terra Soil, following digestion by both Mehlich’s 3 and Morgan’s reagents. Analyses were carried out on the < 2 mm fraction retrieved from the Tellus sample archive. Archive material was not available for all 9921 Tellus sample sites, particularly peat-rich samples, so the number of samples sites for which Terra Soil data are available is somewhat lower than that for Tellus samples. When the Tellus and Terra Soil datasets are combined, there are 9911 Tellus sample sites for which both ICPar and Mehlich’s 3 data are available. Morgan’s data are available for 9903 sites.

Terra Soil samples were analysed by ICP-OES following Mehlich’s 3 digestion and concentrations are reported in mg/kg, allowing direct comparison to ICPar data. However, Mehlich’s 3 reagent is a relatively weak extractant, much weaker than aqua regia, and reported concentrations are thus much lower than those for ICPar. Morgan’s data are reported as mg/L and cannot be compared directly to either ICPar or Mehlich’s 3 data.

Mehlich’s 3 data are reported for 11 elements (in **RED** in table below), Morgan’s for just K and P. Individual geochemical assessments have been completed for the Terra Soil project for the following elements:

ICPar and Mehlich’s 3:	Ca, Cu, Fe, Mg, Mn, Zn
ICPar only:	As, Cd, Cr, Pb, Hg

In addition, a high-level review of Morgan's data is included below for completeness.

Ag	**Al**	As	Ba	Be	Bi	**Ca**	Cd	Ce	**Co**	Cr	Cs	**Cu**	**Fe**	Ga
Hf	Hg	In	**K**	La	Li	**Mg**	**Mn**	Mo	Na	Nb	Ni	**P**	Pb	Rb
S	Sb	Sc	Se	Sn	Sr	Th	Ti	Tl	U	V	W	Y	**Zn**	Zr

4. Base maps

The following maps provide details of bedrock geology and other potential controls on soil chemistry that have been incorporated into the data exploration for the geochemical assessments. These potential controls are referred to throughout the text and the maps are provided here for reference purposes.

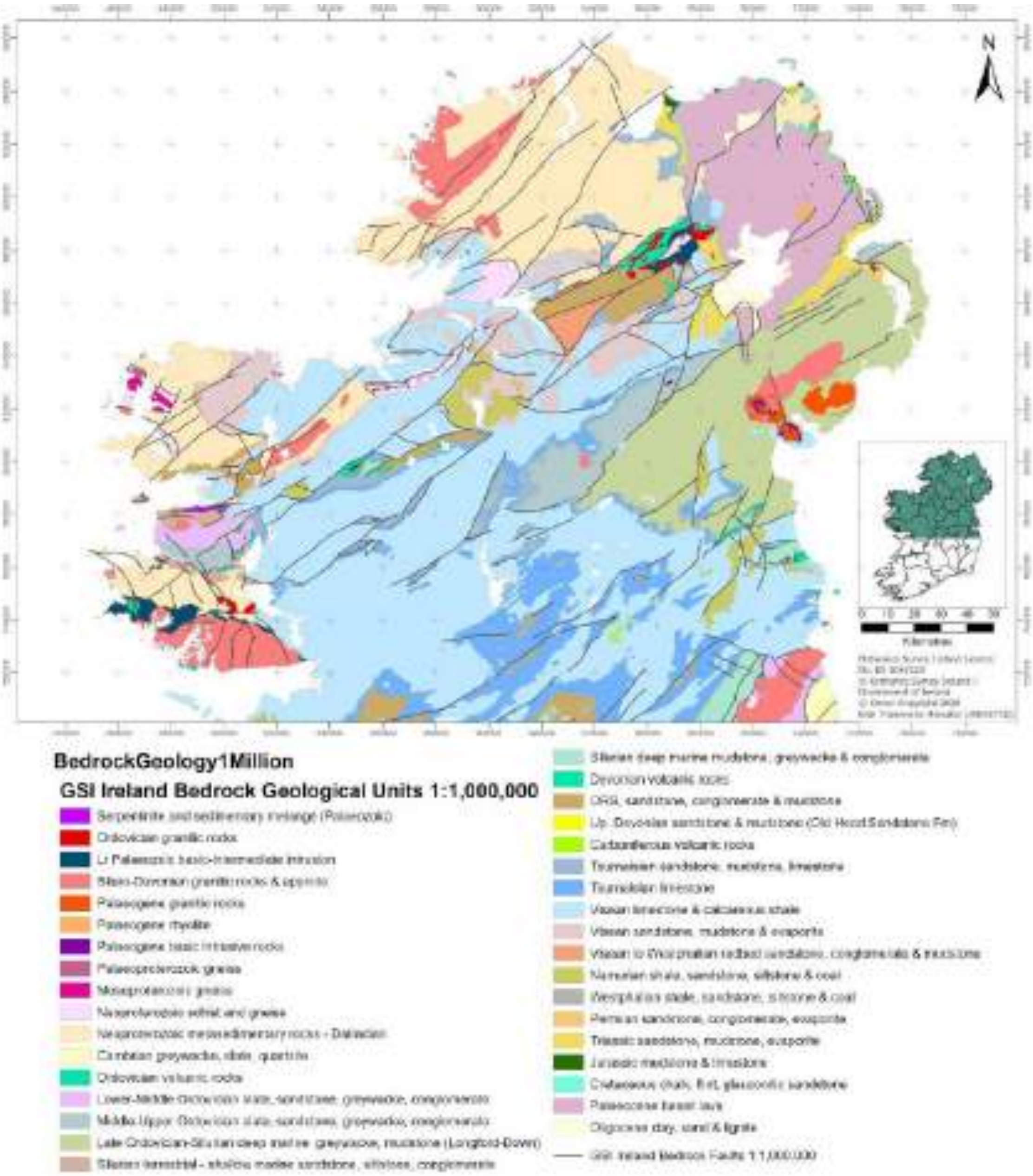


Figure 3: Bedrock geology of northern part of Ireland

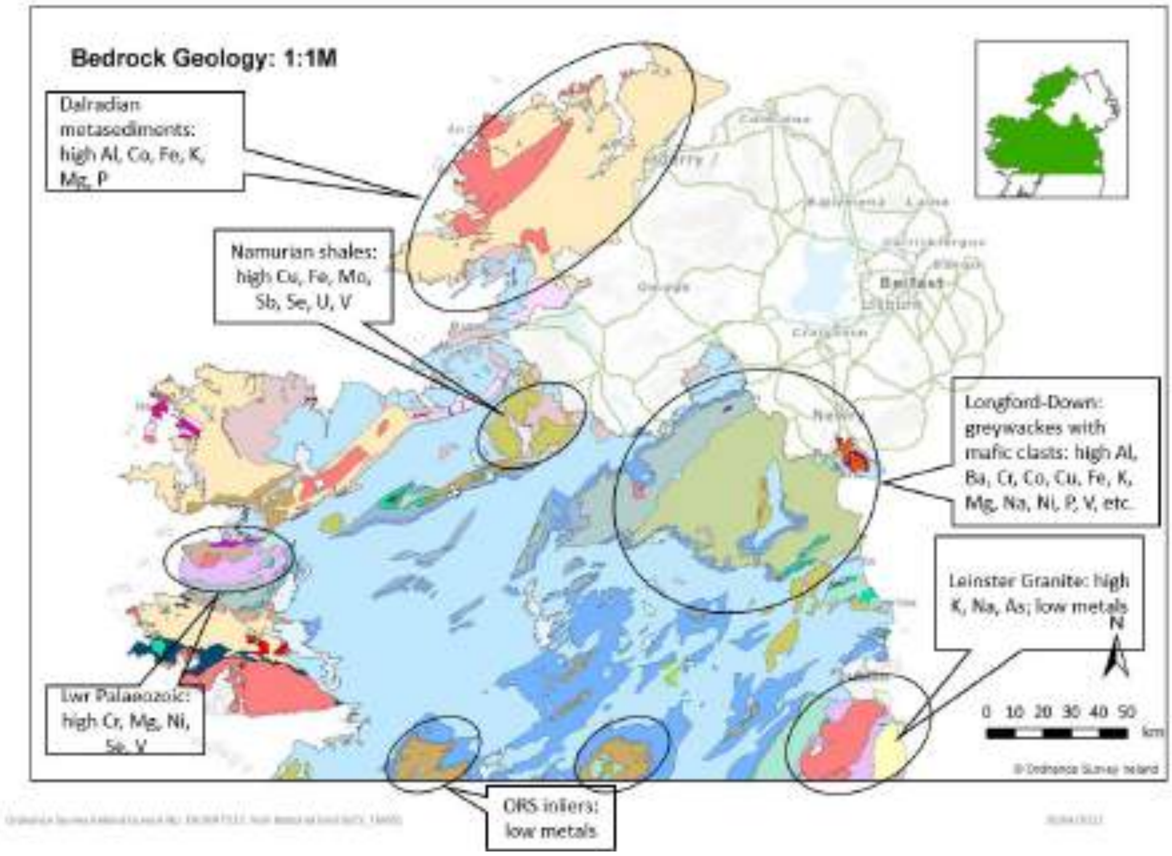


Figure 4: Bedrock geology of study area in northern part of Ireland: potential influence of bedrock on soil geochemistry (1)

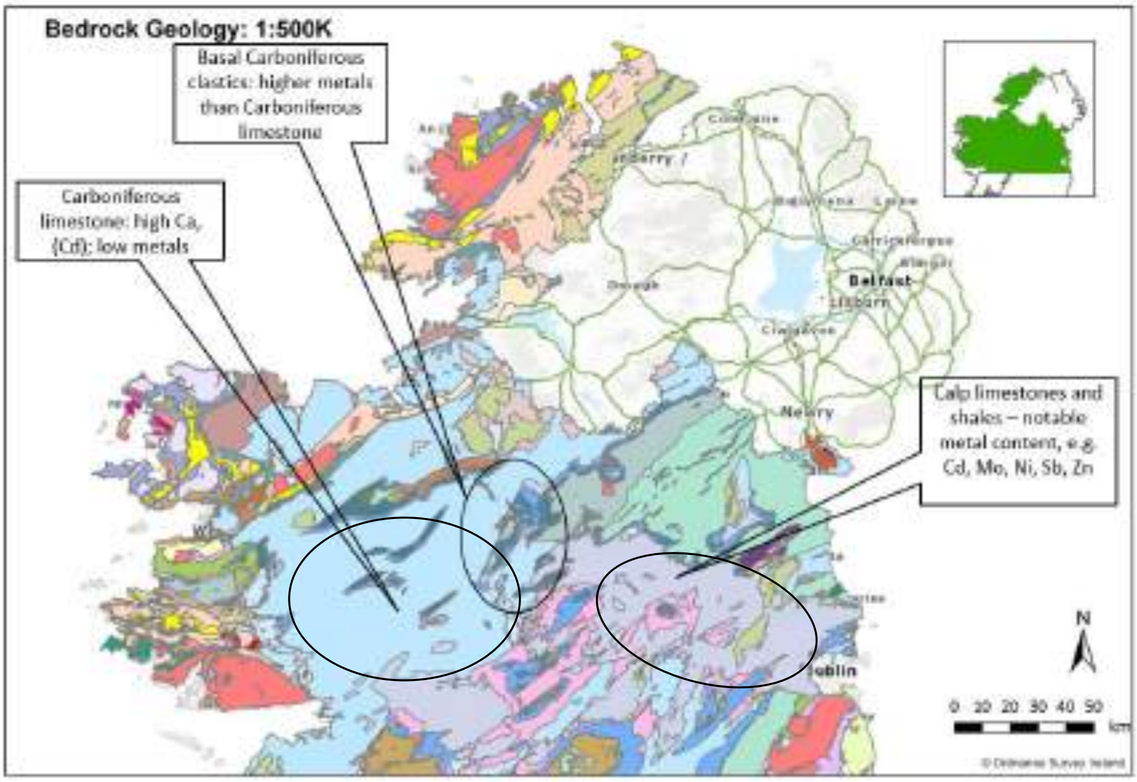


Figure 5: Bedrock geology of study area in northern part of Ireland: potential influence of bedrock on soil geochemistry (2)

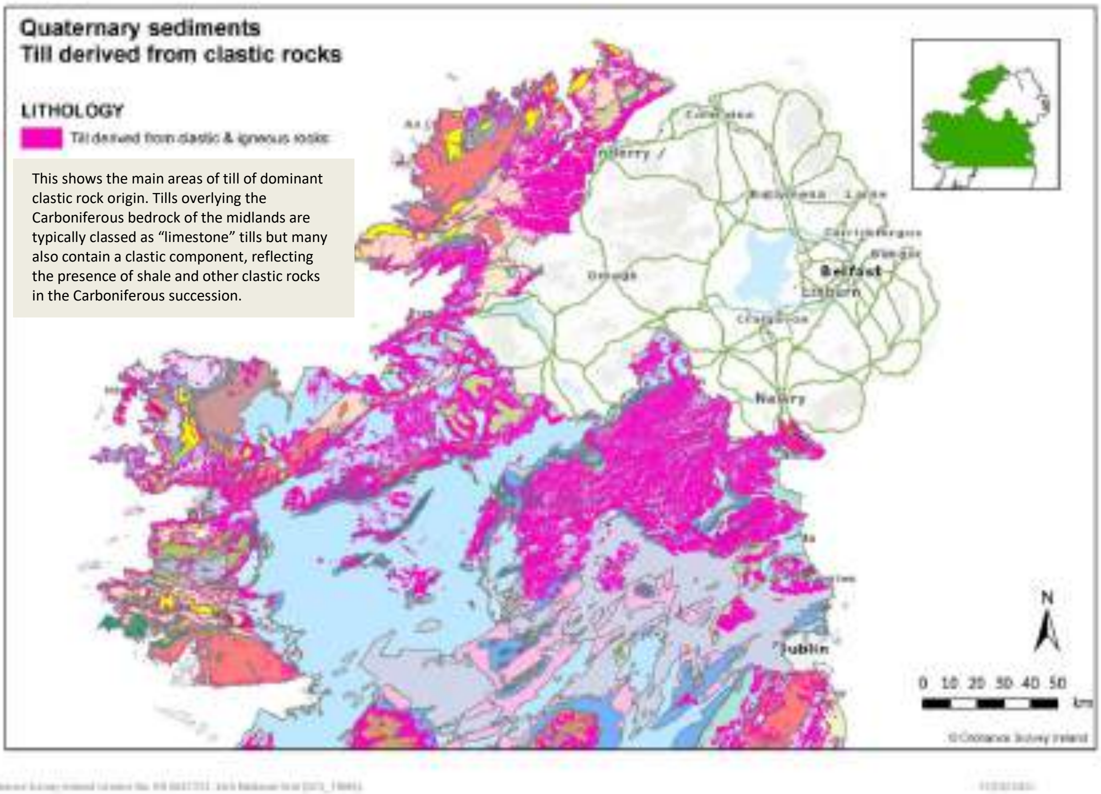


Figure 6: Quaternary geology of study area in northern part of Ireland: potential influence of surficial sediments on soil geochemistry

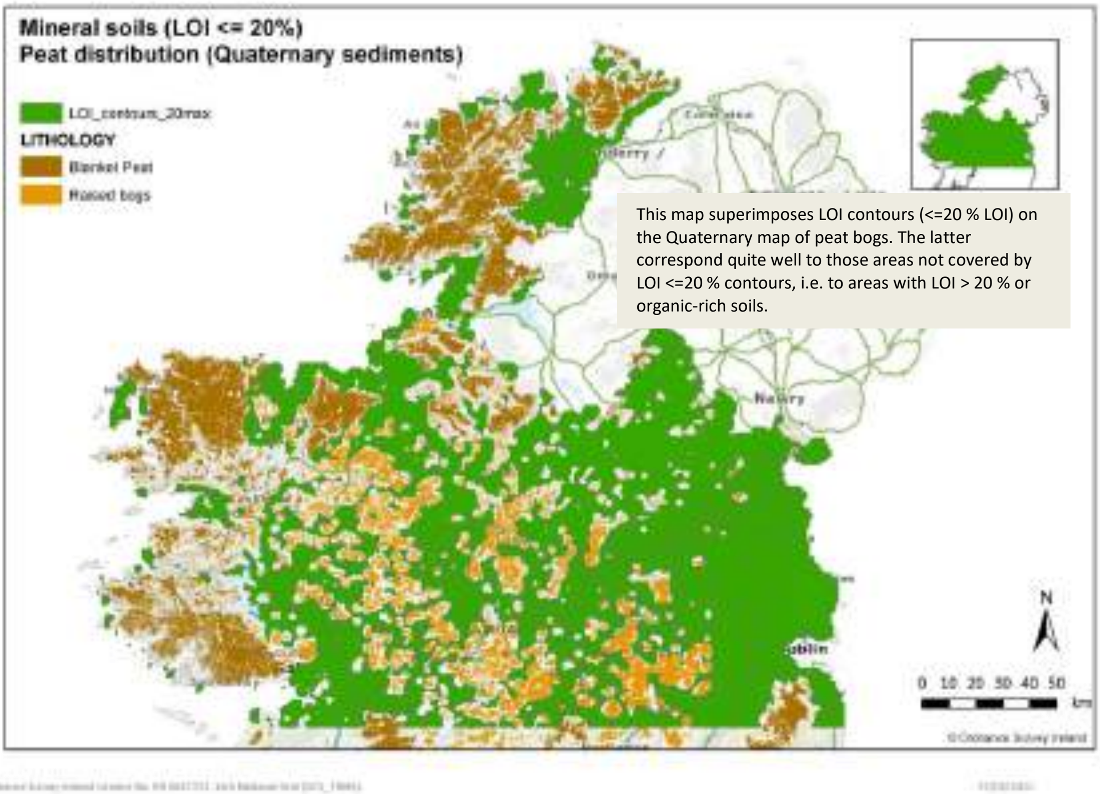


Figure 7: Loss-on-ignition of study area in northern part of Ireland: <=20% LOI (mineral soils) overlaid to areas of peat in Quaternary mapping

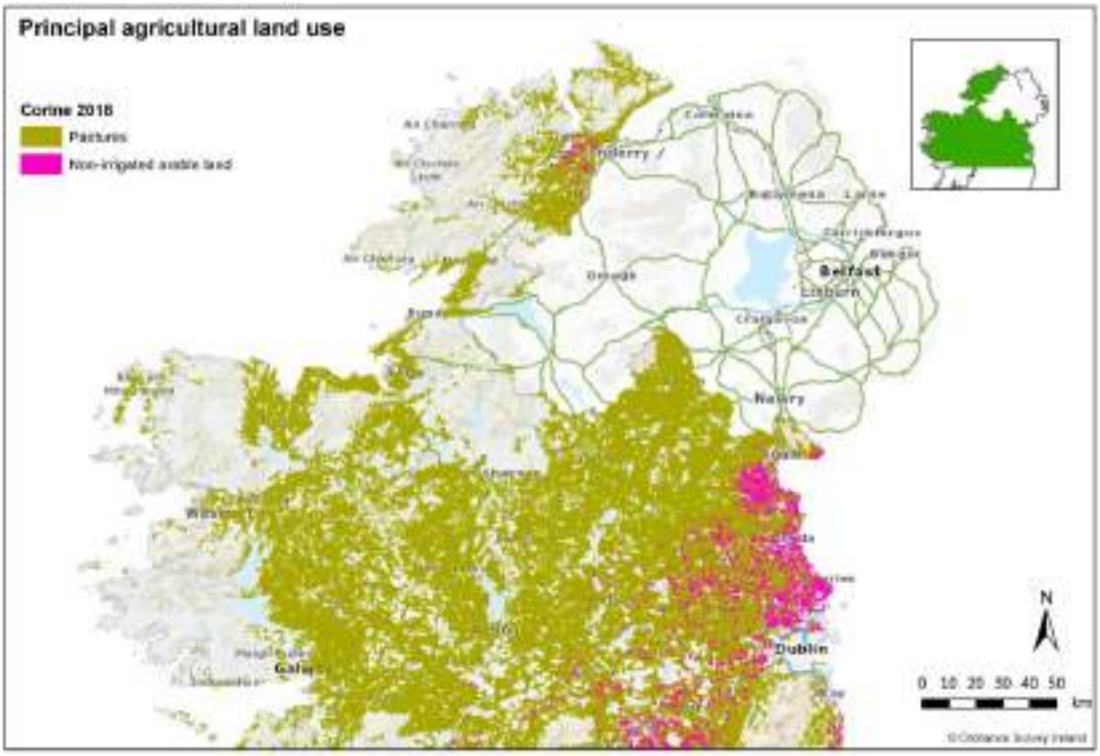


Figure 8: Principal agricultural areas as mapped by Corine correspond well to areas with dominant mineral soil type.

5. Mapped distribution: Terra Soil Mehlich's 3 data v Tellus ICPar data

Comparing the mapped distribution of Mehlich's 3 (hereafter referred to as "M3") and ICPar data provides initial insight into factors that control soil geochemistry. While ICPar analysis of soil does not yield "near-total" concentrations for most elements, nevertheless in many cases a sufficient proportion of elements from rock-forming minerals is extracted by the relatively strong digestion achieved by *aqua regia* so that soil concentrations determined using ICPar typically display a recognizable geogenic signature. Moreover, work by GSI and others over many years has helped understand the range of other controls that can affect the regional geochemistry of soil and other media, including diffuse and point-source anthropogenic contamination.

Given that the ICPar data distribution is relatively well understood, comparing M3 maps to ICPar maps provides significant insight into the potential controls on M3 concentrations in soils in the study area.

Below, a general comparison between ICPar and M3 data is provided for each of the 11 elements common to both analytical methods. The extraction rate data quoted on the maps is based on the XRF data as discussed above. The geology of the study area and distribution of mineral soils, organic-rich soils and peat have been shown above, as context for the discussion.

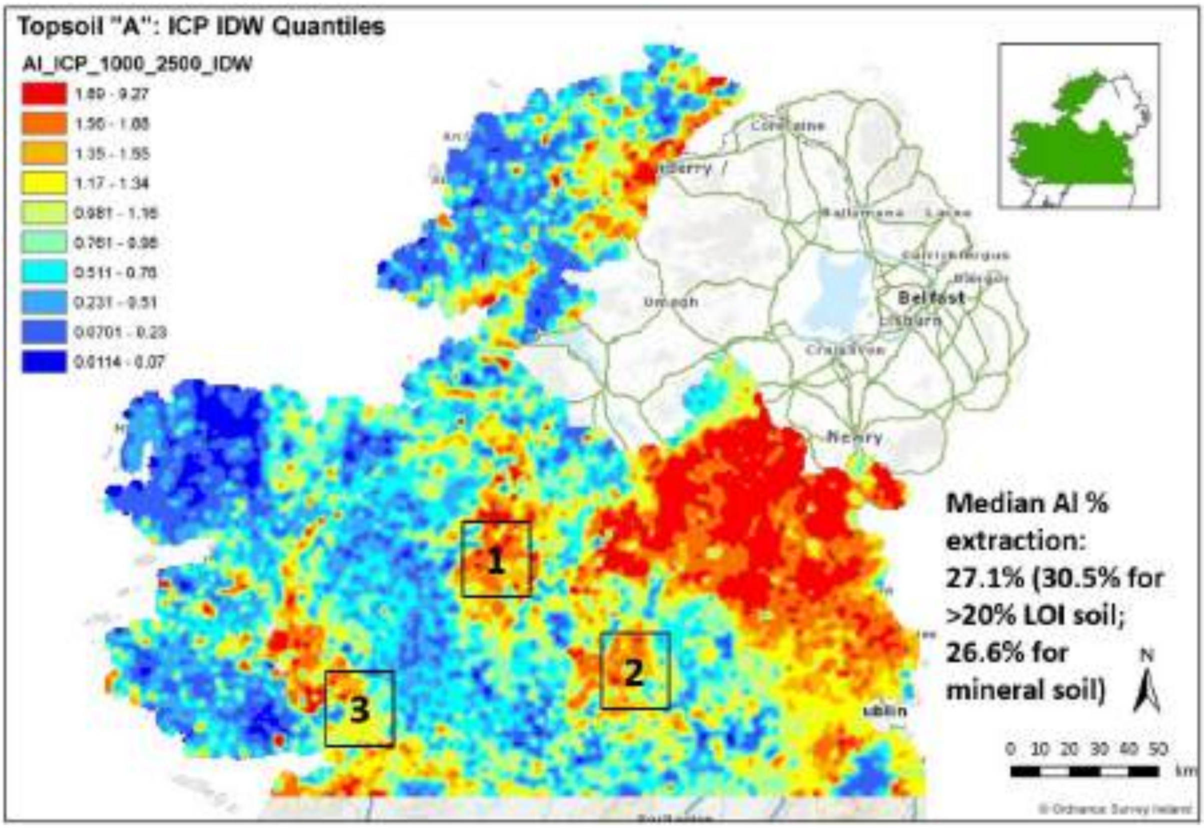


Figure 9: Aluminium ICP aqua regia data

- Despite a relatively low extraction rate for Al in aqua regia, a strong geogenic signature is suggested.
- There is strong coherence between higher Al and bedrock or till dominated by clastic rocks: Dalradian (E Donegal), Lower Palaeozoic sediments (Longford-Down, N Wicklow), Donegal Bay (Carb sandstone till), & Basal Carboniferous clastic rocks (midlands).
- However, even over areas with dominant limestone bedrock in the midlands, Al can be relatively high in soil provided organic content is low – see areas 1, 2 and 3. Bedrock with dominant Carboniferous limestone typically includes at least some clastic layers, especially shale.
- Low Al in areas of peat: NW Donegal, NW Mayo, Connemara, E Galway/Roscommon/E Mayo "corridor", ORS inliers, Dublin-Wicklow mountains.

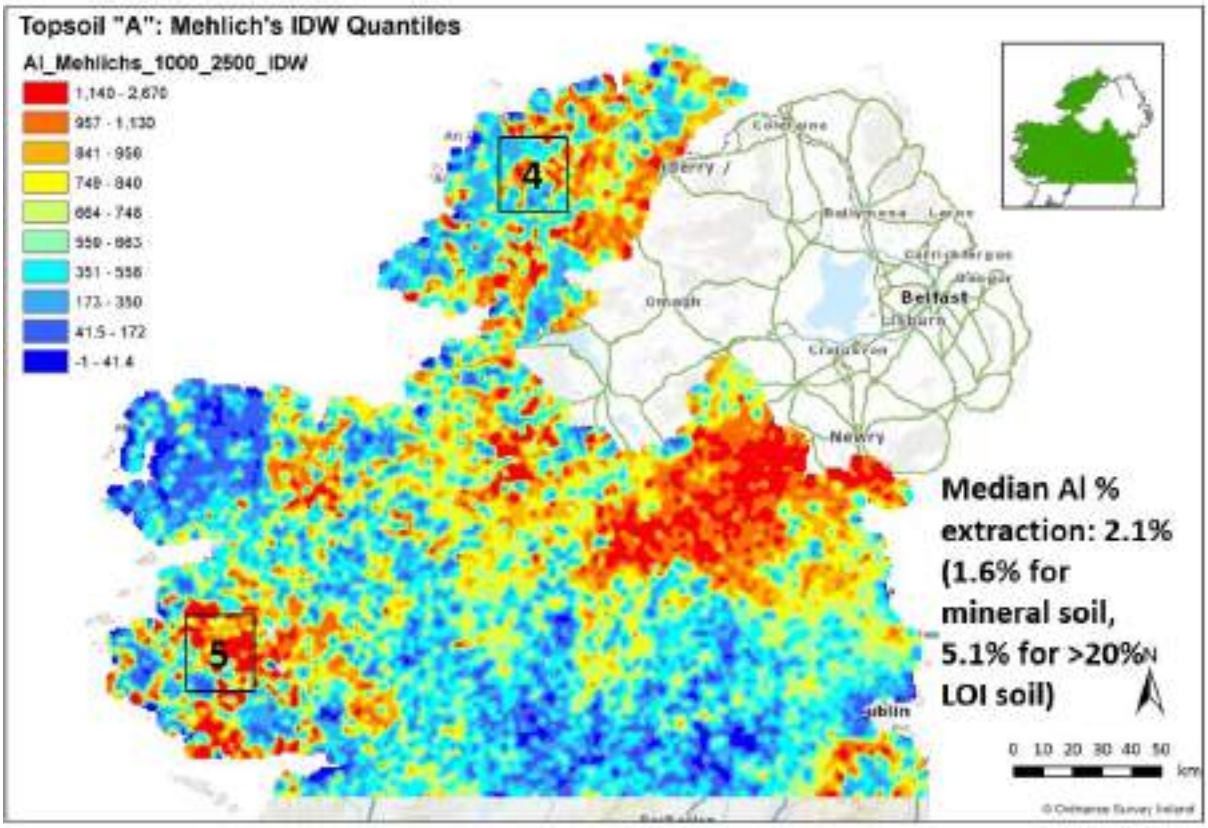


Figure 10: Aluminium ICP M3 data

- The main areas of high Al correlate well with *aqua regia* data: Longford-Down, E Donegal, Donegal Bay, N Wicklow, some midlands and other Carboniferous bedrock areas.
- Low Al over peaty areas and Carboniferous bedrock in midlands.
- Scattered high Al values over upland areas in Galway and Donegal (areas 4, 5) may reflect relatively higher rate of extraction of Al from these samples.

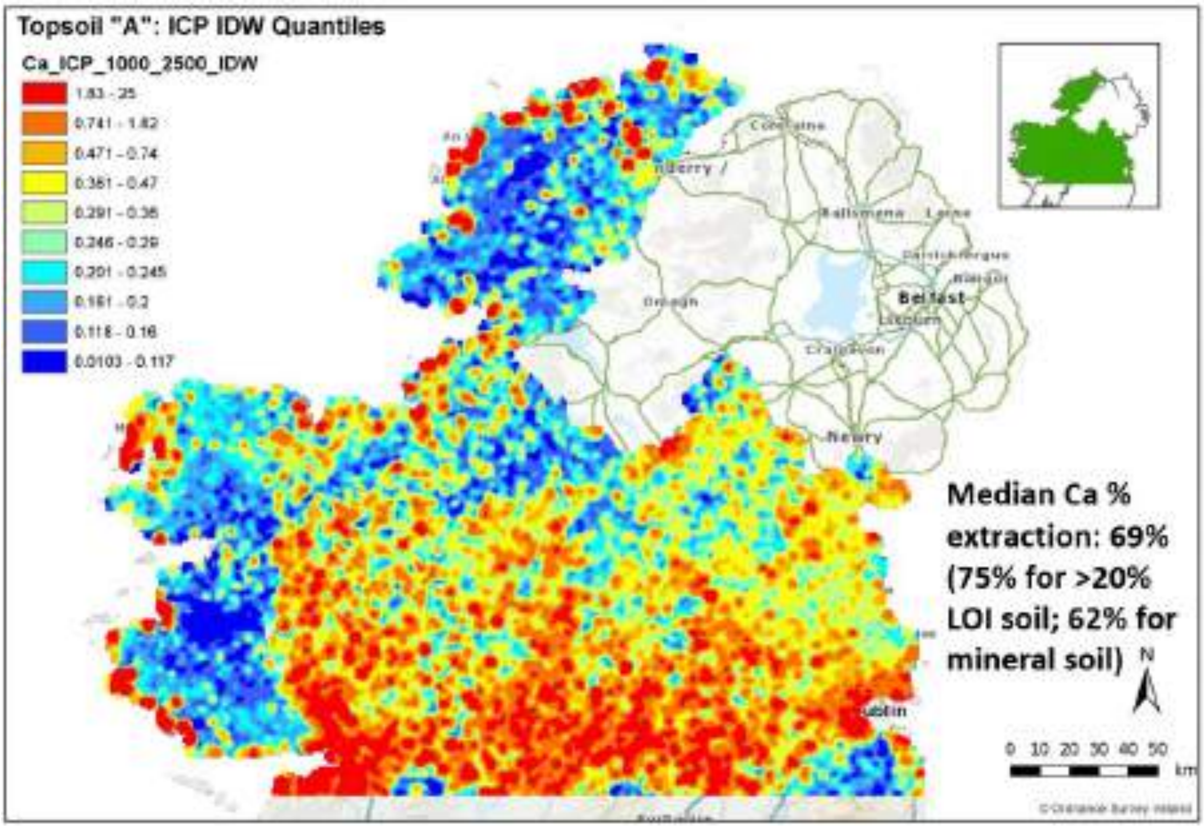


Figure 11: Calcium ICP aqua regia data

- The extraction rate for Ca in *aqua regia* is typically high, hence a good geogenic signature is to be expected.
- There is strong coherence between higher Ca and bedrock or till dominated by Carboniferous limestone and related rocks in the midlands.
- There are relatively lower Ca concentrations in soils over the Longford-Down inlier but these are still generally high in absolute terms.
- High Ca is observed around western coastline on *machairs* (Ca-rich (shelly) sand-based soils).
- Low Ca is observed in areas of peat: NW Donegal, NW Mayo, Connemara, Lough Allen uplands, Dublin-Wicklow mountains, ORS inliers, Ox Mountains inlier. The E Galway / Roscommon/ E Mayo “corridor” visible as a generally low-Ca zone.

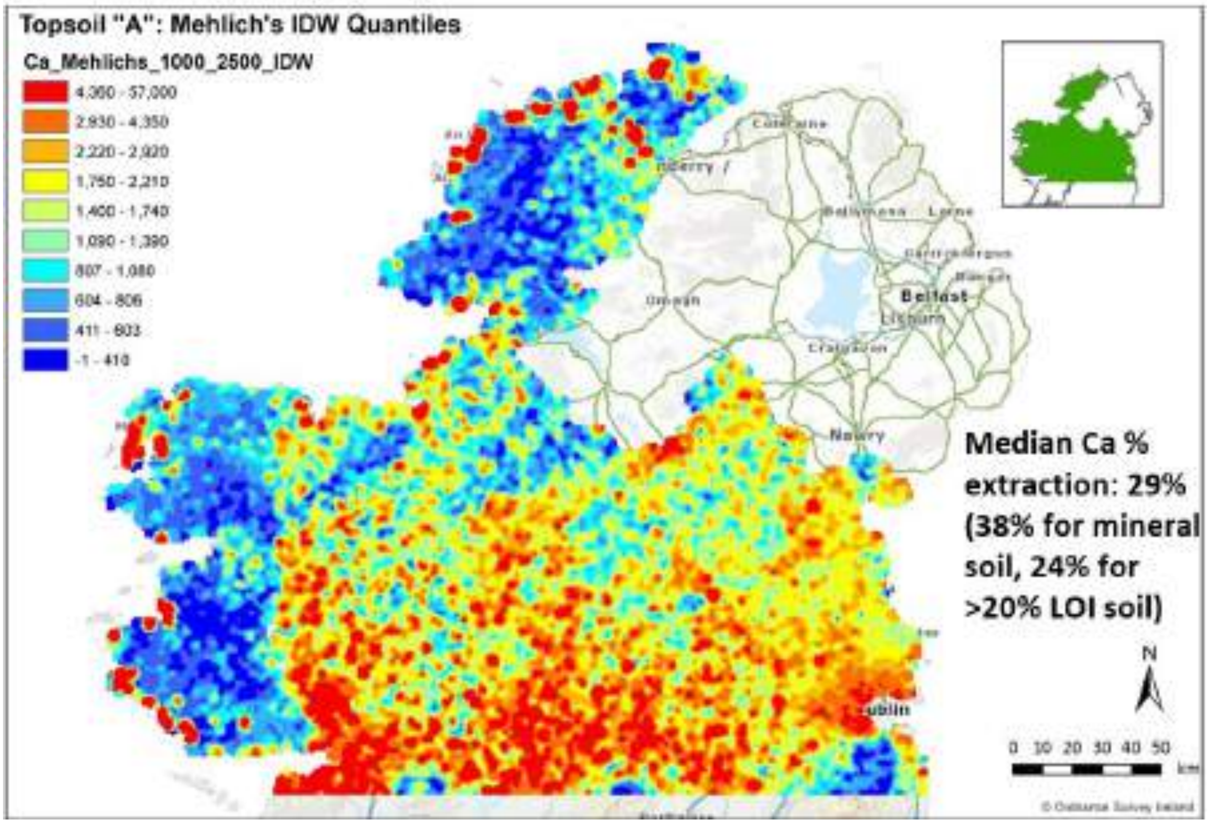


Figure 12: Calcium ICP M3 data

- There is near-identical distribution to that of *aqua regia* data, reflecting a relatively high extraction rate.
- Low Ca is observed over peaty areas (as above).
- Low Ca also over non-peaty areas underlain by Ca-poor clastic rocks (e.g., North Wicklow Lower Palaeozoic metasediments).
- E Galway / Roscommon/ E Mayo “corridor” better defined than for *aqua regia* data, probably because a lower extraction rate for Ca in organic-rich soil heightens the contrast.

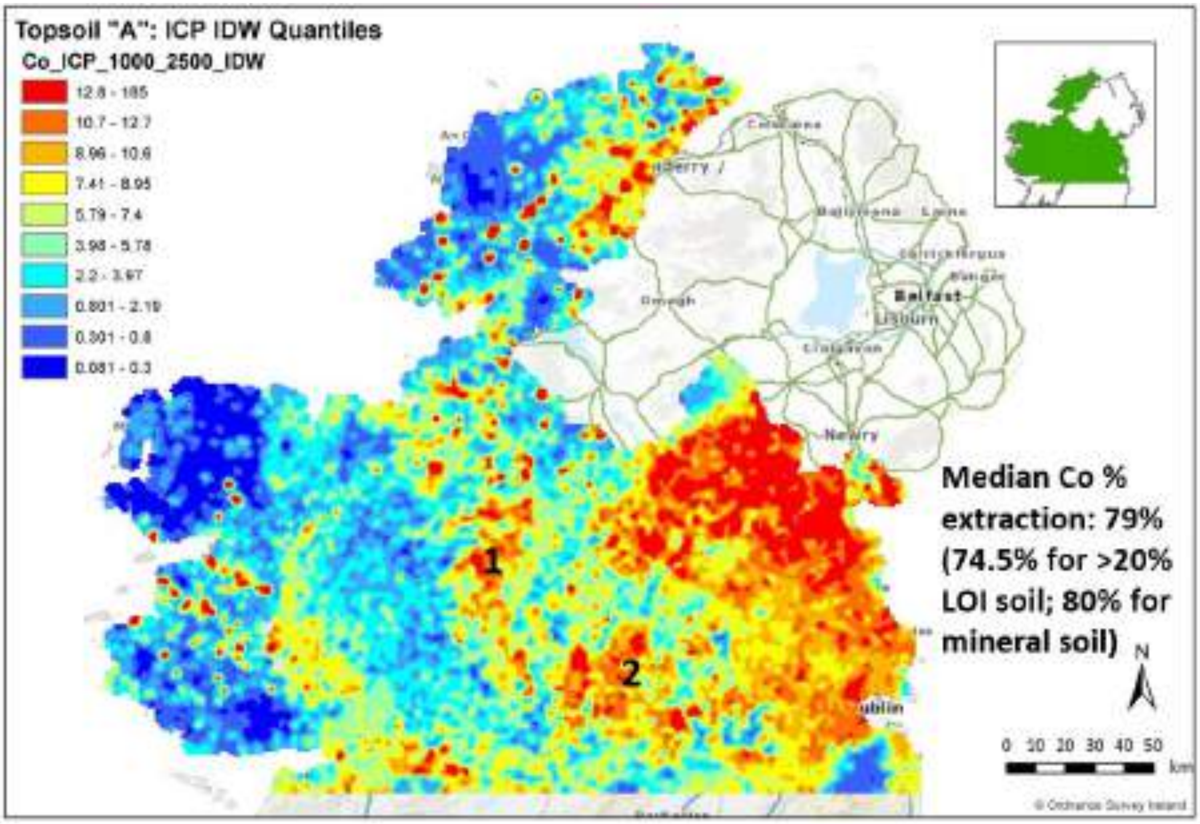


Figure 13: Cobalt ICP aqua regia data

- The extraction rate for Co, in aqua regia, is typically high, hence a good geogenic signature is to be expected.
- There is strong coherence between higher Co and bedrock or till dominated by clastic rocks: Dalradian (E Donegal), Lwr Palaeozoic sediments (Longford-Down, N Wicklow), Carboniferous clastic rocks (midlands).
- The Co distribution is similar to that of Al: even over areas with dominant limestone bedrock in the midlands, Co can be relatively high in soil provided organic content is low – see areas 1 and 2. Bedrock with dominant Carboniferous limestone typically includes at least some clastic layers, especially shale.
- Low Co is observed in areas of peat: NW Donegal, NW Mayo, Connemara, E Galway/Roscommon/E Mayo “corridor”, ORS inliers, Dublin-Wicklow mountains.

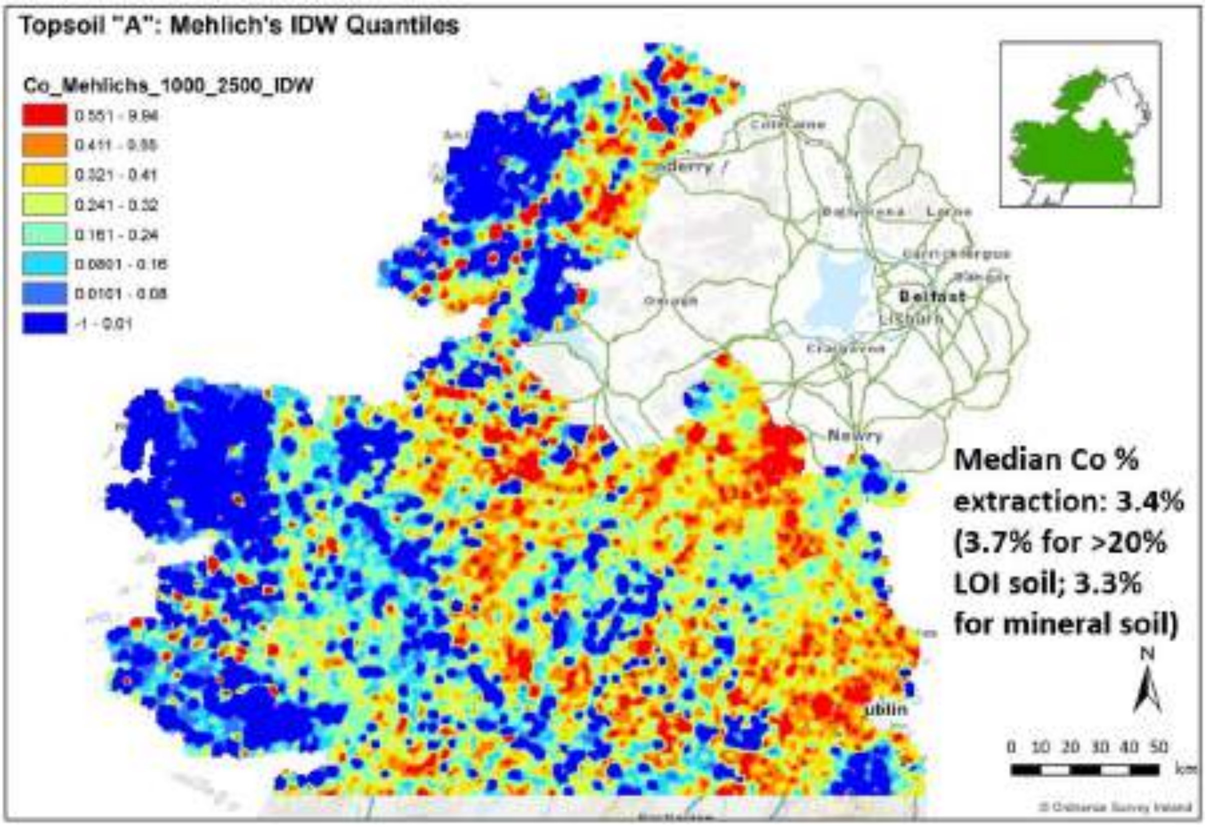


Figure 14: Cobalt ICP M3 data

- In general, areas of high Co correlate well with *aqua regia* data: Longford-Down, E Donegal, N Wicklow, some midlands and other Carboniferous bedrock areas.
- Low Co over peaty areas.
- In general, the distribution of M3 Co is less coherent ("spottier") than M3 Al or Ca – this may reflect, in part, high rate (12 %) of non-detects.

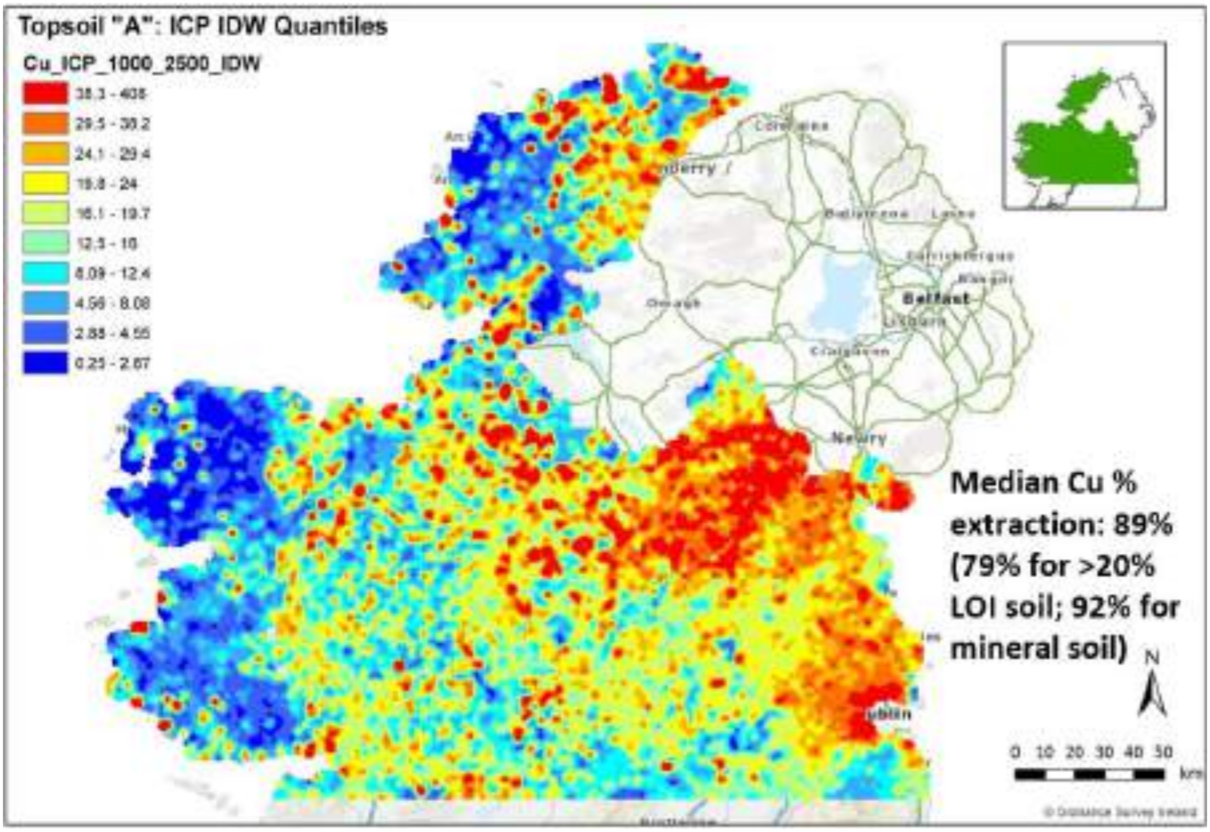


Figure 15: Copper ICP aqua regia data

- The extraction rate for Cu in *aqua regia* is typically high, hence some geogenic signature is to be expected, albeit Cu is not a major component of rock-forming minerals.
- Strong coherence observed between higher Cu and bedrock or till dominated by clastic rocks.
- High Cu in Dublin and Galway peri-urban areas.
- Cu has spottier distribution than elements that are more clearly linked to rock-forming minerals in bedrock hosts, e.g., Al.
- Moderate-to-high Cu is observed over areas with dominant limestone bedrock in the midlands / N Mayo, provided organic content is low.
- Some links to mineralization are suggested (Tynagh, Monaghan mines) but there is no observed strong association between high Cu and known mineral deposits.
- Low Cu is observed in areas of peat: NW Donegal, NW Mayo, Connemara, E Galway/Roscommon/E Mayo “corridor”, ORS inliers, Dublin-Wicklow mountains.

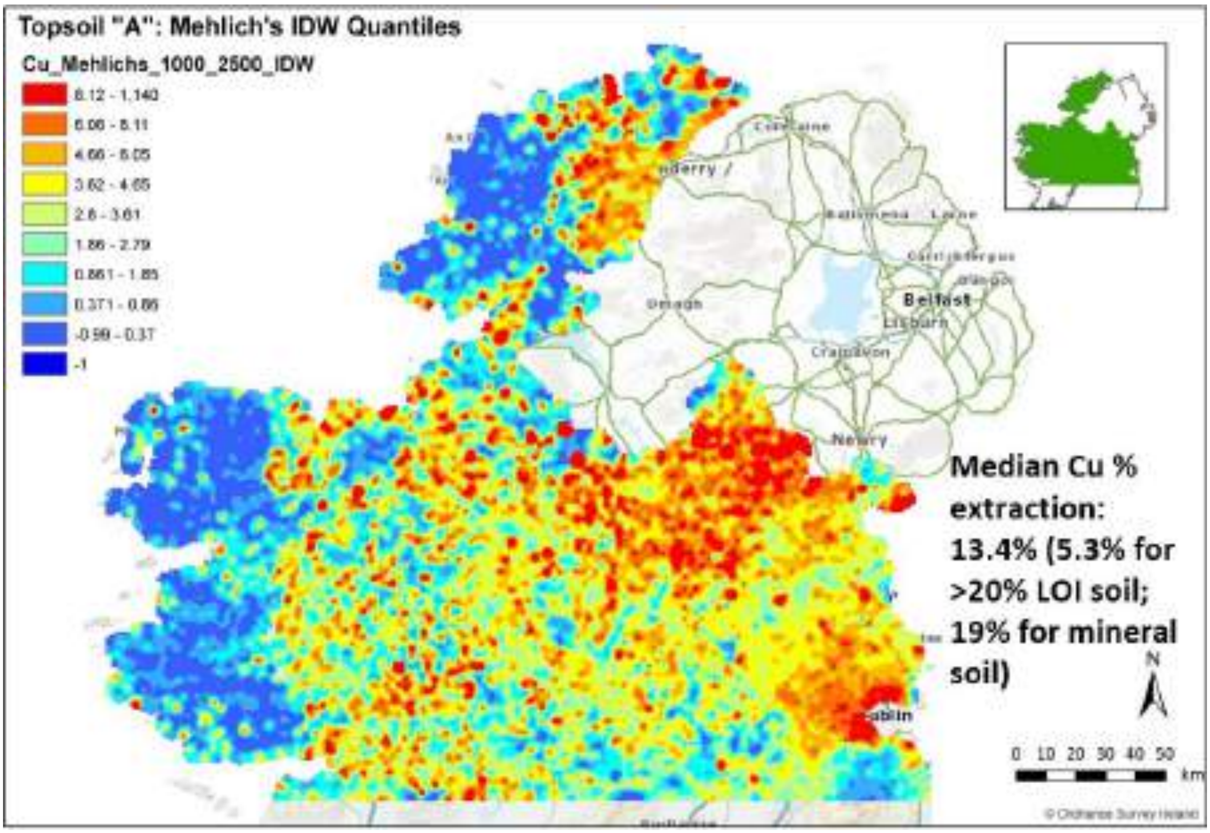


Figure 16: Copper ICP M3 data

- Main areas of high Cu correlate well with *aqua regia* data: Longford-Down, E Donegal, Donegal Bay, some midlands / N Mayo Carboniferous bedrock areas, peri-urban areas.
- Low Cu is observed over peaty areas.
- Again, as for *aqua regia* data, Cu distribution is somewhat spotty.

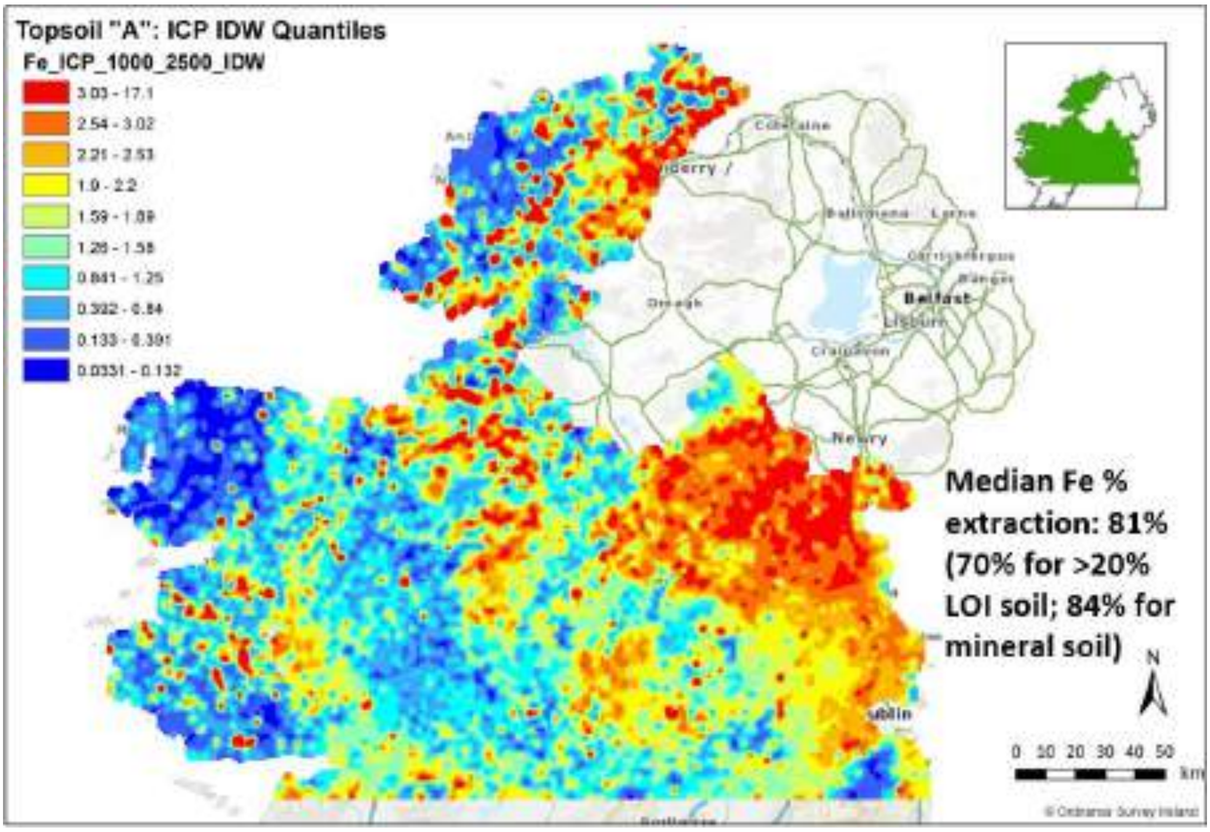


Figure 17: Iron ICP aqua regia data

- The extraction rate for Fe in *aqua regia* is typically high, hence a good geogenic signature is to be expected.
- Strong coherence is observed between higher Fe and bedrock or till dominated by clastic rocks: Dalradian (E Donegal), Lwr Palaeozoic sediments (Longford-Down, N Wicklow), Donegal Bay (Carb sandstone till), Basal Carboniferous clastics (midlands) - a broadly similar distribution to Al.
- Moderate-to-high Fe is observed over areas with dominant limestone bedrock in the midlands / N Mayo, provided organic content is low.
- Low Fe observed in areas of peat: NW Donegal, NW Mayo, Connemara, ORS inliers, Dublin-Wicklow mountains, E Galway/Roscommon/E Mayo “corridor”.

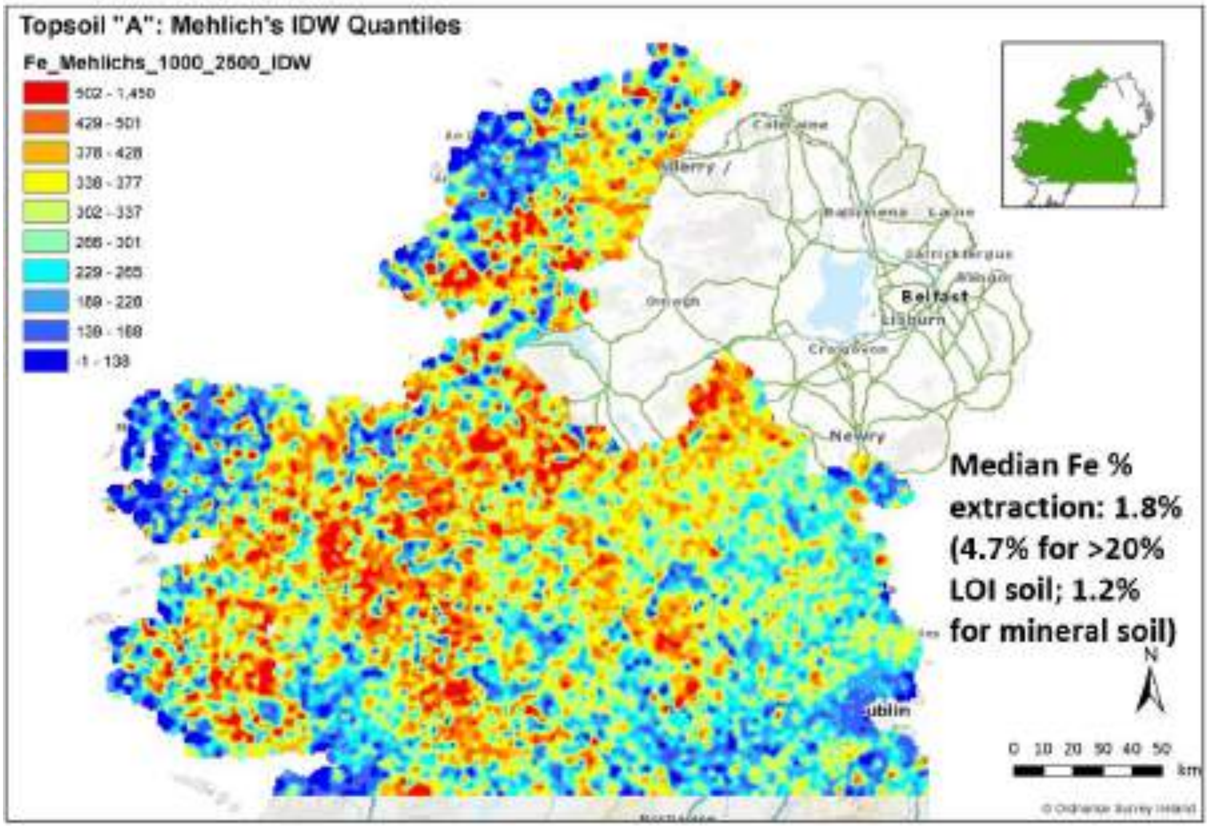


Figure 18: Iron ICP M3 data

- The overall Fe extraction rate for M3 is quite low but is much higher (x4) for peaty soils than for mineral soils, contributing to a significant change in Fe distribution for M3 data compared to *aqua regia* data.
- Almost a reversal of patterns observed: high Fe over peat-rich areas (midlands, E Galway/Roscommon/E Mayo "corridor", Connemara, parts of NW Mayo and NW Donegal).
- Relatively low Fe is observed over some areas dominated by clastic rocks, notably Longford-Down.

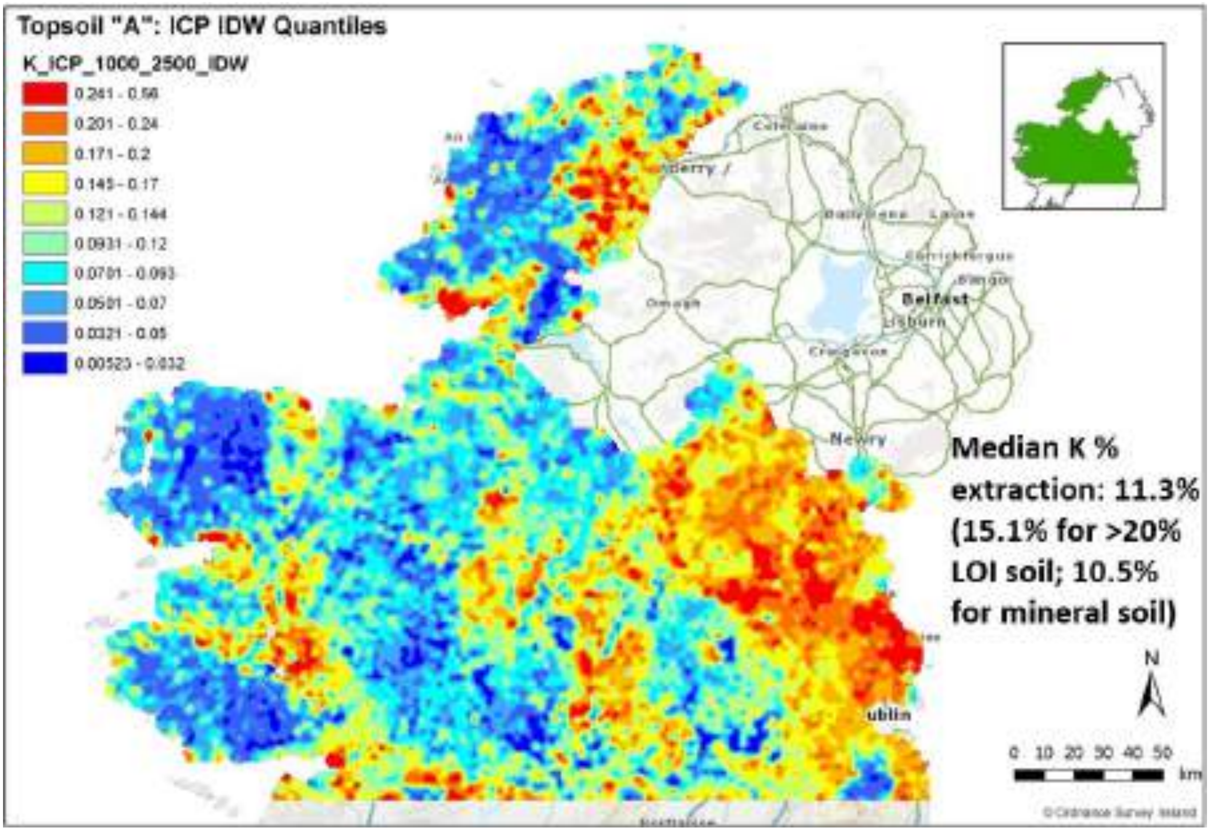


Figure 19: Potassium ICP aqua regia data

- The extraction rate for K in *aqua regia* is typically low because a high proportion of K is hosted by feldspar or other silicates that are poorly digested by aqua regia. Nevertheless, a geogenic signature can be observed.
- There is strong coherence between higher K and bedrock or till dominated by clastic rocks: Dalradian (E Donegal), Lower Palaeozoic sediments (Longford-Down, N Wicklow), Donegal Bay (Carb sandstone till), Basal Carboniferous (midlands), etc., so similar distribution to Al, as expected given the association of K and Al in many minerals common to clastic rocks (feldspars, micas, etc.).
- Low K in areas of peat: NW Donegal, NW Mayo, Connemara, E Galway/Roscommon/E Mayo “corridor”, midlands raised bogs, ORS inliers, Dublin-Wicklow mountains.

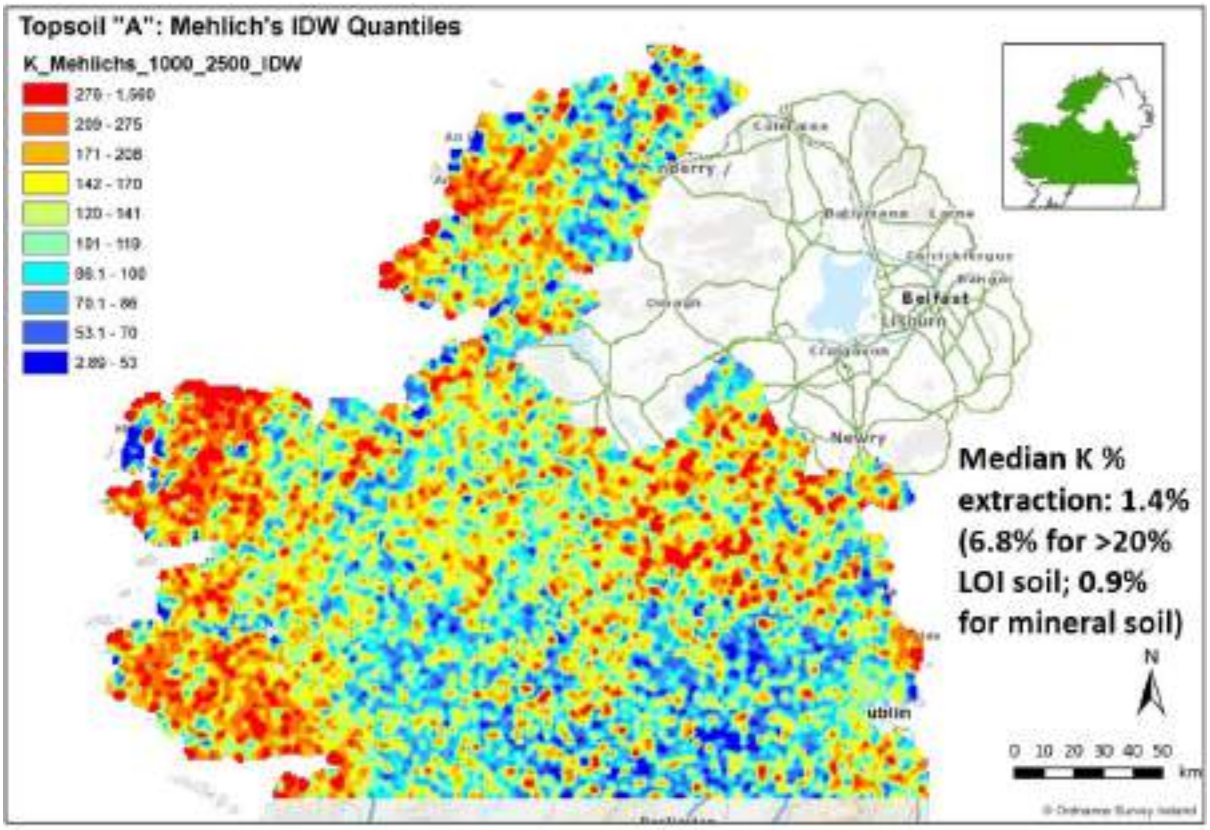


Figure 20: Potassium ICP M3 data

- As with Fe, the extraction rate for K in peaty soils is much higher (x7) than for mineral soils, leading to significant change in K distribution for M3 data compared to *aqua regia* data.
- Almost a reversal of patterns observed for *aqua regia* data: high K over peat-rich areas (Connemara, NW Mayo and NW Donegal), E Galway/Roscommon/E Mayo "corridor" less apparent.
- High K in north Dublin (Skerries) – link to tillage?
- M3 K data distribution is somewhat spotty.

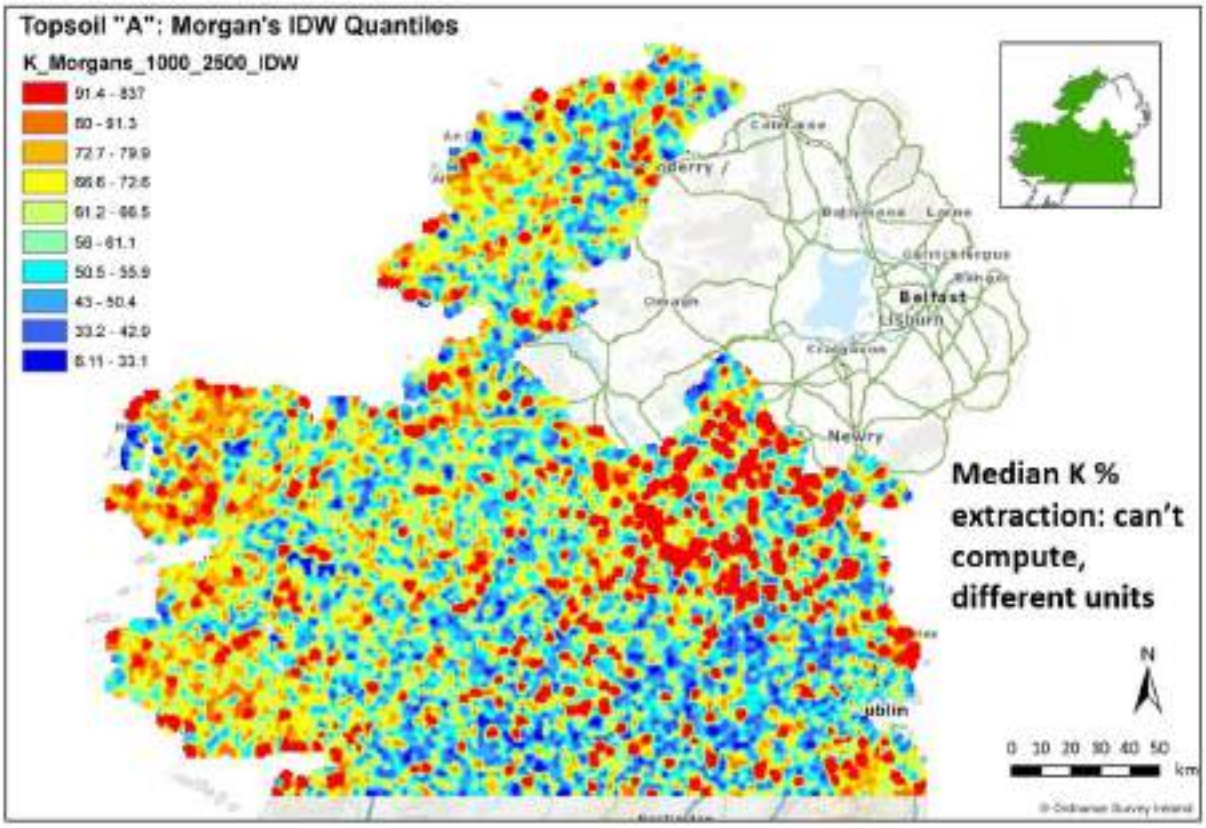


Figure 21: Potassium ICP Morgan's data

- Distribution of Morgan's K is spatially very incoherent ("spotty"), pointing to influence of extraction and/or source of reported K.
- Generally high over some areas of clastic bedrock or till dominated by clastic rocks (Longford-Down, N Wicklow) but not others (e.g., E Donegal, Donegal Bay).
- High K in north Dublin (Skerries) – link to tillage farms?
- High K over peat-rich areas (Connemara, NW Mayo and NW Donegal).
- E Galway/Roscommon/E Mayo "corridor" less apparent.
- Morgan's K has broadly similar distribution to that of M3 K.

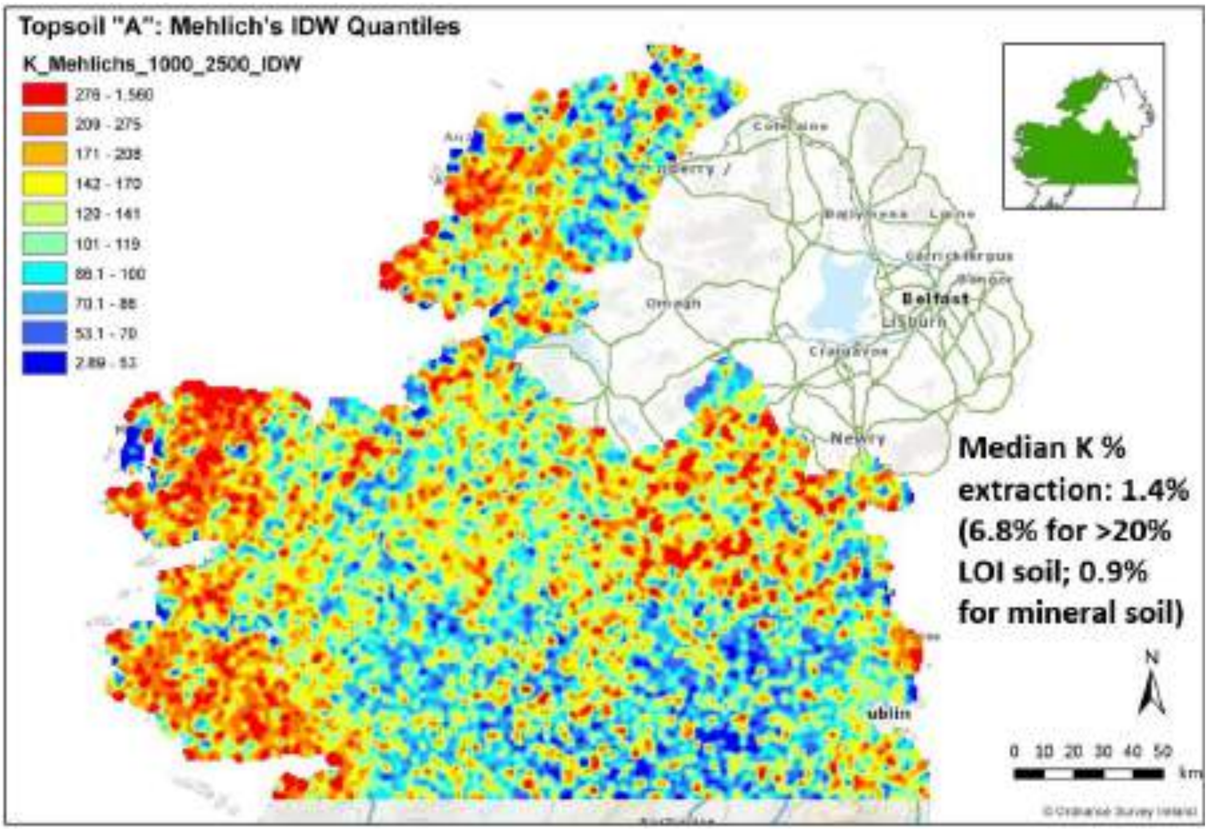


Figure 22: Potassium ICP M3 data

- Extraction rate for peaty soils much higher (x7) than for mineral soils, leading to significant change or reversal in K distribution for M3 data compared to *aqua regia* data.
- High K over peat-rich areas (Connemara, NW Mayo and NW Donegal). High over some clastic-rich areas (Longford-Down mainly) but not others (e.g., E Donegal).
- High K in north Dublin (Skerries) – link to tillage farms?
- M3 K data distribution is somewhat spotty.

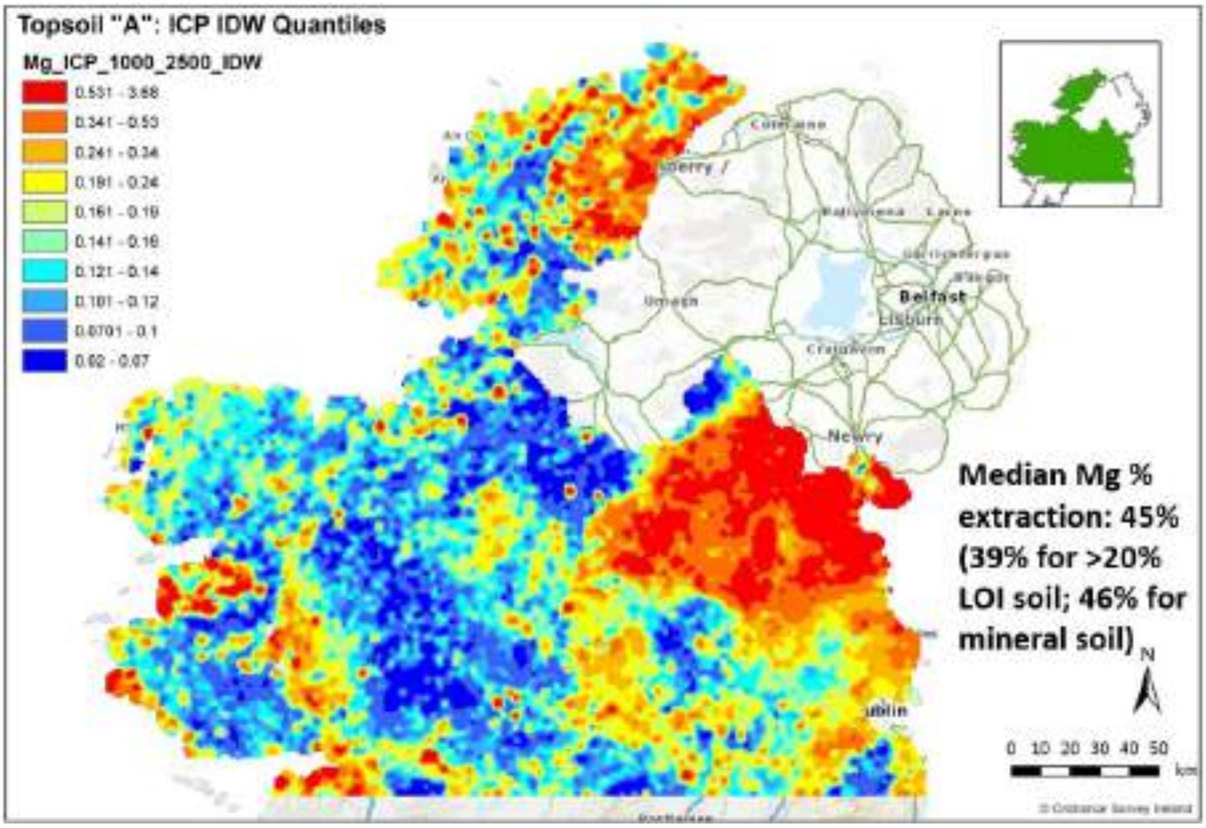


Figure 23: Magnesium ICP aqua regia data

- There is strong coherence between higher Mg and bedrock or till dominated by clastic rocks: Dalradian (E Donegal), Lower Palaeozoic sediments (Longford-Down, N Wicklow), S Mayo Trough & SW Connemara (ultramafic / mafic intrusive rocks), midlands Carboniferous (dolomite? clastics?)
- Low Mg is observed in areas of peat: NW Donegal, NW Mayo, Connemara, E Galway/Roscommon/E Mayo “corridor”, ORS inliers, Dublin-Wicklow mountains.
- The extraction rate for mineral soils may be a little higher than for organic-rich soils, perhaps providing enhanced contrast in maps.

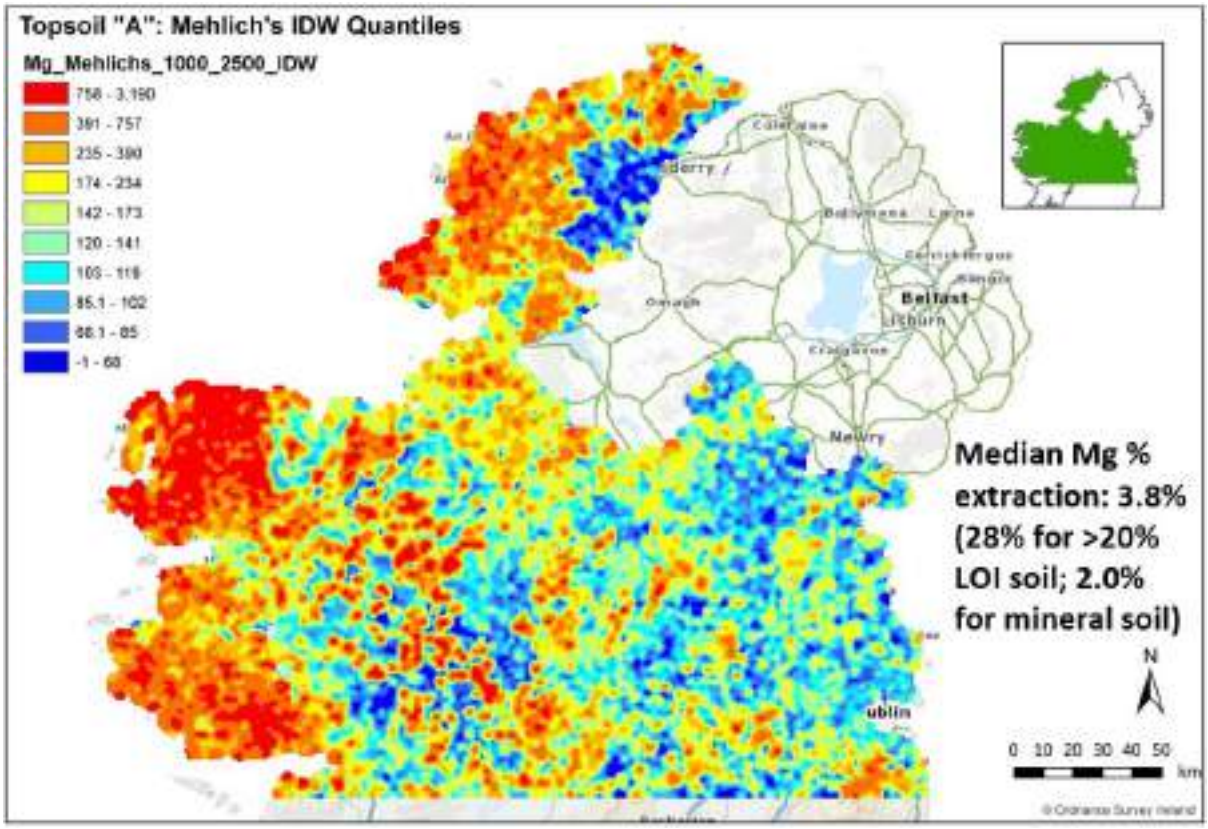


Figure 24: Magnesium ICP M3 data

- Extraction rate for peaty soils is apparently much higher (**x14**) than for mineral soils, leading to a significant change in Mg distribution for M3 data compared to *aqua regia* data.
- There is almost a reversal of patterns observed for aqua *regia* data: high Mg is observed over peat-rich areas (Connemara, NW Mayo, NW Donegal, Dublin-Wicklow mountains, Lough Allen uplands, E Galway/Roscommon/E Mayo "corridor").
- Low Mg is observed over some areas dominated by clastic rocks, notably the Longford-Down Inlier and the Dalradian bedrock of E Donegal).

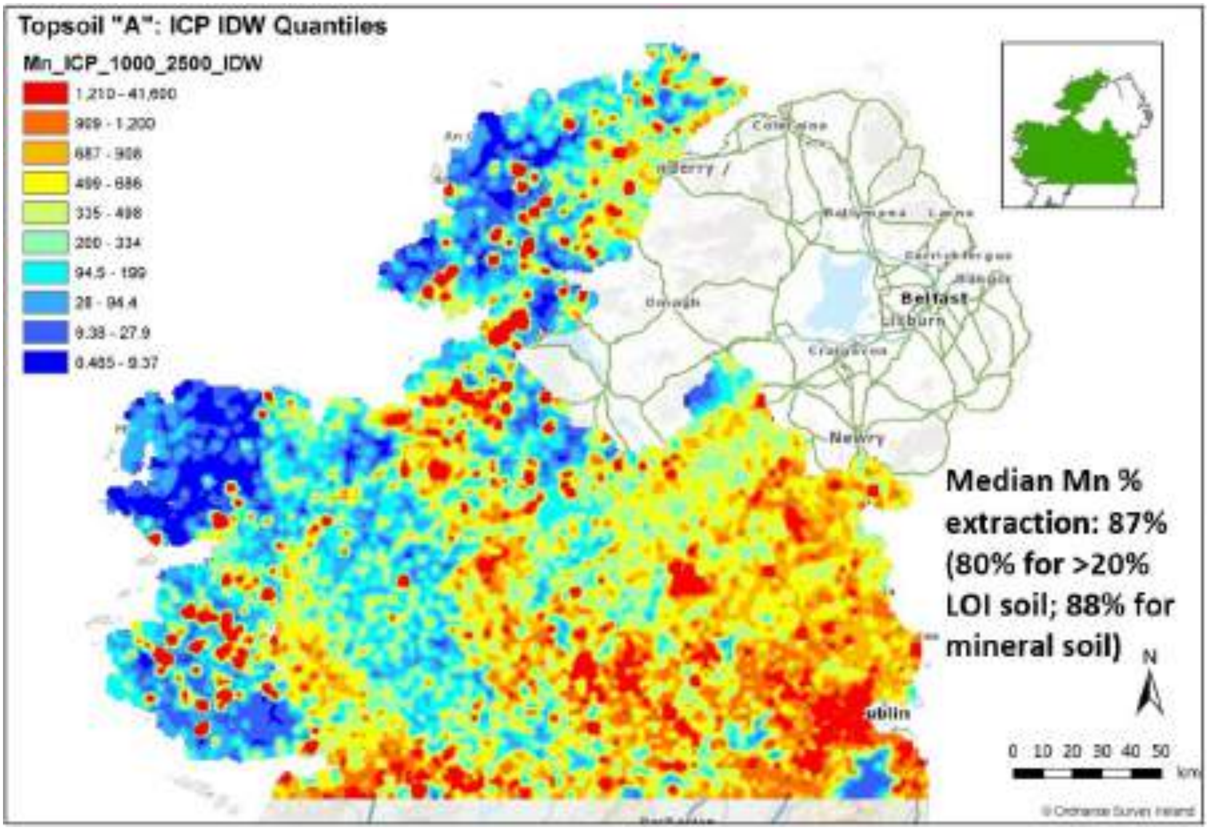


Figure 25: Manganese ICP aqua regia data

- There is general coherence between higher Mn and bedrock or till dominated by clastic rocks.
- Low Mn is observed in areas of peat: NW Donegal, NW Mayo, Connemara, E Galway/Roscommon/E Mayo “corridor”, ORS inliers, Dublin-Wicklow mountains.
- In soils, Mn’s behaviour depends on pH/Eh conditions: under oxidizing conditions it forms hydrous oxides that co-precipitate with other transition elements.
- Many single-point anomalies or small clusters of anomalies (NW Donegal, Connemara), representing some of the highest recorded Mn concentrations in the region, have no evident geological or other obvious control and may reflect precipitation of Mn under local oxidizing conditions.

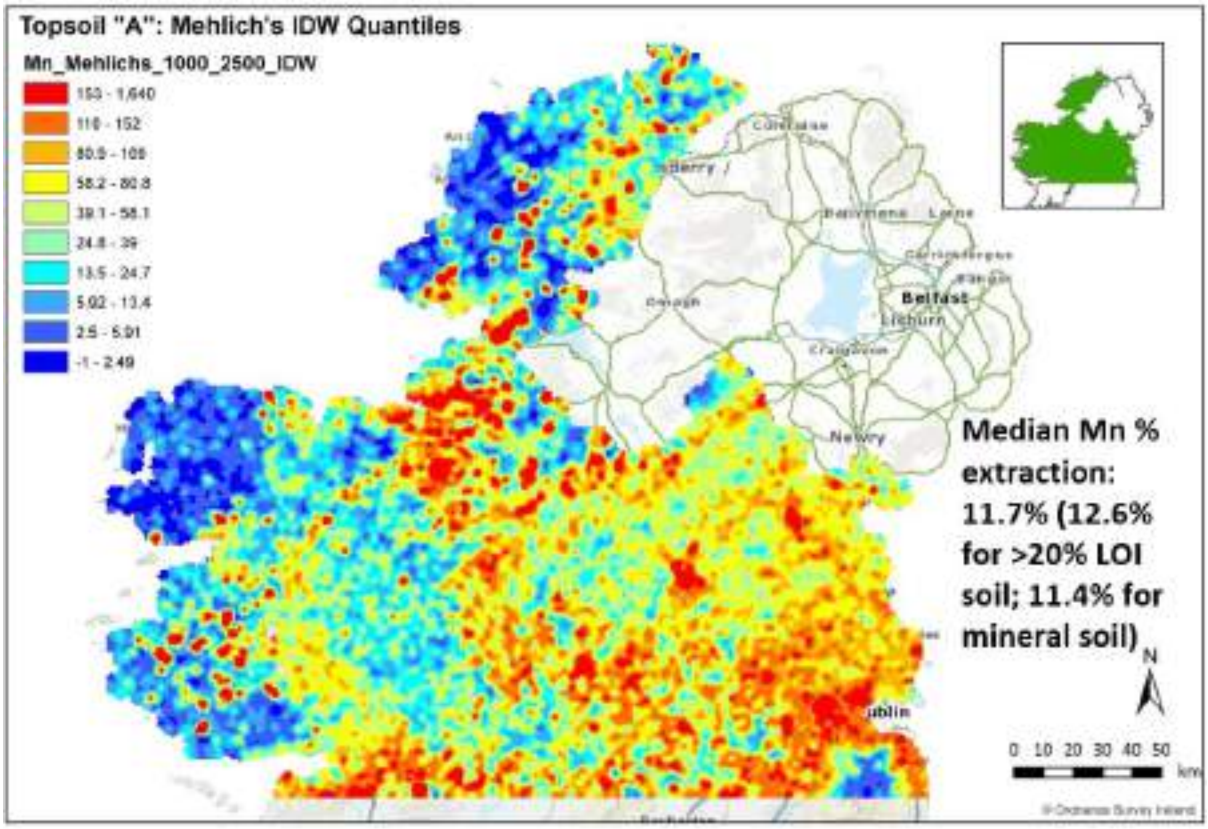


Figure 26: Manganese ICP M3 data

- M3 data display almost identical distribution to that of *aqua regia* data.
- For both *aqua regia* and M3 extractions there is little difference between extraction rates for mineral and organic-rich soils – this removes one cause of variable distribution between *aqua regia* and M3 as observed for other elements.

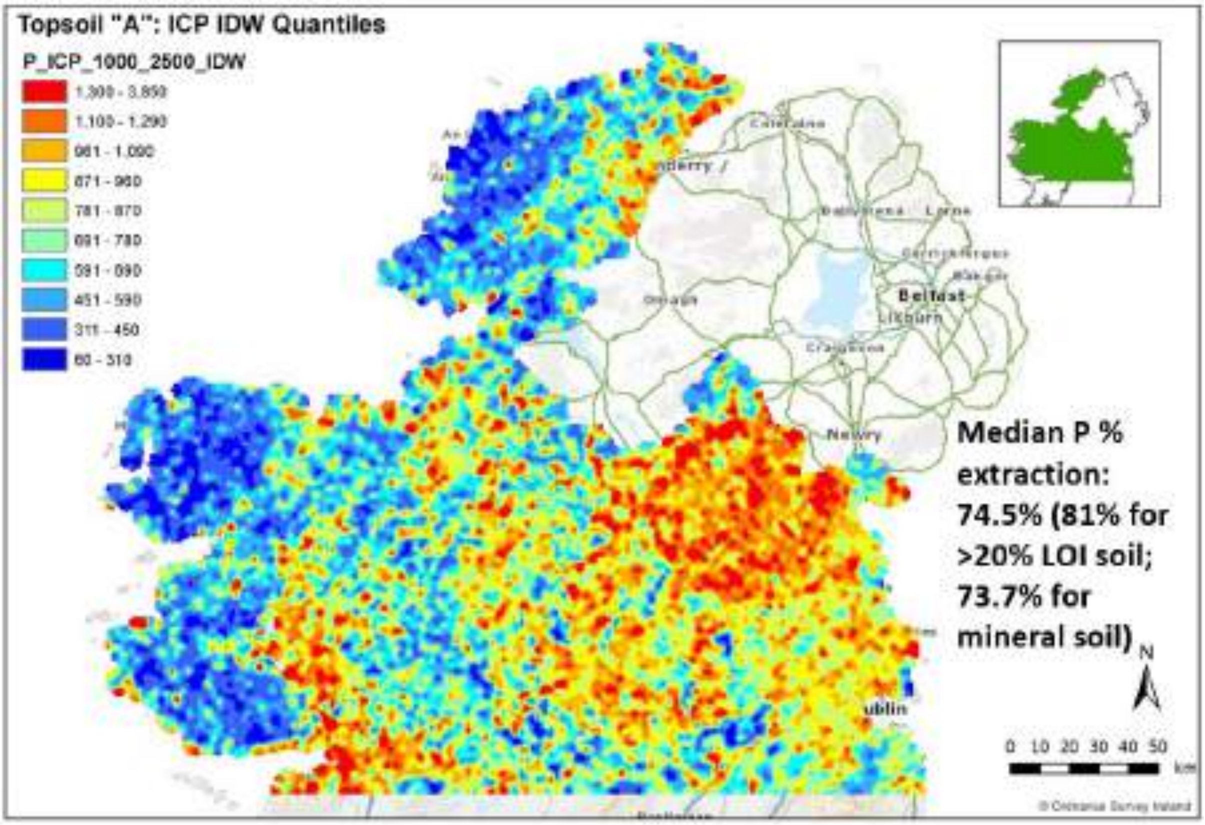


Figure 27: Phosphorus ICP aqua regia data

- There is general coherence between higher P and bedrock or till dominated by clastic rocks: Dalradian (E Donegal), Lower Palaeozoic sediments (Longford-Down, N Wicklow), but distribution is spotty.
- Distribution can also be seen as coincident with pasture or arable land.
- High P observed in north Dublin (Skerries) – link to tillage farms?
- Low P is observed in areas of peat: NW Donegal, NW Mayo, Connemara, E Galway/Roscommon/E Mayo "corridor", ORS inliers, Dublin-Wicklow mountains.

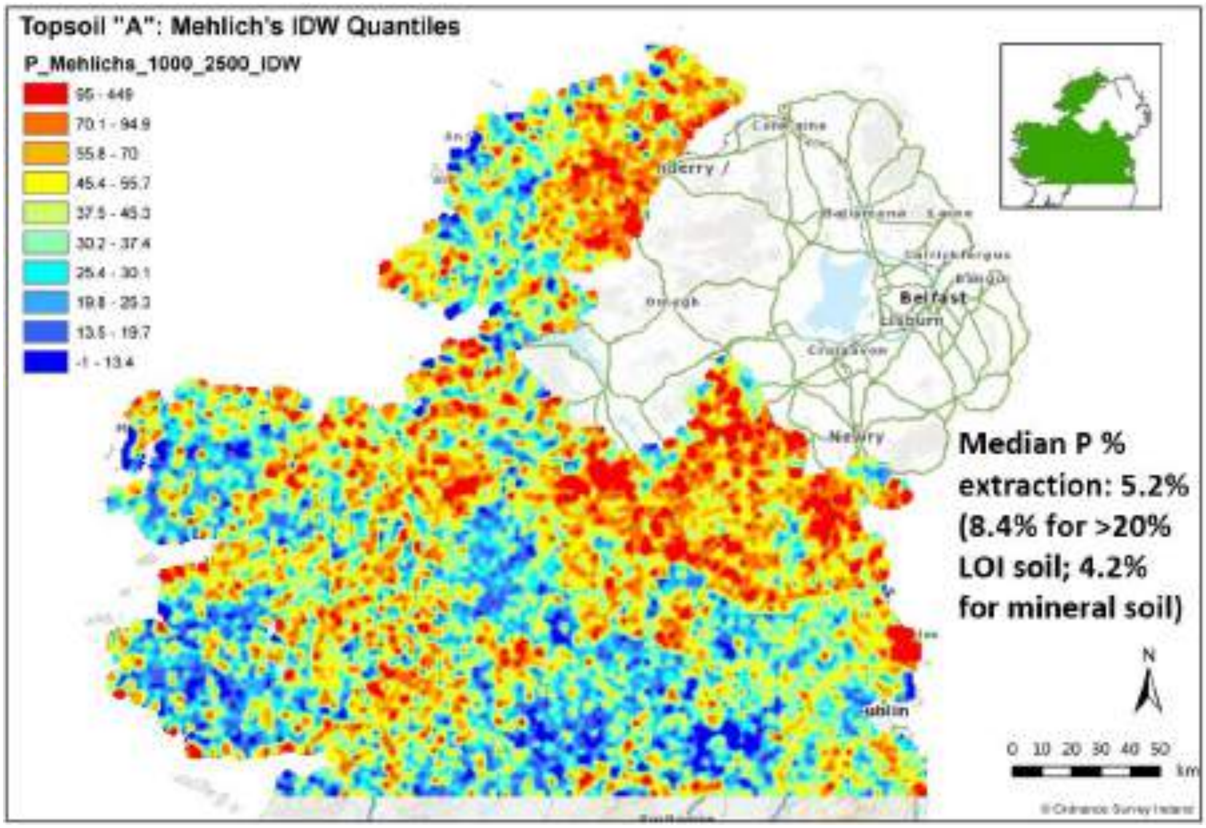


Figure 28: Phosphorus ICP M3 data

- Spotty data, less coherence than observed for *aqua regia* data.
- There is a partial reversal of the distribution observed for *aqua regia* data – high P in E Galway/Roscommon/E Mayo "corridor" and scattered high P in other peaty areas (NW Donegal, Mayo, Connemara).
- The main areas of high soil P correlate well with *aqua regia* data: Longford-Down, E Donegal, north Dublin (Skerries).

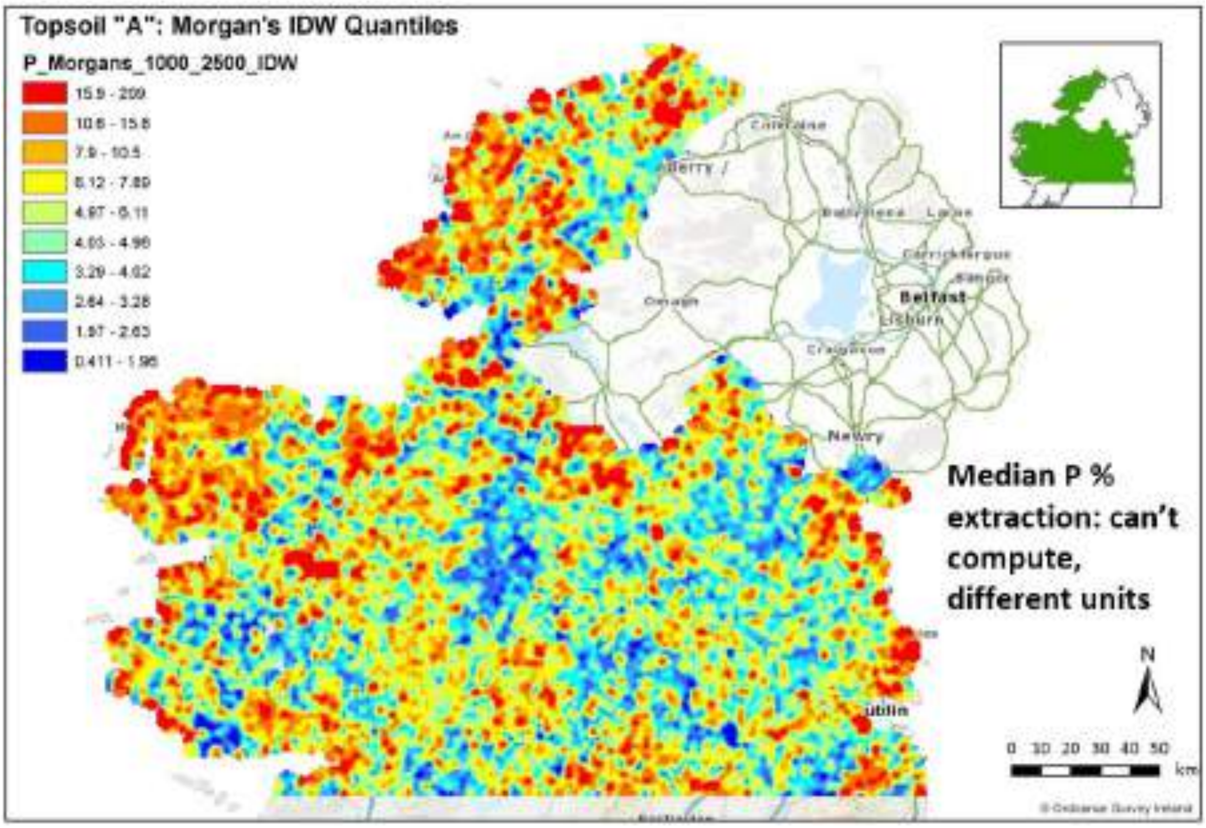


Figure 29: Phosphorus ICP Morgan's data

- Spotty data, less coherence than *aqua regia* data.
- Partial reversal of distribution seen for *aqua regia* data – high P in E Galway/Roscommon/E Mayo "corridor" and in other peaty areas (NW Donegal, Mayo, Connemara, Dublin-Wicklow mountains).
- Main areas of high P that correlate well with *aqua regia* data are areas of tillage (north Dublin, Louth).

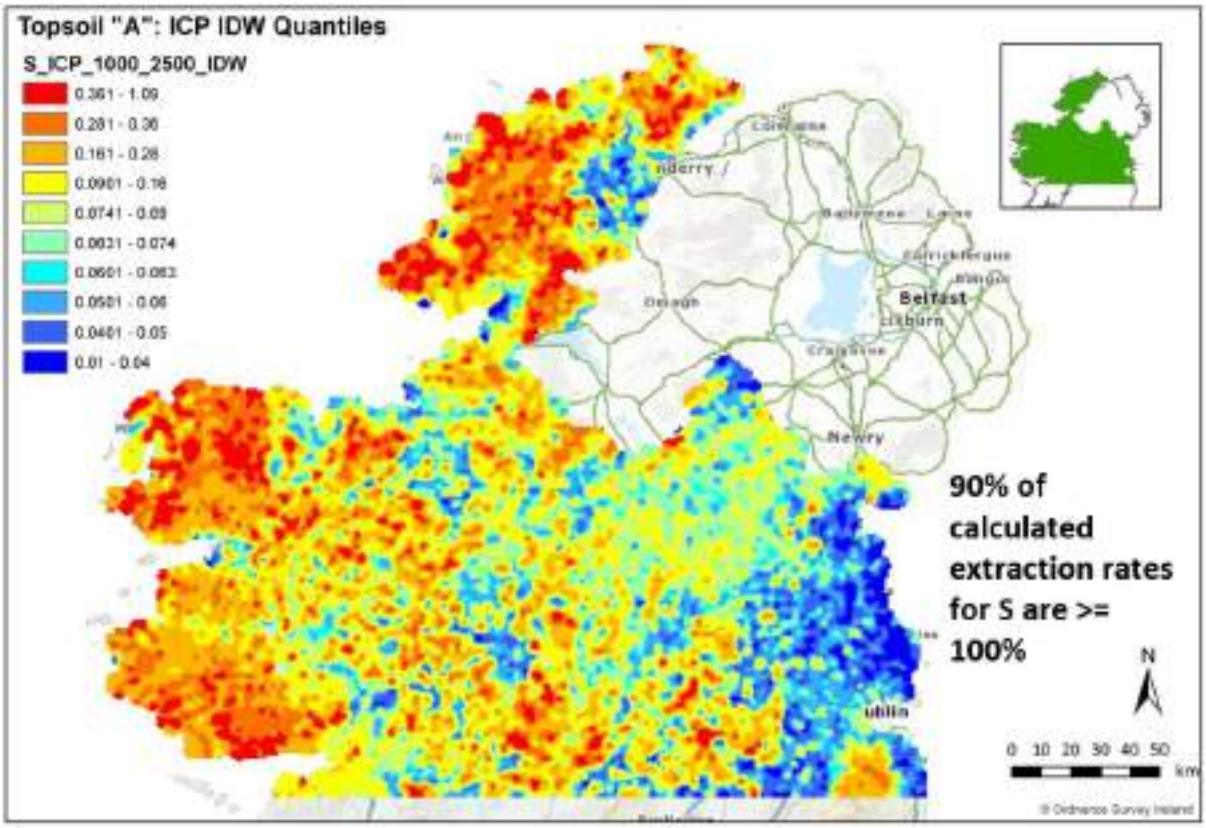


Figure 30: Sulphur ICP aqua regia data

- There is strong coherence between measured high S and peaty areas, especially upland blanket bog.
- Relatively low S is observed in mineral soil.

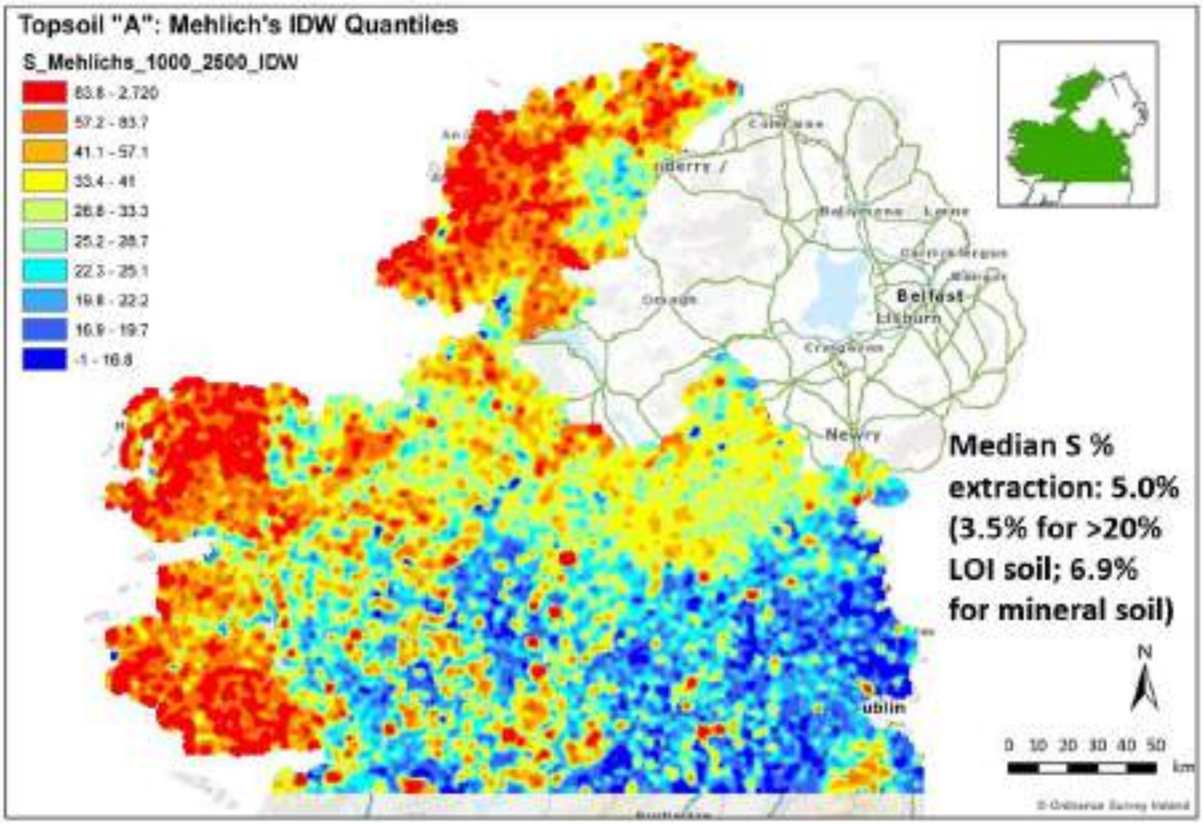


Figure 31: Sulphur ICP M3 data

- The main areas of high S correlate well with *aqua regia* data, i.e. blanket bogs and some parts of midlands.

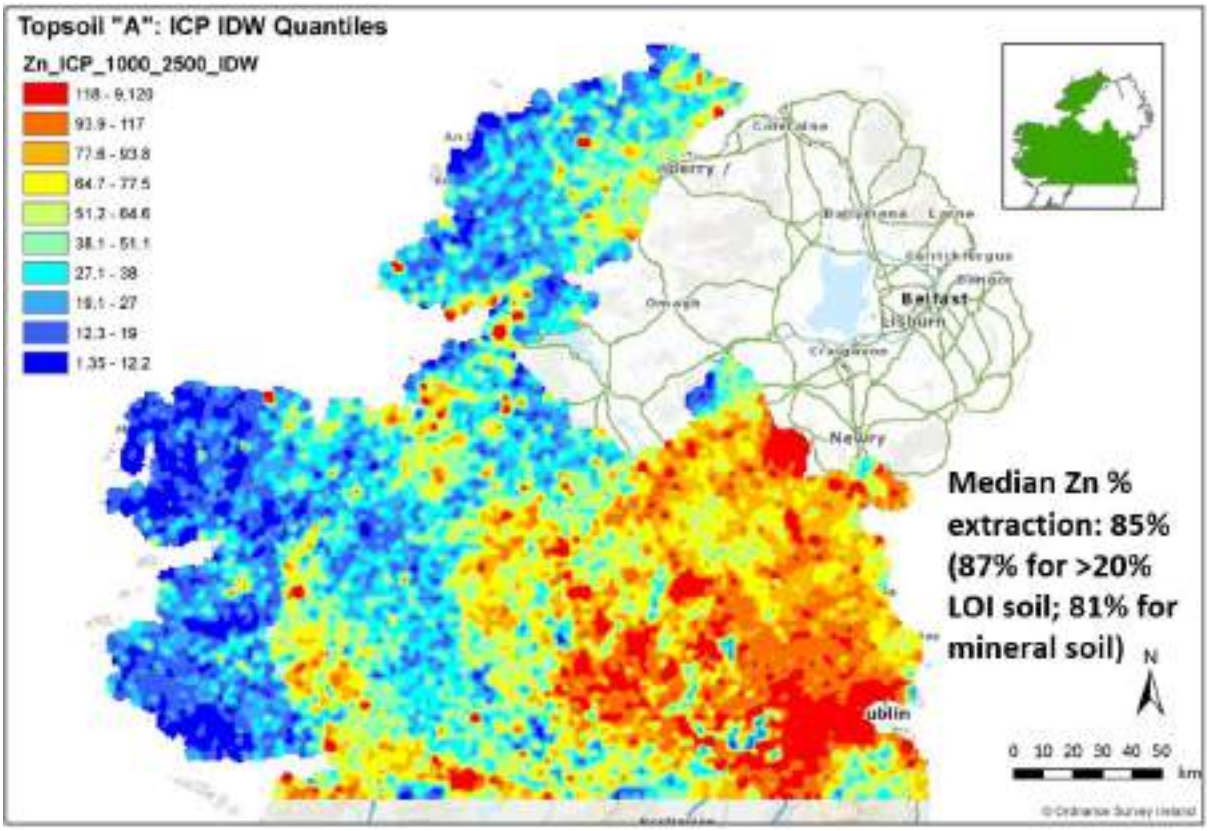


Figure 32: Zinc ICP aqua regia data

- Higher Zn concentrations are widely distributed in mineral soils, with particularly high concentrations in the Longford-Down Inlier and E Midlands.
- In E Midlands, high Zn is associated with Carboniferous lithologies, especially basal Carboniferous clastics and overlying Waulsortian and Calp limestone.
- High Zn concentrations are also associated with known mineral occurrences (e.g. Tynagh in Co. Galway, Monaghan mines).
- Low Zn is observed in areas of peat: NW Donegal, NW Mayo, Connemara, E Galway/Roscommon/E Mayo “corridor”, Lough Allen uplands, ORS inliers, Dublin-Wicklow mountains.

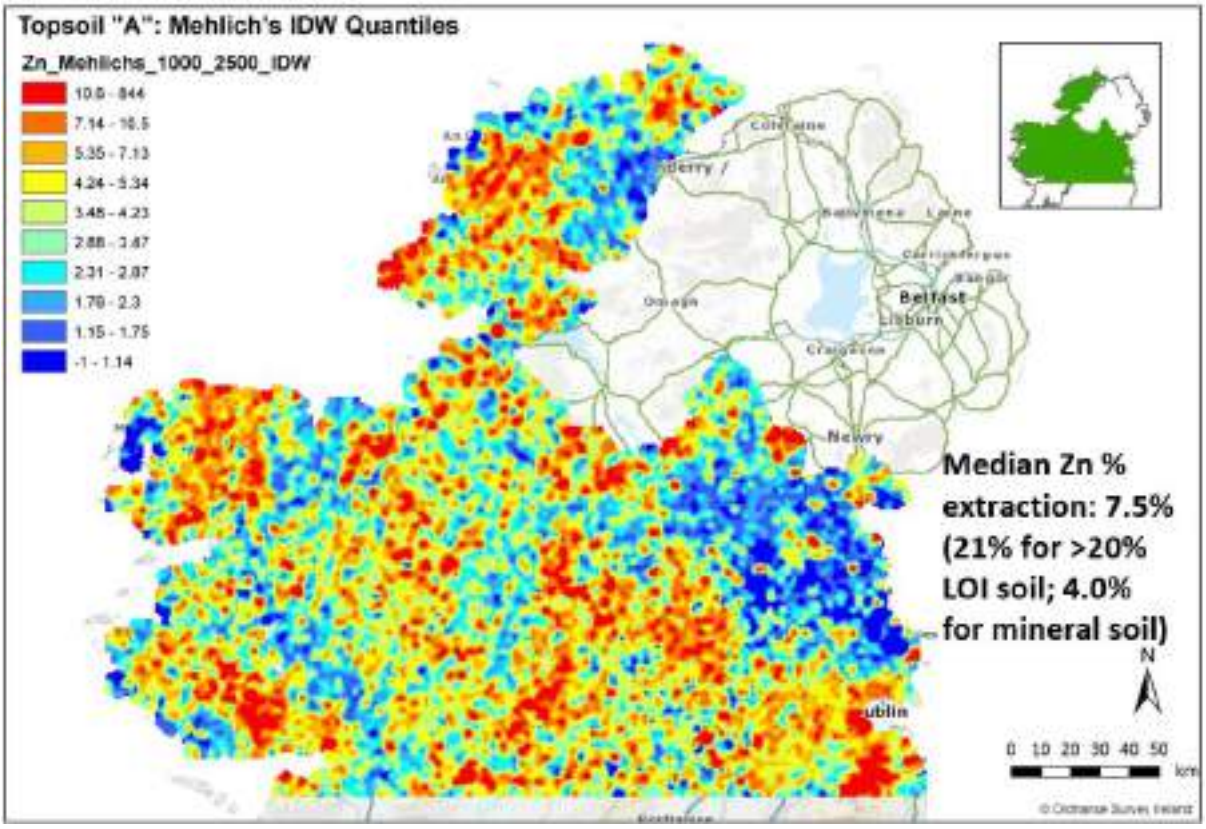


Figure 33: Zinc ICP M3 data

- M3 Zn data display almost the reverse of the distribution seen for *aqua regia* data.
- Relatively high Zn is observed over peaty areas (NW Donegal, NW Mayo, Connemara, E Galway/Roscommon/E Mayo "corridor", Dublin-Wicklow mountains, midlands raised bogs).
- Lower Zn is observed over clastic bedrock areas such as Longford-Down (apart from area around Monaghan mines) and E Donegal.
- The observed patterns may at least be partly explained by much higher (**x5**) M3 extraction rate for Zn in peaty soil compared to mineral soil.

6. Influence of organic matter (OM) on element extraction rates and their measured concentrations

The estimates of median extraction rates given in the preceding section and in the table below for the various elements using M3 reagent, based on a comparison of M3 and XRF data, are necessarily an approximation given that they reflect a specific collection of samples that are not wholly representative of the range of different soil compositions in the study area. Nevertheless, they provide useful additional insights to help understand the mapped distributions of M3 data.

The maps of M3 and ICPar data for the 11 elements analysed by both methods, as presented in the previous section, typically display either (i) a similar distribution for a given element or (ii) distributions that are essentially the reverse of each other. In the latter case, the most striking feature of each map is that areas underlain predominantly by peat bog, which, as reflected in the ICPar maps, generally have very low absolute element concentrations, appear on the M3 maps to have relatively high element concentrations. This reversal of the expected distribution is observed for Fe, K, Mg and Zn. Each of these elements is characterized by a significantly higher estimated rate of M3 extraction for soil rich in OM (LOI > 20 %) compared to mineral soil (table, below). The suggestion is that the high rate of extraction for OM-rich soils in M3 reagent compensates for the low absolute element concentrations that naturally occur in these soils, leading to a much higher proportion of element in the M3 extract. Whether this *alone* explains the observed mapped distribution is not clear but differential extraction rates for M3 reagent undoubtedly contribute significantly to the observed mapped distribution of Fe, K, Mg and Zn.

Element	**M3 Extraction rate (median, %)**			**Mapped distribution**	
	Organic-rich soil (A)	**Mineral soil (B)**	**Ratio A/B**	**Similar to ICPar**	**Reverse of ICPar**
Al	5.1	1.6	3.19	*	
Ca	24	38	0.63	*	
Co	3.7	3.3	1.12	*	
Cu	5.3	19	0.28	*	
Fe	4.7	1.2	3.92		*
K	6.8	0.9	7.56		*
Mg	28	2	14.0		*
Mn	12.6	11.4	1.11	*	
P	8.4	4.2	2.00		
S	3.5	6.9	0.51	*	
Zn	21	4	5.25		*

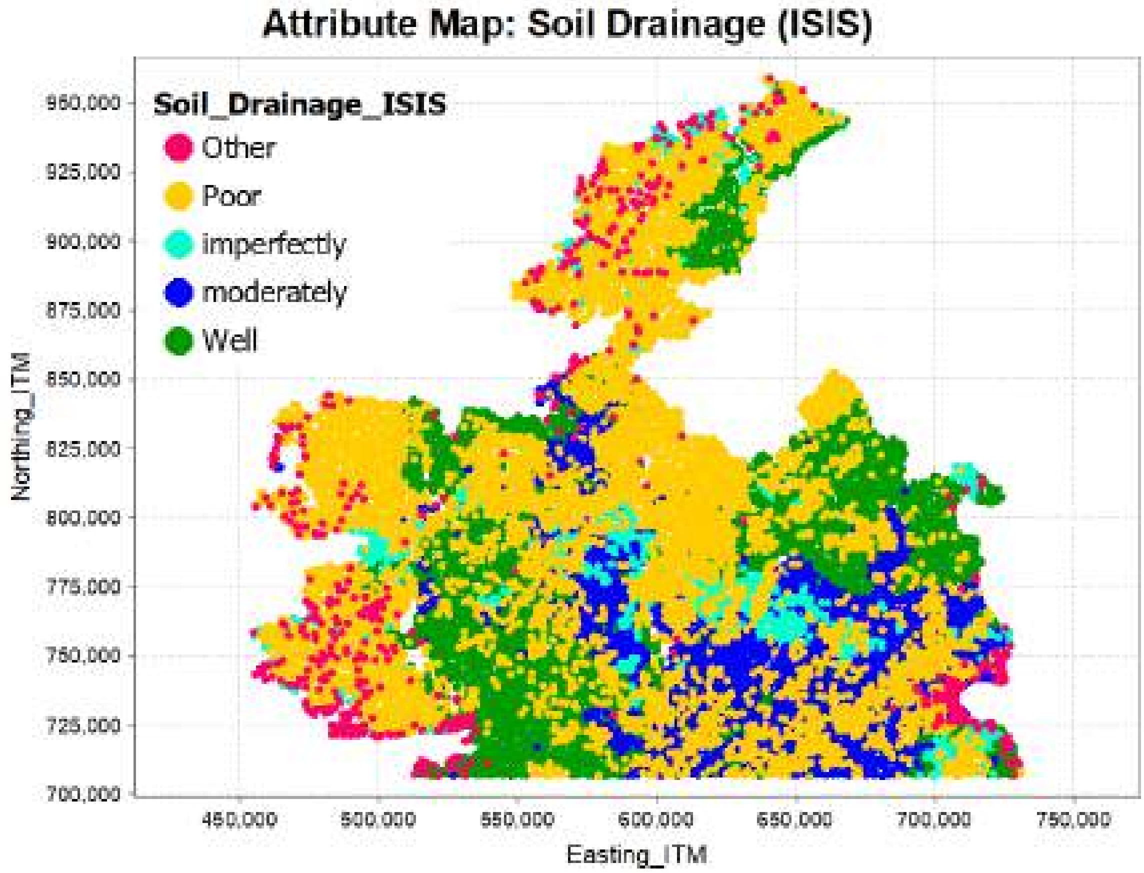
7. Soil attributes – drainage and texture (ISIS)

Soil drainage and texture attributes used in the geochemical assessments are derived from the 1:250,000-scale Irish Soil Information System (ISIS) map. Soil drainage, in particular, is considered to have a predominant influence on soil processes, given the relatively wet prevailing soil conditions in Ireland.

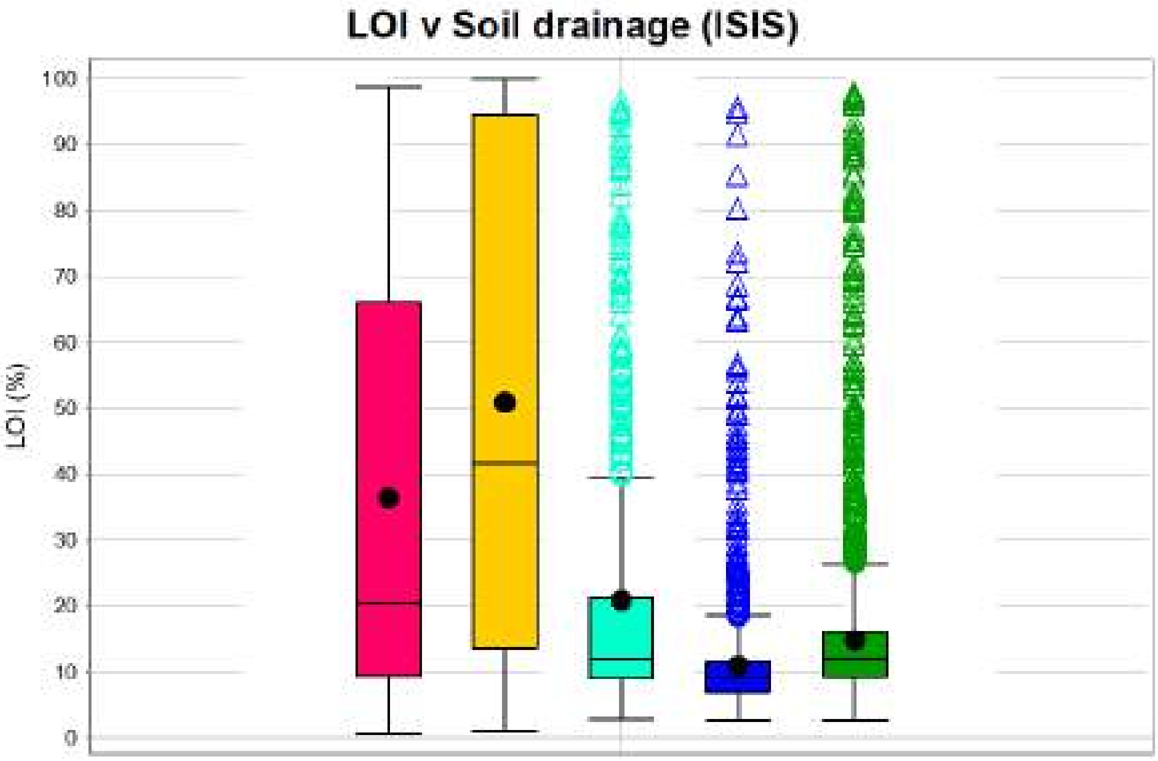
ISIS soil drainage categories are "Poor", "Imperfectly", "Moderately", "Well" and "Other". The map (Figure 35a) indicates the distribution of these categories. Of the soil samples collected in the study region, 49 % are in the "Poor" category and of these 52 % are classified as peat on the GSI Quaternary map. The bulk of better-drained soils ("Moderately" and "Well") are located in the midlands where mineral soils predominate. The boxplots of soil LOI v the ISIS soil drainage classification emphasises how the better-drained soils correlate with low OM content (high LOI) and, conversely, high mineral content.

Because the drainage classes partly reflect the OM content of the soils, the relationship between specific elements and soil drainage classes is also a reflection of their OM content. Thus, better-drained soils with higher mineral content generally have higher As, Ca (ICPar + M3), Cd, Cr, Cu (ICPar + M3), Fe ICPar, Mg ICPar, Mn (ICPar + M3), Zn ICPar. Elements that tend to display higher concentrations in OM-rich soils (Fe_M3, Mg_M3, Zn_M3) appear to have a positive association with the "Poor" drainage class. See following pages for boxplots of specific elements classified by soil drainage class.

This points to the general difficulty of linking measured soil chemical composition to specific soil characteristics, given the numerous and sometimes confounding properties of soil that are reflected in the different soil classifications, notably OM content. In addition, soil maps such as those produced for ISIS have been compiled at a relatively coarse scale (1:250,000), necessarily introducing further uncertainty into modelling of the spatial data.

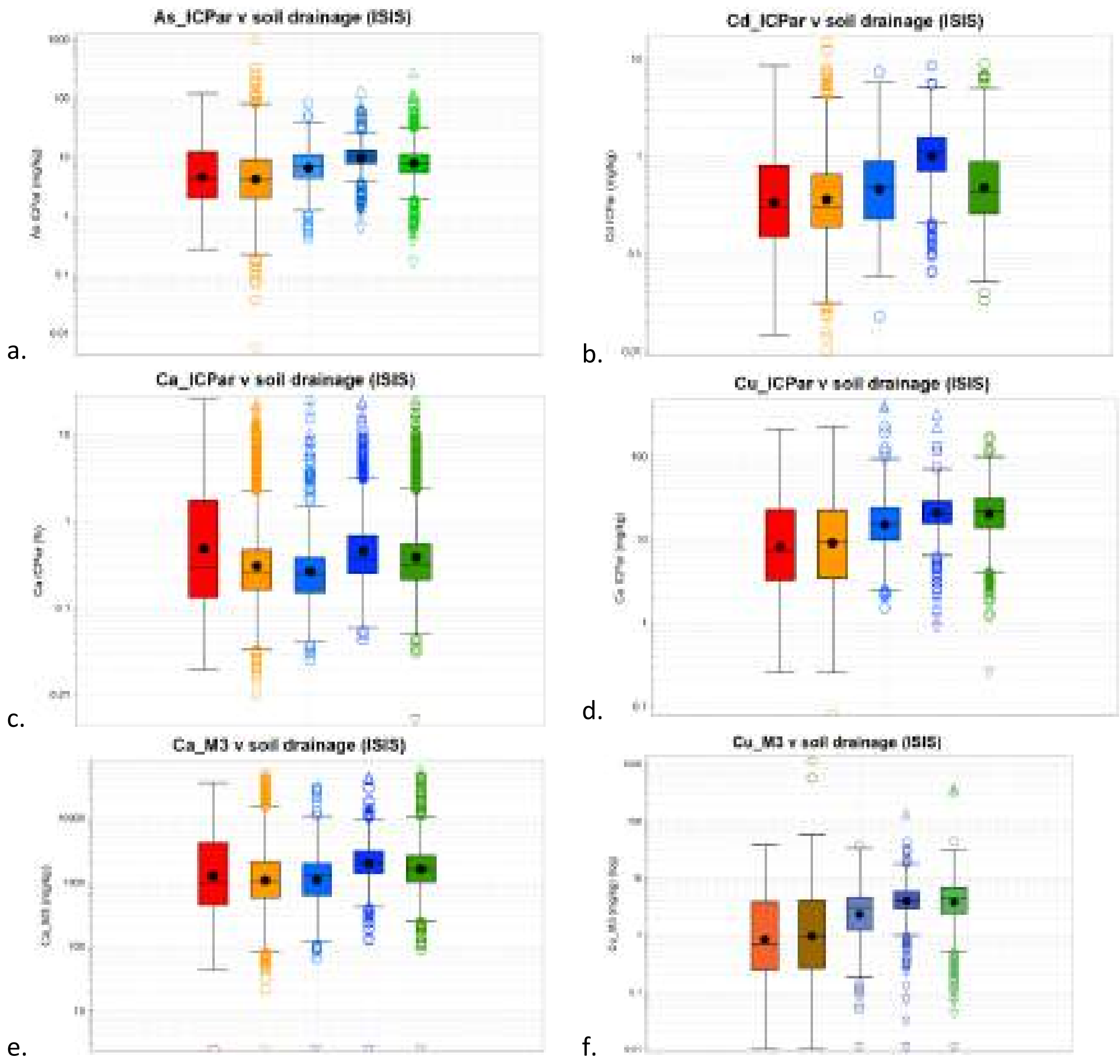


a.



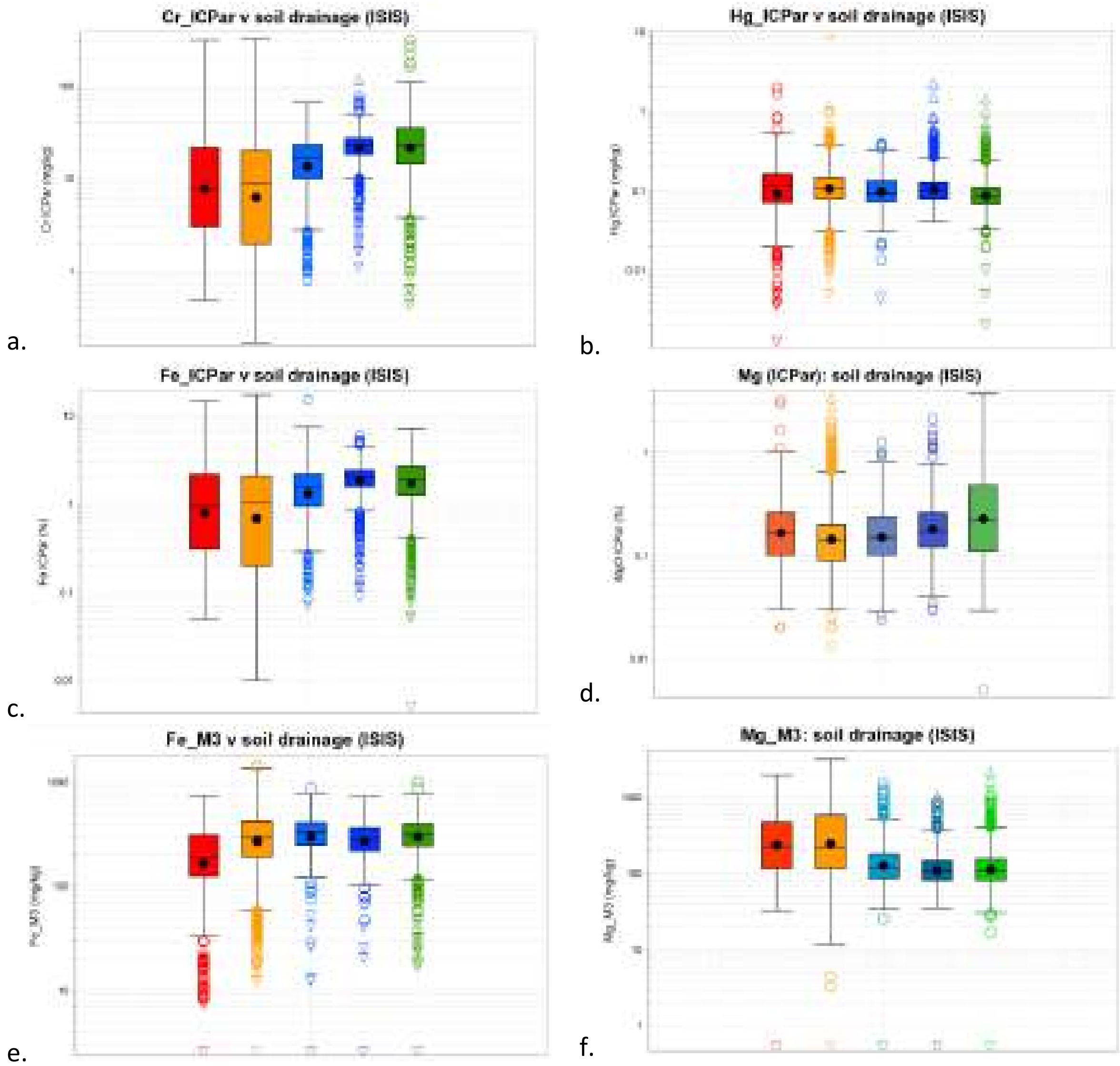
b.

Figure 34: Distribution of soil drainage compared to LOI data in a. map form and b. box plot comparison



Soil_Drainage_ISIS
- Other
- Poor
- imperfectly
- moderately
- Well

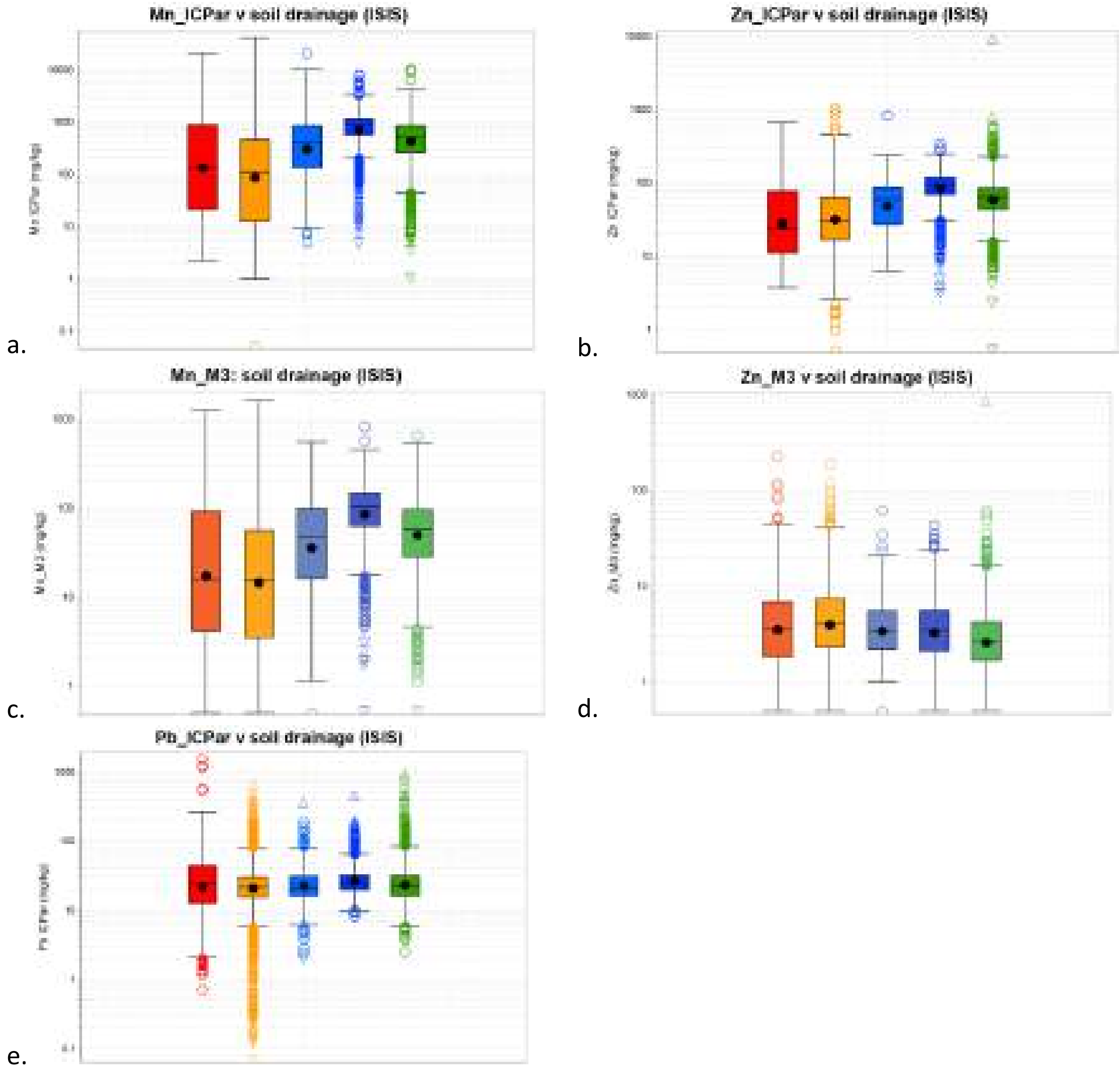
Figure 305: a. As ICPar, b. Cd ICPar, c. Ca ICPar, d. Cu ICPar, e. Ca M3, f. Cu M3 v Soil drainage (ISIS)



Soil_Drainage_ISIS

- Other
- Poor
- imperfectly
- moderately
- Well

Figure 316: a. Cr ICPar, b. Hg ICPar, c. Fe ICPar, d. Mg ICPar, e. Fe M3, f. Mg M3 v Soil drainage (ISIS)



Soil_Drainage_ISIS
- Other
- Poor
- imperfectly
- moderately
- Well

Figure 32: a. Mn ICPar, b. Zn ICPar, c. Mn M3, d. Zn M3, e. Pb ICPar v Soil drainage (ISIS)

ISIS soil texture categories are “Alluvium”, “Clayey”, “Coarse loamy”, “Fine loamy”, “Loamy”, “Sandy” and “Peat”. The map (Figure 39) indicates the distribution of these categories. Some of the categories have a quite restricted distribution, notably (i) the clayey class, which is mostly found around Lough Allen where Carboniferous shale and sandstone bedrock predominates;(ii) the sandy class, which largely comprises marine sand deposits (machairs, dunes) and (iii) the loamy class which is mostly found overlying clastic rocks in east Donegal and Mayo. The fine loamy class accounts for the bulk of the mineral soils in the region, particularly over the midlands (bedrock of Carboniferous limestone and Lower Palaeozoic clastic rocks in the Longford-Down Inlier).

Because of this distribution, the texture classes partly reflect bedrock composition in addition to specific soil compositions (peat, marine sands) and the relationship between texture and element concentrations reflects this. Low element concentrations are typically associated with peat and sandy texture classes. The sandy class is very restricted and includes only 38 samples. The abundance of shelly fragments and absence of significant amounts of lithic material in these marine sand deposits results in relatively low concentrations of As, Cd, Cr, Cu, Fe, Hg, Mn, Pb, Zn. By the same token, this composition gives rise to relatively high concentrations of Ca (ICPar and M3), expected given the abundance of marine shell fragments in these sands, and Mg_M3, but not Mg ICPar. The latter suggests that sandy soils have a source of readily leachable Mg, possibly from marine aerosols.

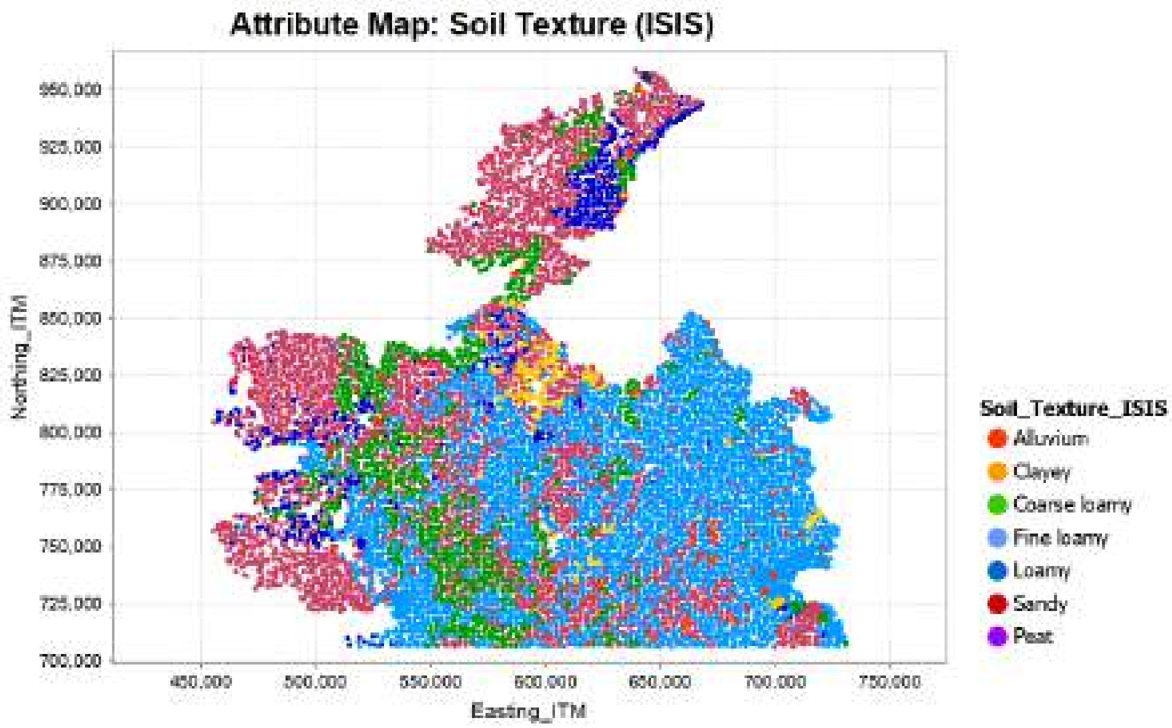
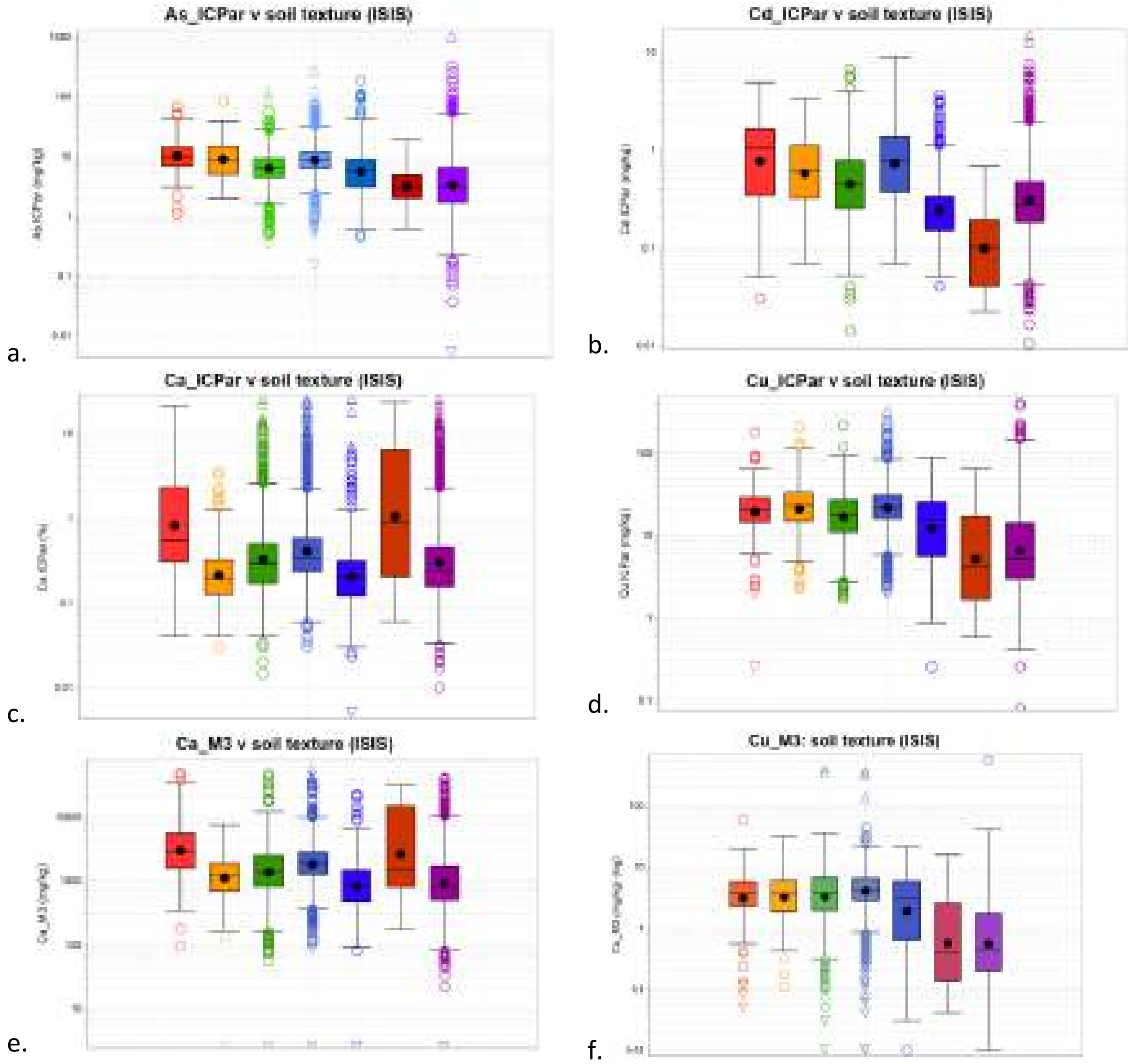


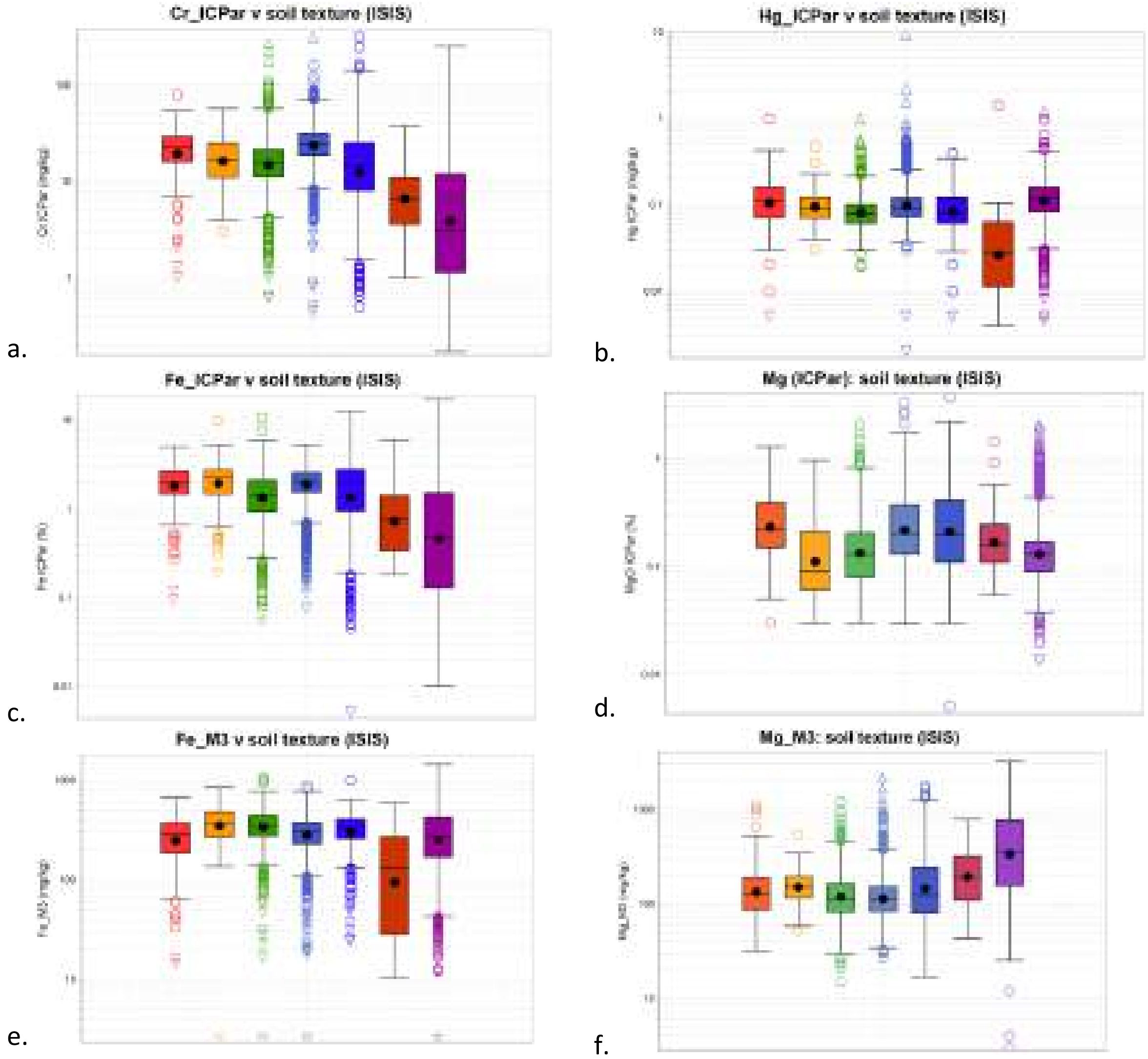
Figure 38: Soil texture map (ISIS)



Soil_Texture_ISIS

- Alluvium
- Clayey
- Coarse loamy
- Fine loamy
- Loamy
- Sandy
- Peat

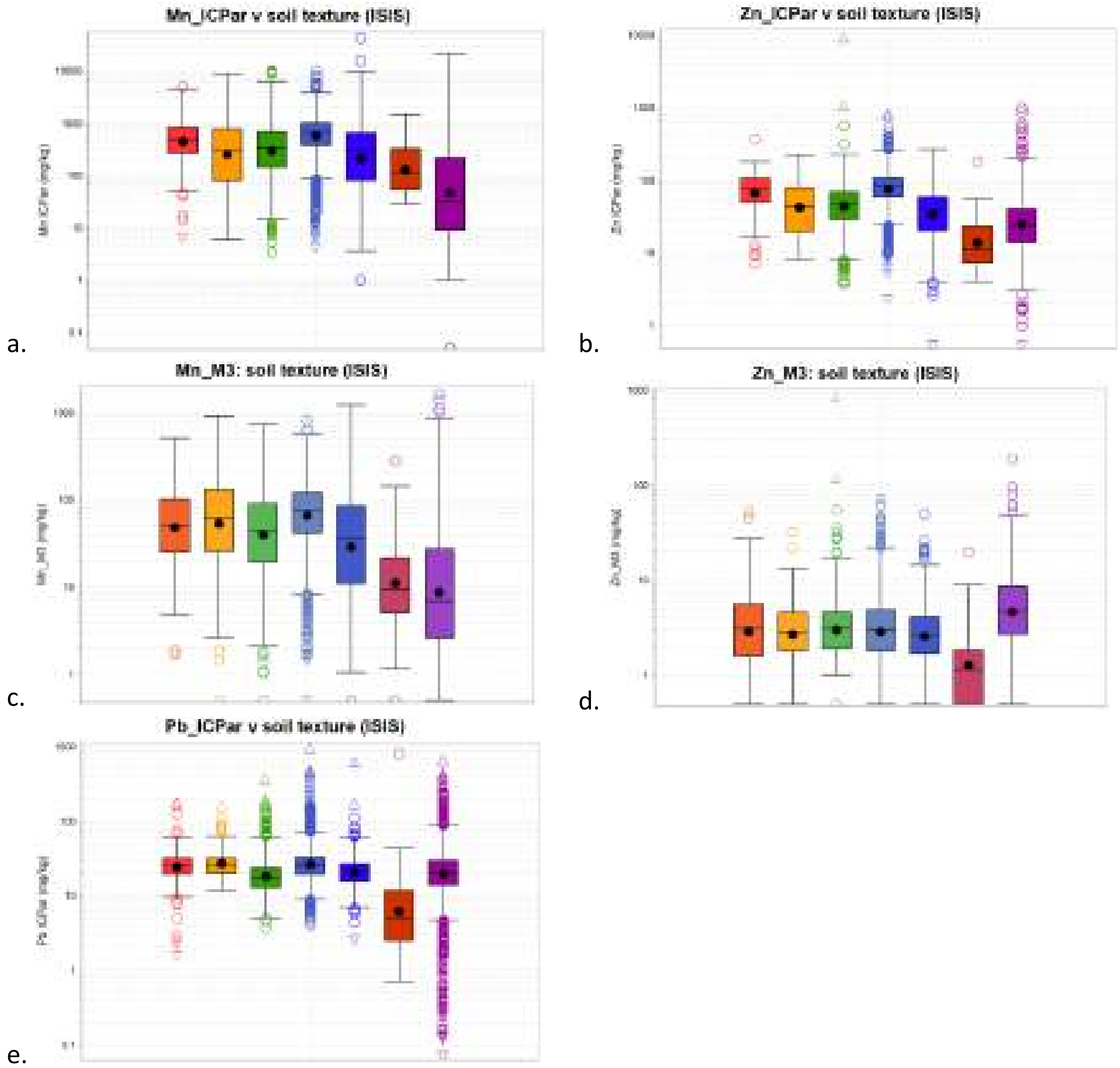
Figure 39: a. As ICPar, b. Cd ICPar, c. Ca ICPar, d. Cu ICPar, e. Ca M3, Cu M3 v soil texture (ISIS)



Soil_Texture_ISIS

- Alluvium
- Clayey
- Coarse loamy
- Fine loamy
- Loamy
- Sandy
- Peat

Figure 330: a. Cr ICPar, b. Hg ICPar, c. Fe ICPar, d. Mg ICPar, e. Fe M3, Mg M3 v soil texture (ISIS)



Soil_Texture_ISIS

- Alluvium
- Clayey
- Coarse loamy
- Fine loamy
- Loamy
- Sandy
- Peat

Figure 41 a. Mn ICPar, b. Zn ICPar, c. Mn M3, d. Zn M3, e. Pb ICPar v soil texture (ISIS)

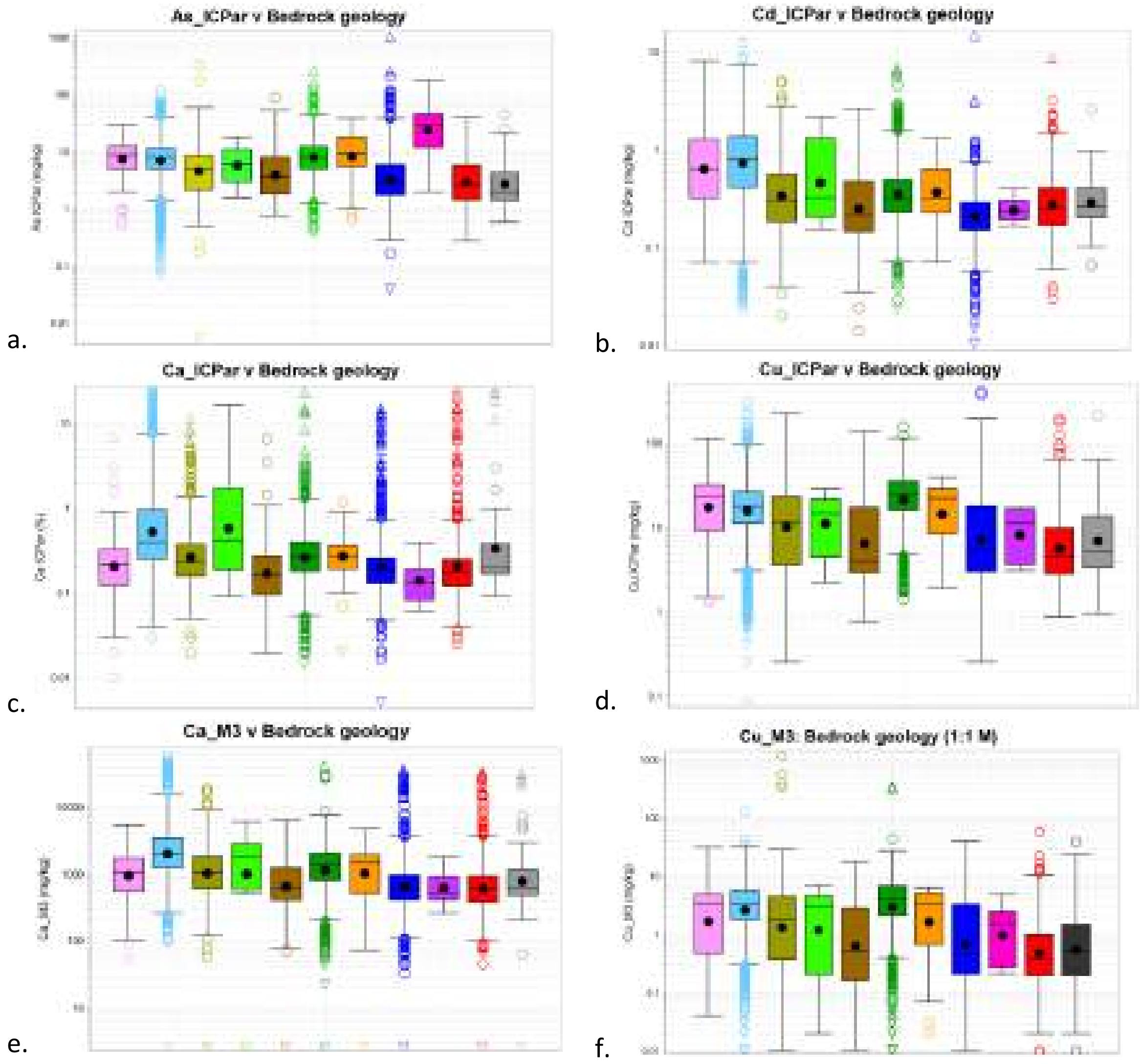
8. Geological attributes: Bedrock composition and Quaternary class

Bedrock geology exerts a significant control on soil composition in the study area, albeit other factors, notably OM content, can mask its influence.

Relatively high concentrations of some elements (Cr, Cu, Fe, Mg, Zn) characterize soils overlying the Longford-Down Inlier, where greywackes have a distinctive composition that reflects in part their content of mafic igneous lithic clasts. Similarly, the limestone-dominated Lower Carboniferous succession in the midlands underlies soils that typically have relatively high concentrations of Ca, Mg, Cd and Zn.

More localized instances of element enrichment in soil occur where specific bedrock types are found. These include (i) the high Cr and Mg concentrations in soil overlying serpentinite of the Deer Park Complex on the shore of Clew Bay in County Mayo and in soils across the South Mayo Lower Palaeozoic succession, (ii) high As in soil around the Au-As mineralization in the Croagh Patrick area and (iii) high Pb and Zn related to Zn-Pb mineralization in County Monaghan and near Tynagh in County Galway.

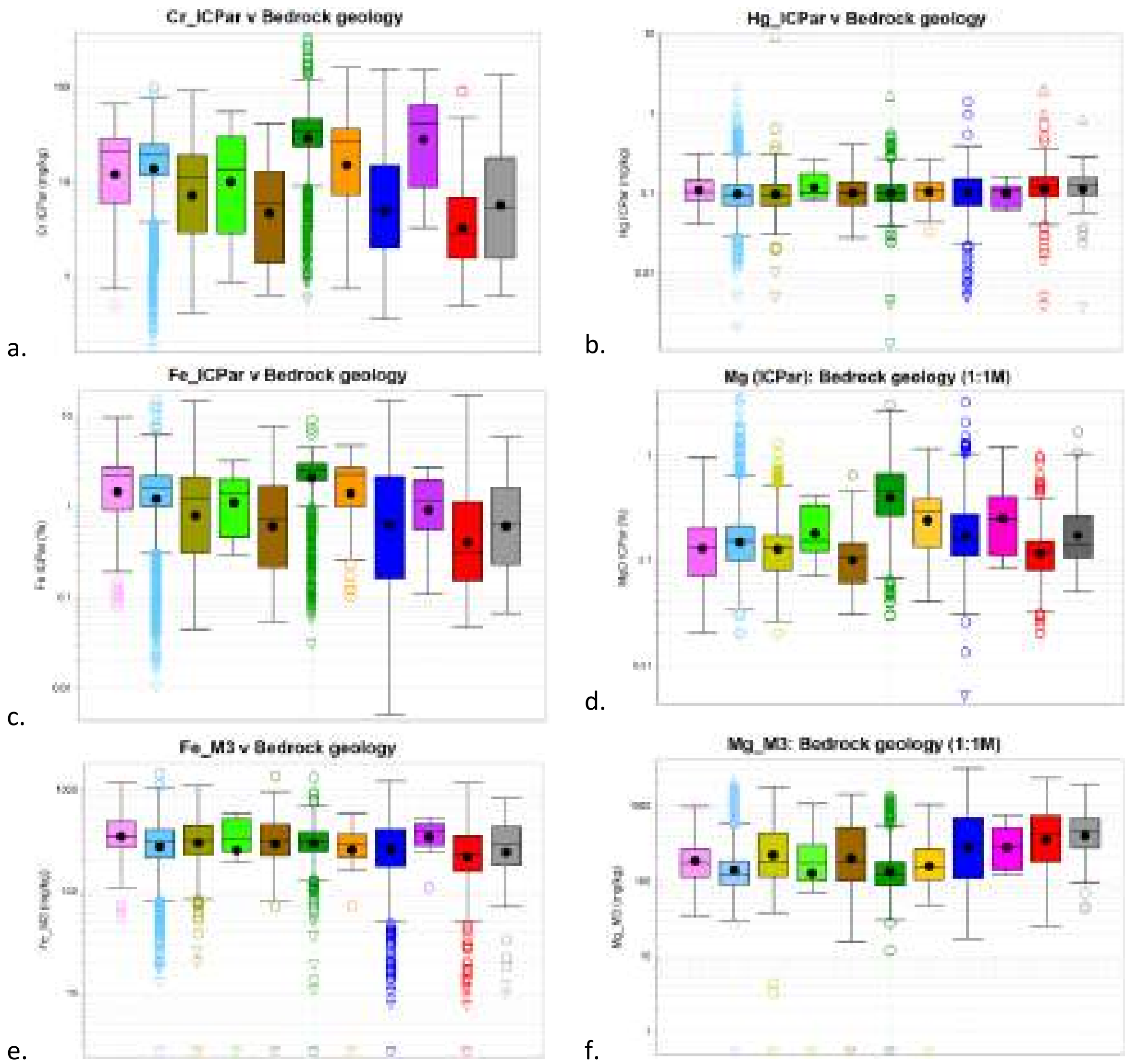
Other bedrock units in the study area, notably granitic rocks, Proterozoic (Dalradian) metasediments and ORS sandstones typically underlie soils that have relatively low element concentrations. This reflects the fact that these rocks generally occur in upland areas (Dublin-Wicklow mountains, Connemara, N Mayo and Donegal) where blanket bog is the dominant soil type. Peat or OM-rich soil is generally depleted in mineral content leading to low absolute element concentrations.



Bedrock (GSI 1M)

- Namurian rocks
- Carboniferous limestone
- Carboniferous clastics
- Devonian-Carboniferous volcanics
- Devonian clastics
- Lr. Palaeozoic clastics
- Ordovician volcanics
- Proterozoic schist, gneiss
- Serpentinite, melange
- Granitic rocks
- Mafic intrusive rocks

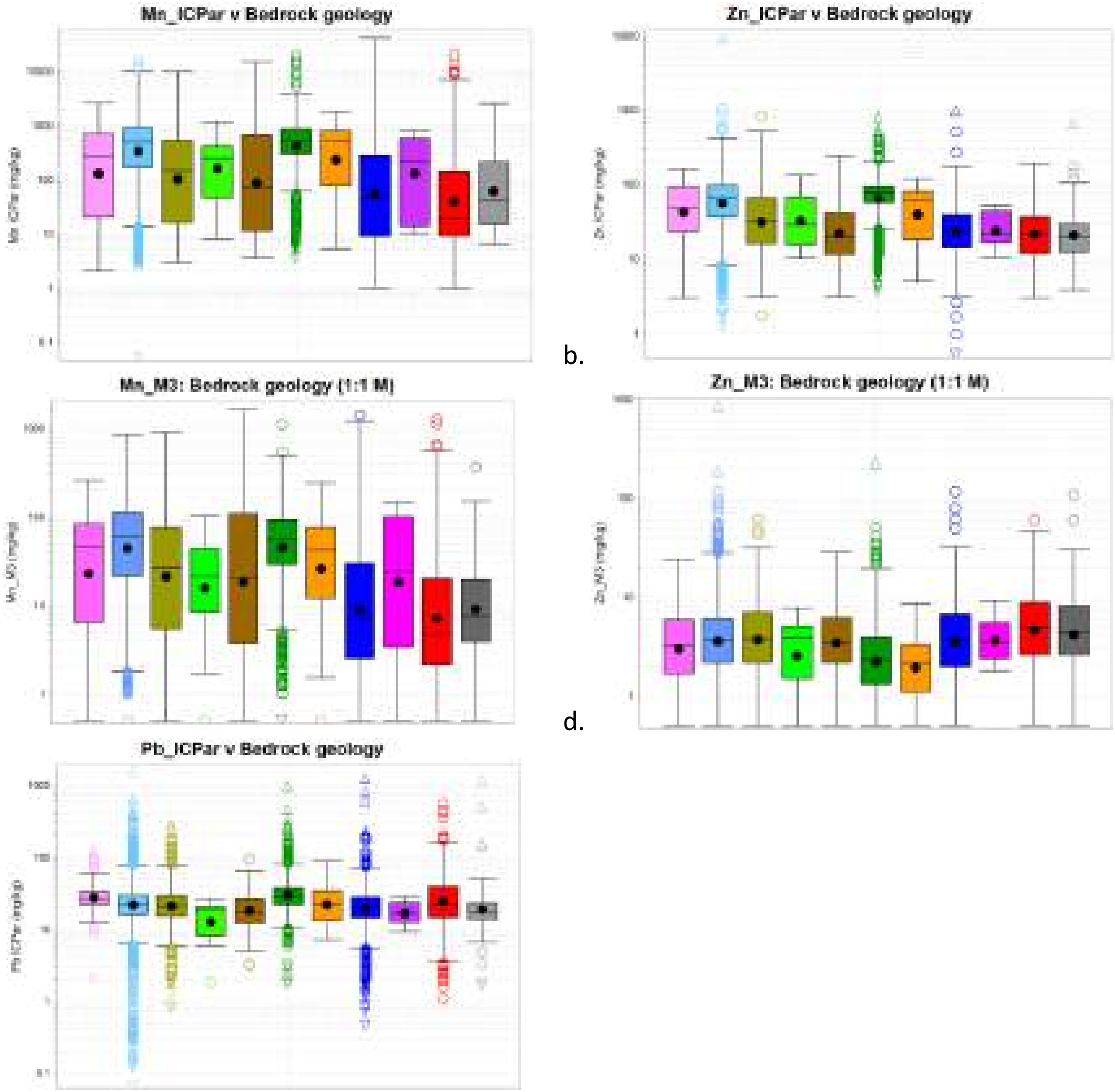
Figure 42: a. As ICPar, b. Cd ICPar, c. Ca ICPar, d. Cu ICPar, e. Ca M3, f. Cu M3 v Bedrock geology



Bedrock (GSI 1M)

- Namurian rocks
- Carboniferous limestone
- Carboniferous clastics
- Devonian-Carboniferous volcanics
- Devonian clastics
- Lr. Palaeozoic clastics
- Ordovician volcanics
- Proterozoic schist, gneiss
- Serpentinite, melange
- Granitic rocks
- Mafic intrusive rocks

Figure 43: a. Cr ICPar, b. Hg ICPar, c. Fe ICPar, d. Mg ICPar, e. Fe M3, f. Mg M3 v bedrock geology



Bedrock (GSI 1M)

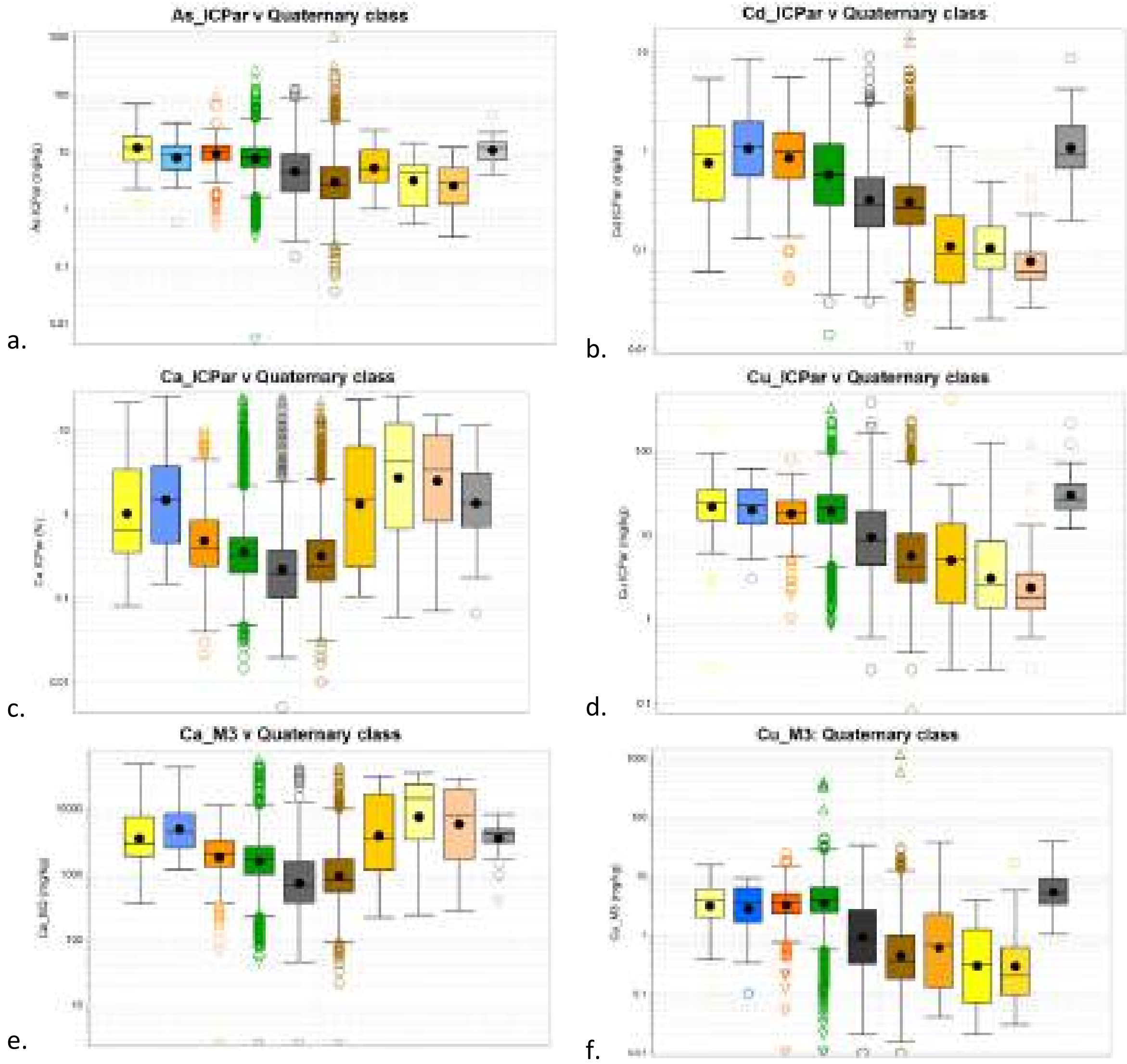
- Namurian rocks
- Carboniferous limestone
- Carboniferous clastics
- Devonian-Carboniferous volcanics
- Devonian clastics
- Lr. Palaeozoic clastics
- Ordovician volcanics
- Proterozoic schist, gneiss
- Serpentinite, melange
- Granitic rocks
- Mafic intrusive rocks

Figure 44: a. Mn ICPar, b. Zn ICPar, c. Mn M3, d. Zn M3, e. Pb ICPar v bedrock geology

Quaternary sediments are classified according to their process of formation and, as such, do not necessarily reflect variation in the chemical composition of soils. In the boxplots below, it is striking how the main Quaternary classes (tills, sand and gravel, alluvium and lacustrine deposits), which comprise 58 % of the area, display very similar medians and ranges for numerous elements. These different sediment types are found across the study area and thus share similar bedrock sources. Nevertheless, the boxplots for Quaternary class do display greater overall variation than is observed for bedrock geology because the classes include sediments of very distinctive composition, such as marine sands and peat.

Samples in the four main Quaternary classes, together with urban samples, generally have relatively high element concentrations (As, Cd, Cu, Cr, Fe, Hg, Mn, Pb, Zn), as measured by ICPar, reflecting the fact that soils in these classes are dominantly mineral soils. In contrast, low element concentrations typically characterize soils in the Quaternary classes that include peat, beach sands, windblown sands and dunes. In the case of the sand deposits, these results largely mirror those for the ISIS texture classification, with "Sandy" soils in the latter largely contained within these Quaternary classes. As with the ISIS "Sandy" class, soils in the corresponding Quaternary classes have relatively high Ca and Mg, reflecting the marine influence (mainly shelly fragments).

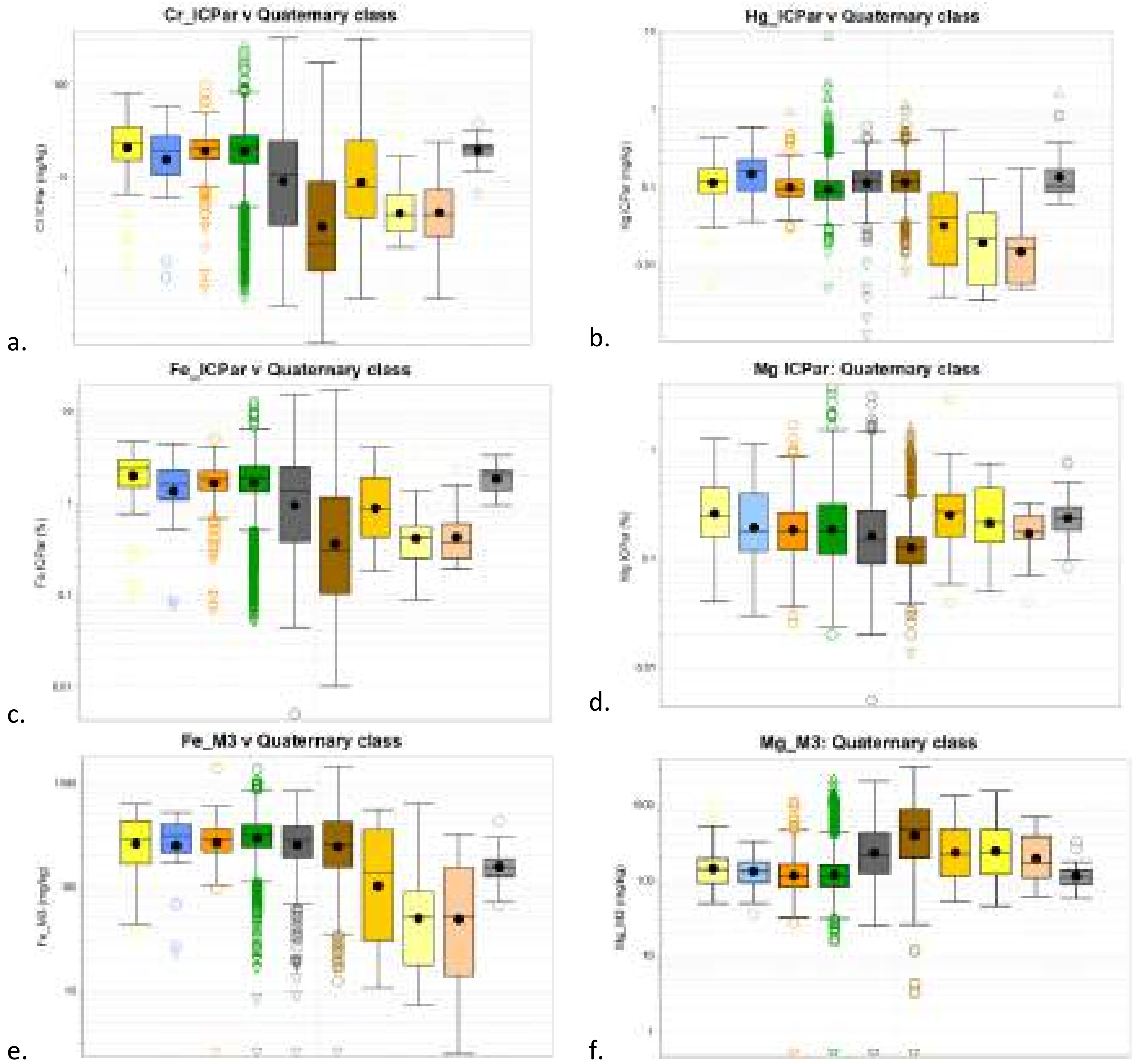
Mercury is an element for which the Quaternary classification provides somewhat more information. In general, the typically very low concentration of Hg in soil combined with relatively poor analytical reproducibility means that discrimination among samples can be poor for this element. For Quaternary sediments, peat and urban soil have relatively high Hg, apparently reflecting both anthropogenic contamination and the tendency of organic matter to bind Hg. Beach and dune sands have distinctly lower Hg.



Quat class

- Alluvium
- Lacustrine
- Sand & Gravel
- Till
- Rock
- Peat
- Beach, marine
- Windblown sands
- Windblown sands and dunes
- Urban

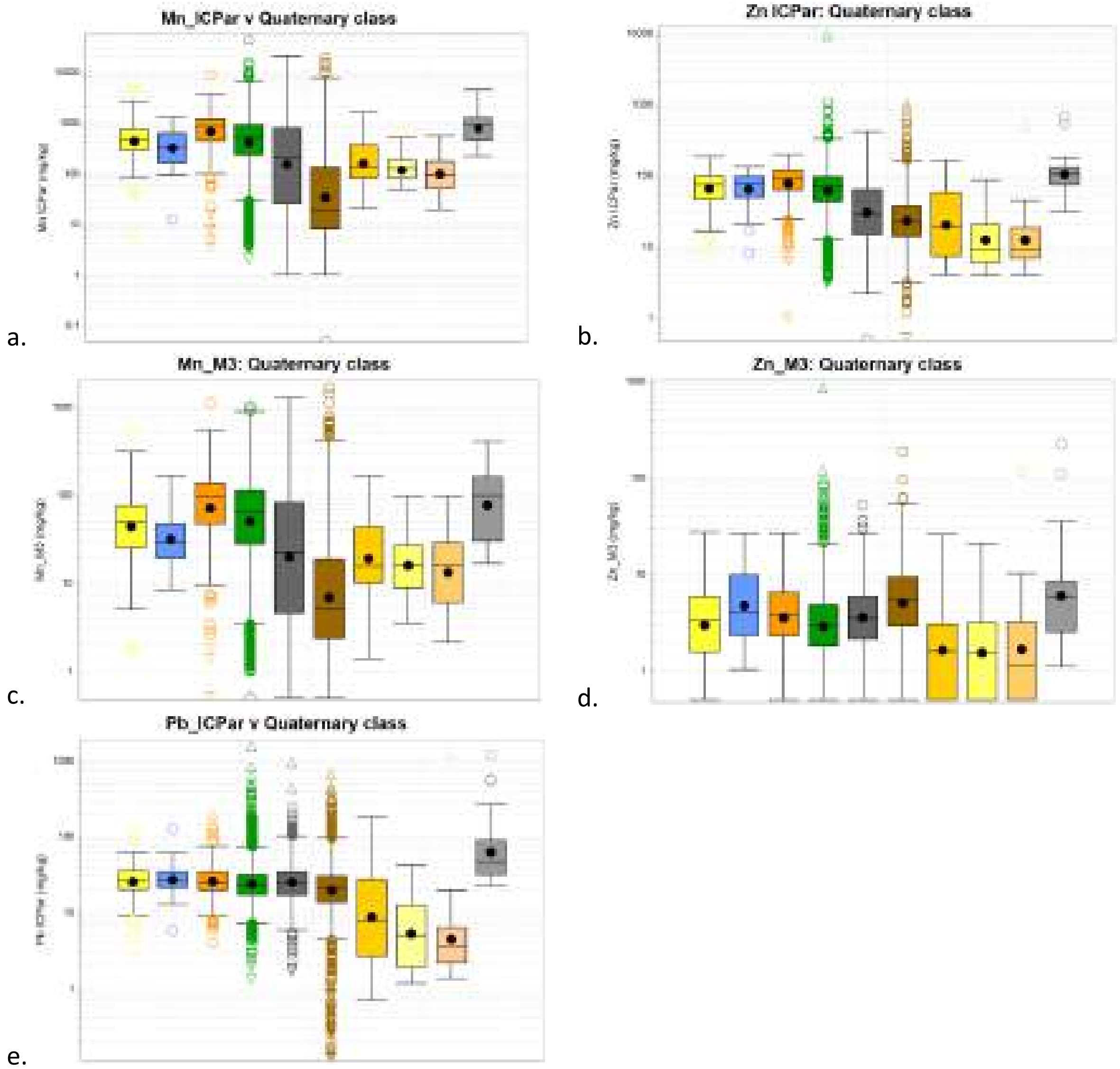
Figure 45: a. As ICPar, b. Cd ICPar, c. Ca ICPar, d. Cu ICPar, e. Ca M3, f. Cu M3 v Quaternary classes



Quat class

- Alluvium
- Lacustrine
- Sand & Gravel
- Till
- Rock
- Peat
- Beach, marine
- Windblown sands
- Windblown sands and dunes
- Urban

Figure 346: a. Cr ICPar, b. Hg ICPar, c. Fe ICPar, Mg ICPar, Fe M3, Mg M3 v Quaternary classes



Quat class

- Alluvium
- Lacustrine
- Sand & Gravel
- Till
- Rock
- Peat
- Beach, marine
- Windblown sands
- Windblown sands and dunes
- Urban

Figure 357: a. Mn ICPar, b. Zn ICPar, c. Mn M3. Zn M3, Pb ICPar v Quaternary classes

9. Land use – Corine data

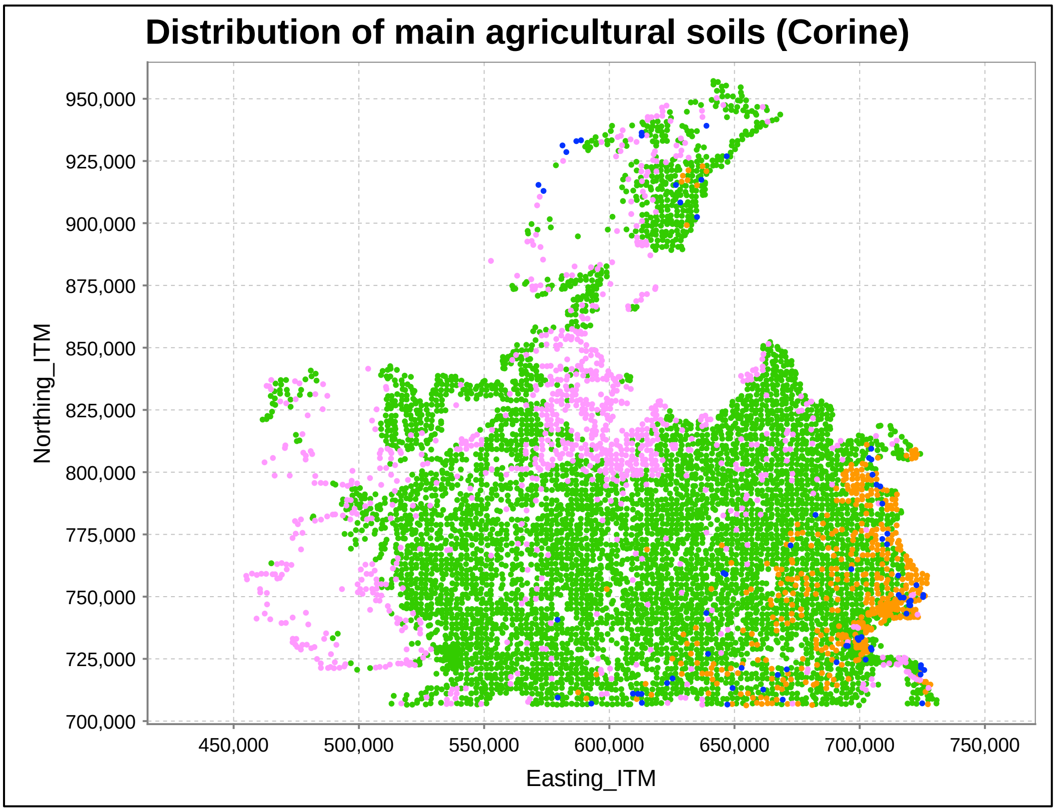
Classifying soils by land use, using Corine data, provides a useful additional perspective on soil chemistry in the study area. In general, the highest element concentrations (As, Ca, Cd, Cr, Cu, Fe, Mg, Mn and Zn), as measured by ICPar, are found in the main agricultural land classes ("pastures", "non-irrigated arable land" and "complex cultivation patterns"). In part, at least, this reflects the fact that such soil is generally mineral soil that naturally contains higher absolute element concentrations (see maps below, showing strong coincidence between distribution of mineral and agricultural soils). An additional factor is that many of these soils overlie the Lower Carboniferous limestone succession, where Ca and Mg are major components of the bedrock and Cd and Zn are important background elements associated with mineralization. By the same token, the Longford-Down Inlier clastic rocks underlying mineral soils in the northeast of the study area are notable for relatively high contents of Cr and Mg.

While the inherent composition of soils in the region provides a general explanation for the observed association between relatively high element concentrations and agricultural soils, it is less easy to identify direct specific agricultural inputs to soil chemistry, at least at the regional scale.

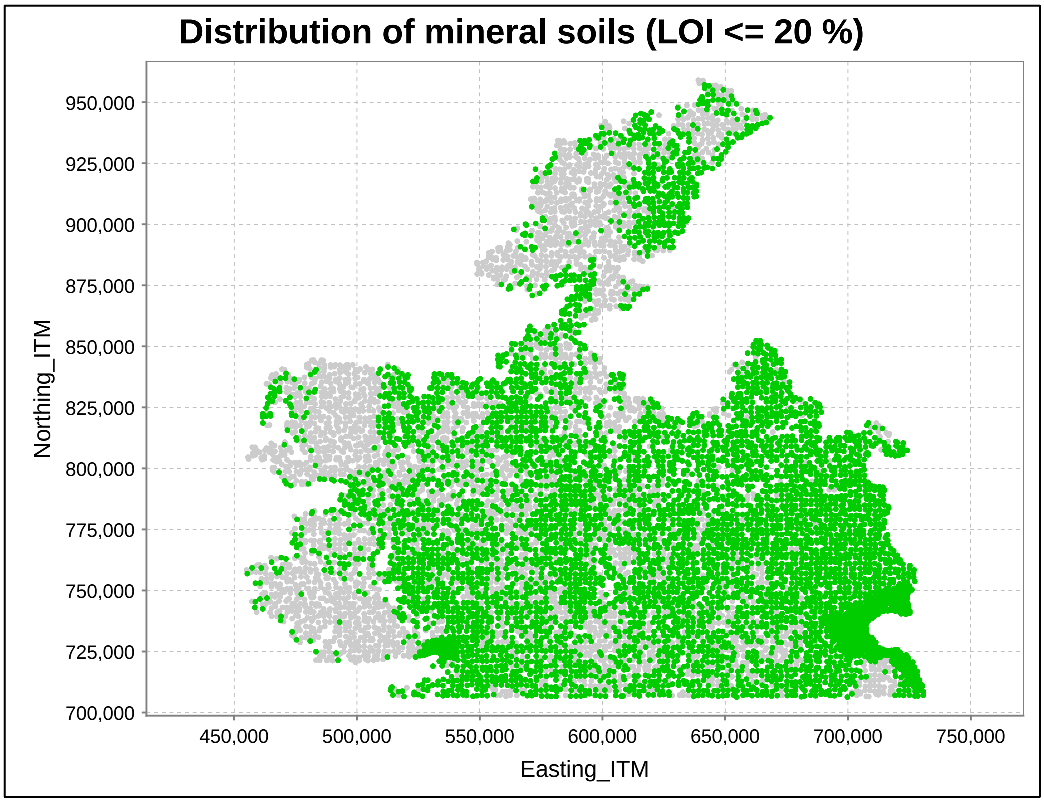
Urban soils also have relatively high concentrations of many of these elements, as well as Hg and Pb. As most of these urban soils, as classified by Corine, are also mineral soils, a similar explanation may be advanced to explain their composition. In the case of Hg and Pb, a more likely source is diffuse anthropogenic contamination, which may also contribute to the content of elements such as As, Cr, Cu, and Zn.

Apart from these urban and agricultural classes, the remaining land use classes typically have relatively low element concentrations, as measured by ICPar, and display ranges and median concentrations that reflect factors such as high OM content (coniferous forests, moors and heathland, peat bogs) or sandy soil (beaches). Exceptions are noted for Ca, for which the highest concentrations have been recorded in beach and dune sands, reflecting their content of marine shells, and Hg, for which samples with significant OM content (coniferous forests, moors and heathland, peat bogs) have a higher concentration.

As discussed previously, for those elements also analysed following extraction with M3 reagent, samples with high OM content may have the higher measured element concentration. This is particularly true for Mg_M3 but is also apparent for Fe_M3.

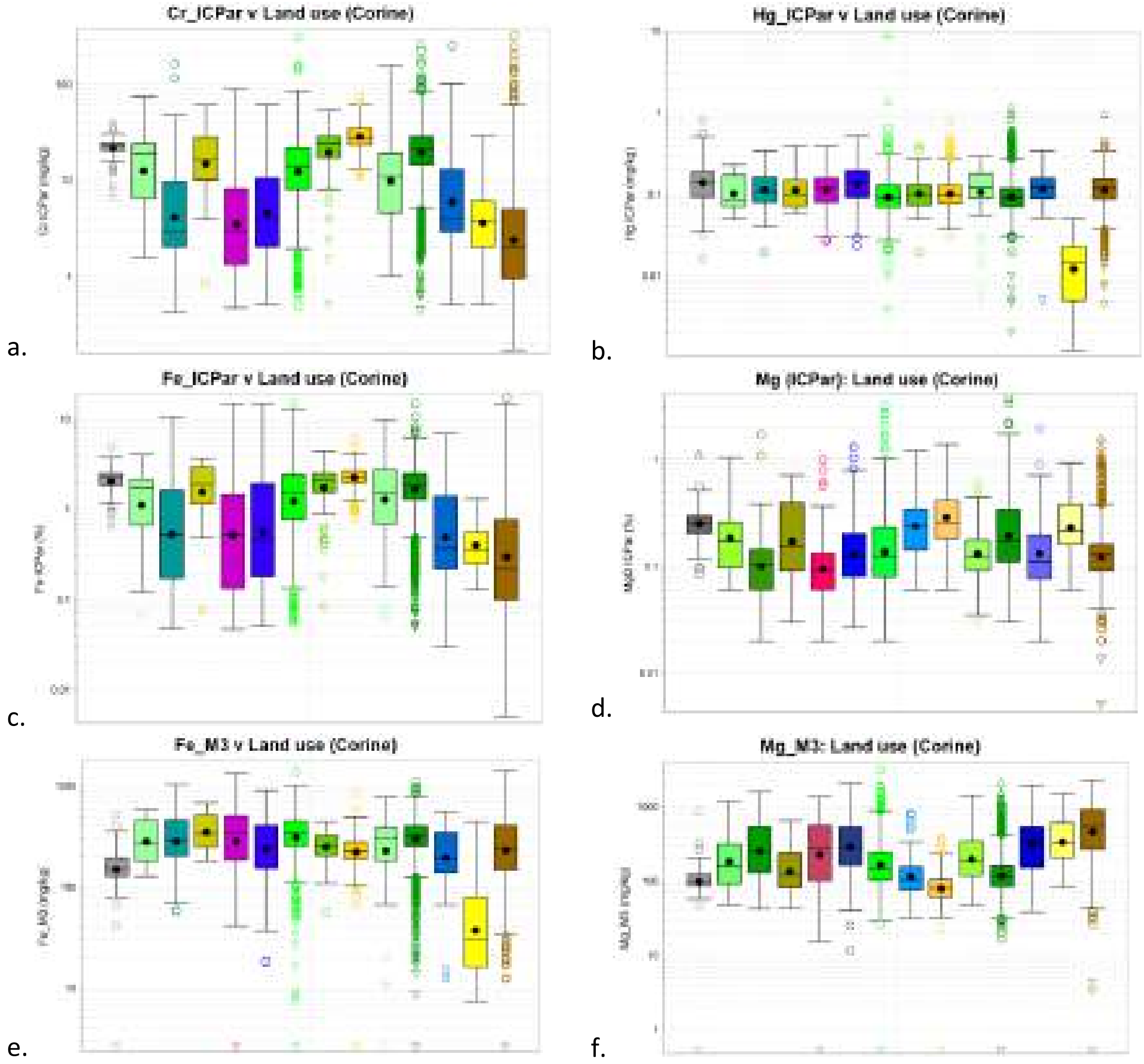


a.



b.

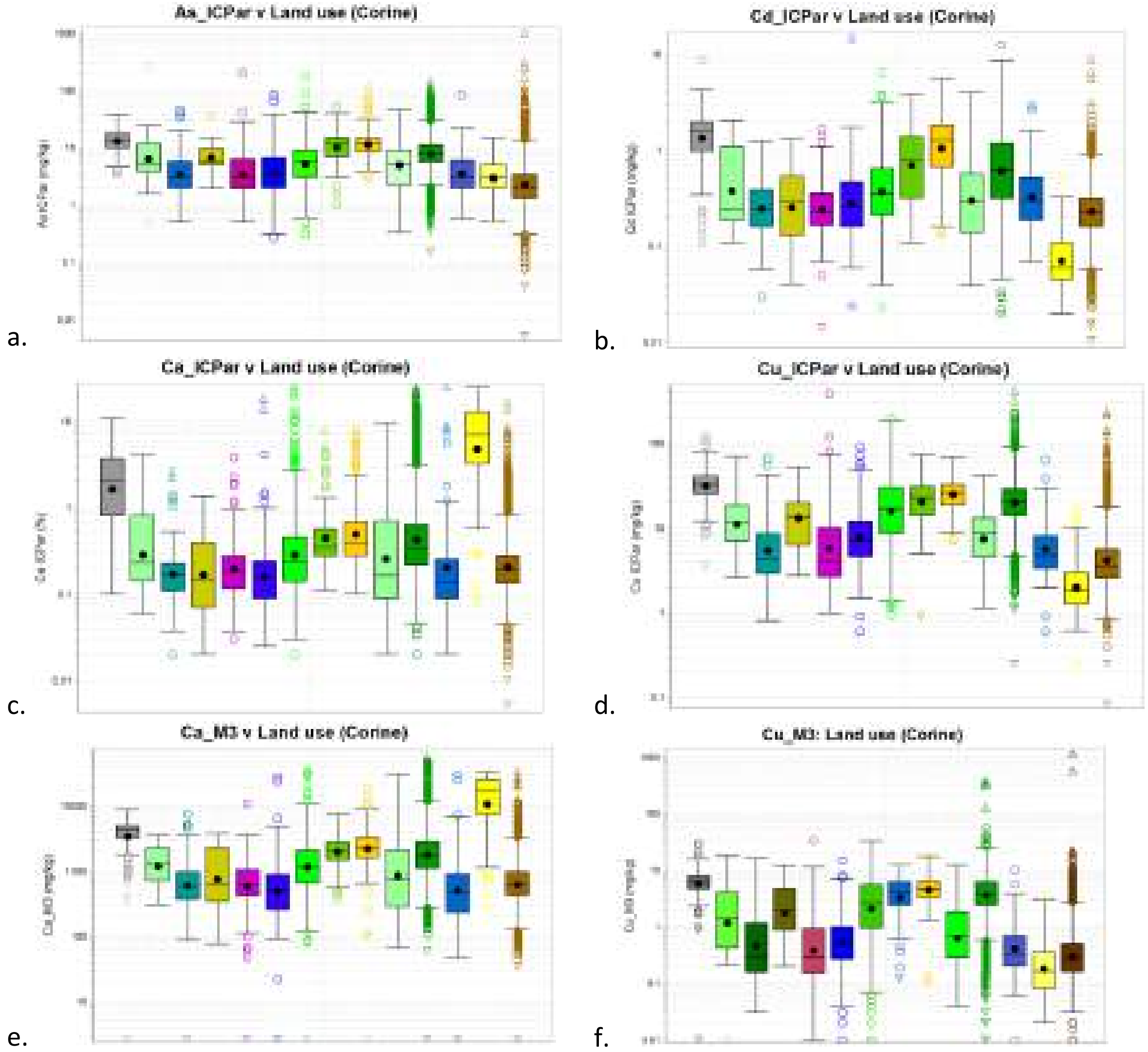
Figure 368: Maps showing the distribution of the main agricultural land classes and mineral soils in the region. The broad coincidence of these distributions is clear.



Corine 2018 class

- Discontinuous urban fabric
- Mixed forest
- Coniferous forest
- Broad-leaved forest
- Transitional woodland-shrub
- Moors and heathland
- Land mainly agriculture
- Complex cultivation patterns
- Non-irrigated arable land
- Natural grasslands
- Pastures
- Sparsely vegetated areas
- Beaches, dunes, sands
- Peat bogs

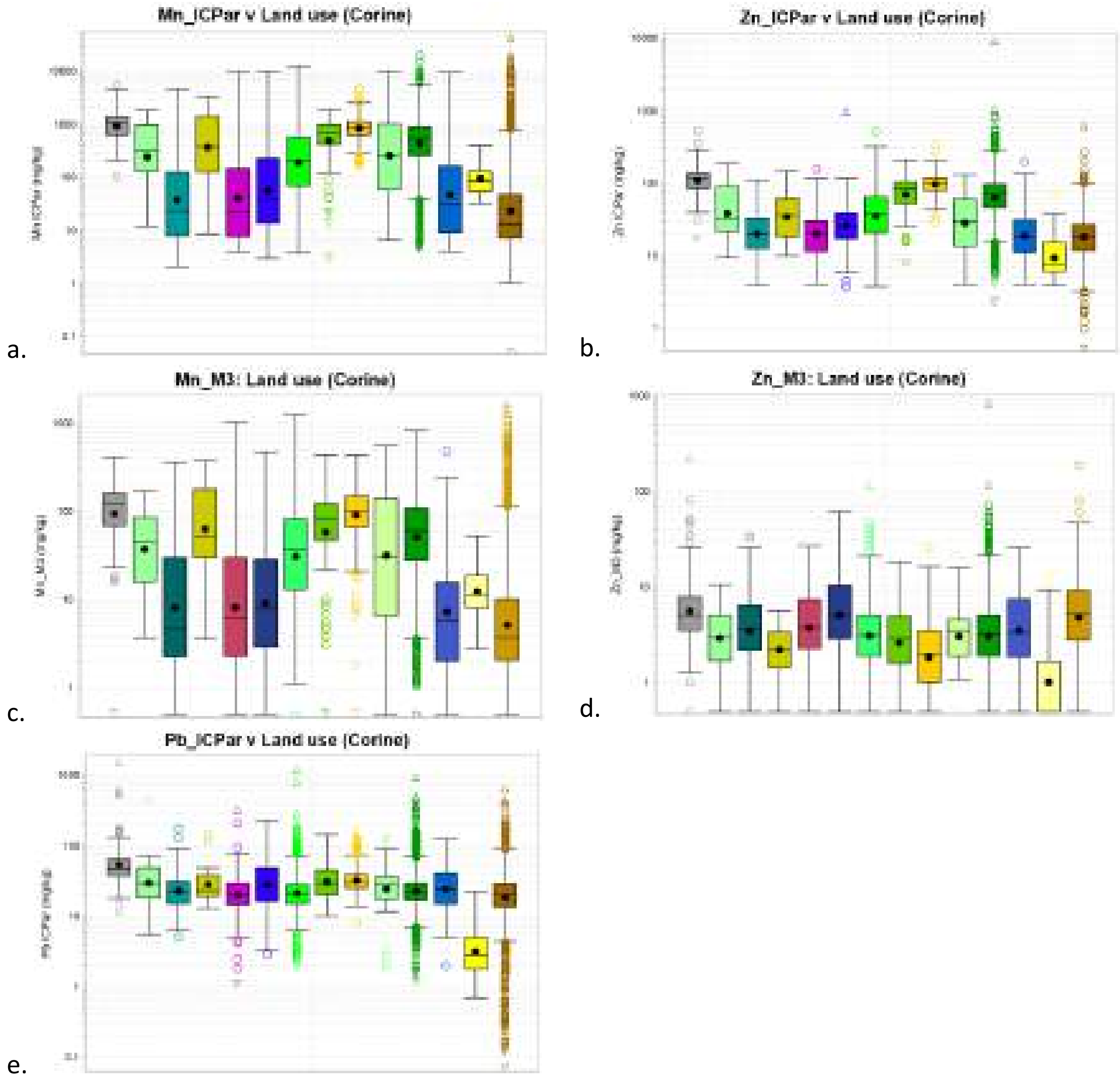
Figure 49: Cr ICPar, Hg ICPar, Fe ICPar, Mg ICPar, Fe M3, Mg M3 v Land use (Corine)



Corine 2018 class

- Discontinuous urban fabric
- Mixed forest
- Coniferous forest
- Broad-leaved forest
- Transitional woodland-shrub
- Moors and heathland
- Land mainly agriculture
- Complex cultivation patterns
- Non-irrigated arable land
- Natural grasslands
- Pastures
- Sparsely vegetated areas
- Beaches, dunes, sands
- Peat bogs

Figure 370: a. As ICPar, b. Cd ICPar, c. Ca ICPar, d. Cu ICPar, e. Ca M3, Cu M3 v Land use (Corine)



Corine 2018 class

- Discontinuous urban fabric
- Mixed forest
- Coniferous forest
- Broad-leaved forest
- Transitional woodland-shrub
- Moors and heathland
- Land mainly agriculture
- Complex cultivation patterns
- Non-irrigated arable land
- Natural grasslands
- Pastures
- Sparsely vegetated areas
- Beaches, dunes, sands
- Peat bogs

Figure 381: a. Mn ICPar, b. Zn ICPar, c. Mn M3, d. Zn M3, e. Pb ICPar v Land use (Corine)

10. Examination of other potential controls

Other potential controls on soil chemistry were considered as part of the geochemical assessments. This included particle size distribution, topography, including elevation and slope, and Pollution Impact Potential, recently developed by the Catchments Unit of the EPA.

Particle Size

The particle size distribution (PSD) of Terra Soil mineral soil samples was determined using IR spectroscopy. In theory these data should correspond, at least for clayey and sandy soils, to the ISIS soil texture data. PSD thus provides an alternative way of examining if any relationship exists between element concentrations and physical soil characteristics. The example of Ca ICPar is shown in the PSD ternary plots below, where the Ca ICPar is classified into five equal concentration bins. In practice, samples classified by five equal percentile bins largely overlap on the ternary plots. However, samples with lower Ca concentrations tend to plot closer to the “sand” vertex, suggesting a broad correlation between lower Ca concentrations and soil with less clay / silt. Note that these plots do not include the high-Ca beach / dune sands that would be expected to show an opposite trend. The remaining elements considered show a similar broad trend whereby finer particle size is associated with higher element concentrations.

Topography

Elevation and slope (degree and direction) were estimated for each sample location using a DEM. These parameters might be anticipated to have an influence on drainage, through run-off, and even the nature of the soil itself, as soil on higher ground exposed to more rain is generally more saturated and acidic. In practice, for most elements it is hard to discern any obvious correlation between element concentrations and topography. In the example of Ca below, there is a tail of high Ca values on flat ground. These appear to be essentially high-Ca samples mainly from areas of Carboniferous limestone in the midlands and *machairs* (sandy soils) around the coast. This is probably the best example of an apparent correlation between topography and element concentration, but it seems clear that this is not a causative relationship.

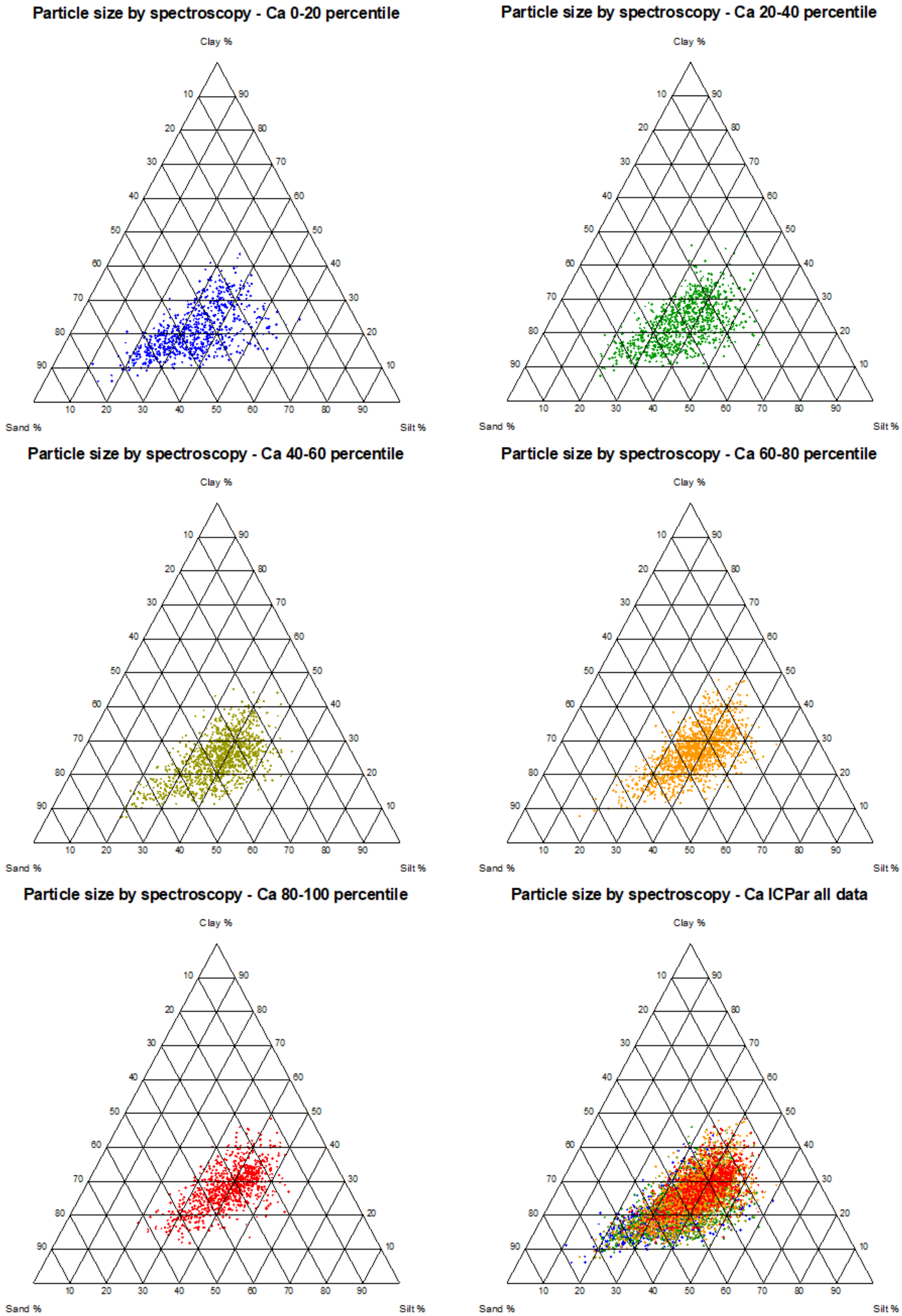


Figure 392: Particle size by spectroscopy

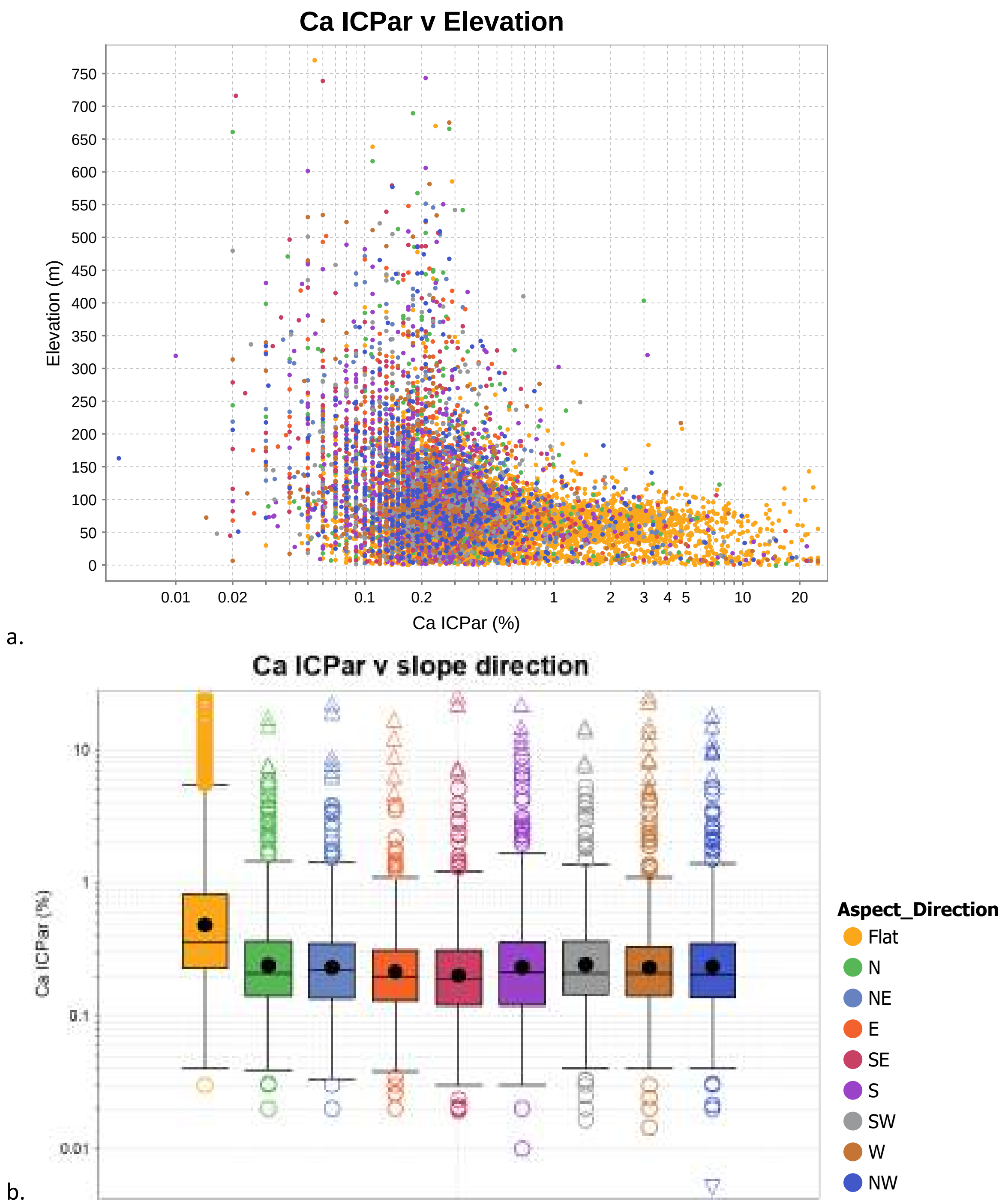


Figure 403: a. Ca ICPar v elevation, b. Ca ICPar v slope direction

Pollutant Impact Potential (PIP)

New maps published by the EPA show areas from which nutrients have a high probability of reaching a water body of interest due to the underlying hydrogeological conditions, i.e., the areas that have significant pathway linkages from the source of pollution or pressure to surface water or groundwater receptors. Susceptibility maps are generated by linking data on soils, subsoils, groundwater vulnerability and aquifer types with nutrient attenuation and transport factors. Pollutant Impact Potential maps have been produced for both P and N (PIP-P and PIP-N). The Tellus geochemical data were classified according to these maps and examined for any possible correlation.

Pollutant Impact Potential for phosphorus (PIP-P) is dependent on pollutant sources (e.g., high stocking rates, fertilizer application) and soil drainage. A high rank (1, 2 or 3) implies the highest potential for P-rich run-off and reflects a combination of high-P sources (e.g., high stocking rates) and poor drainage. In contrast, PIP-P ranks 6 and 7 should reflect well-drained soil with lower stocking rates / fertilizer application. In the example of Ca ICPar below the concentration for ranks 1, 2 and 3 is notably higher than for ranks 4 to 7, particularly ranks 4 and 5, consistent with suggestions above that high Ca is associated with agricultural land (pasture) and, thus, fertilizer application and presumably liming. The same pattern is observed for Ca_M3, albeit much more muted.

Pollutant Impact Potential for nitrogen (PIP-N) differs from that for phosphorus because N loss occurs through well-drained soils and groundwater pathways. A high rank (1, 2 or 3) implies a combination of high-N sources (e.g., high stocking rates, arable land) and good drainage. Little variation in Ca is observed across the first six PIP-N ranks but rank 7 is associated with notably lower Ca. For other elements (Cd, As, Cr) a lower concentration for PIP Rank 7 appears to be related to the predominance of peaty soil in this class and this may explain the observed pattern for Ca also.

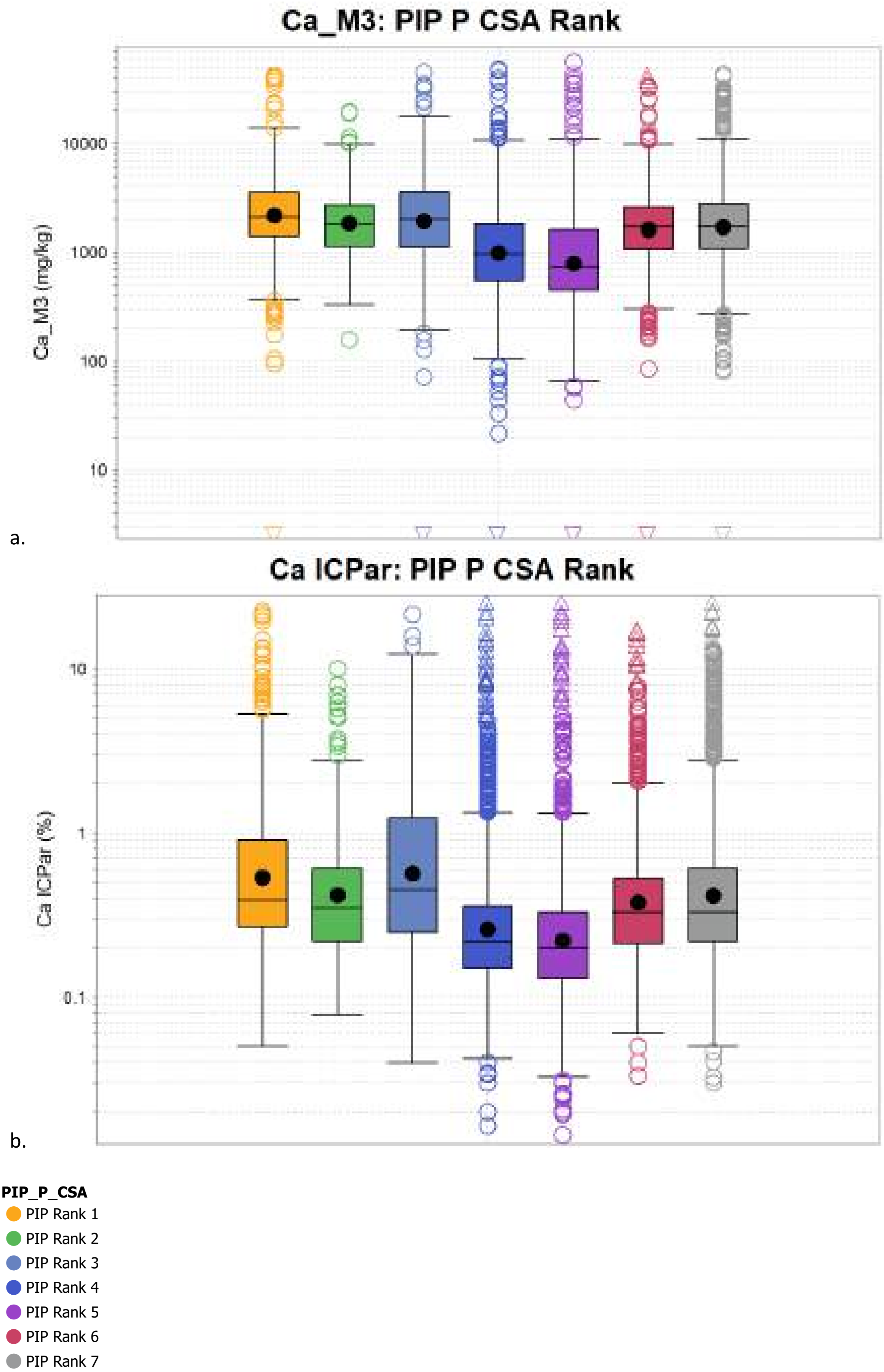


Figure 414: a. Ca M3: PIP P CSA rank, b. Ca ICPar: PIP P CSA rank

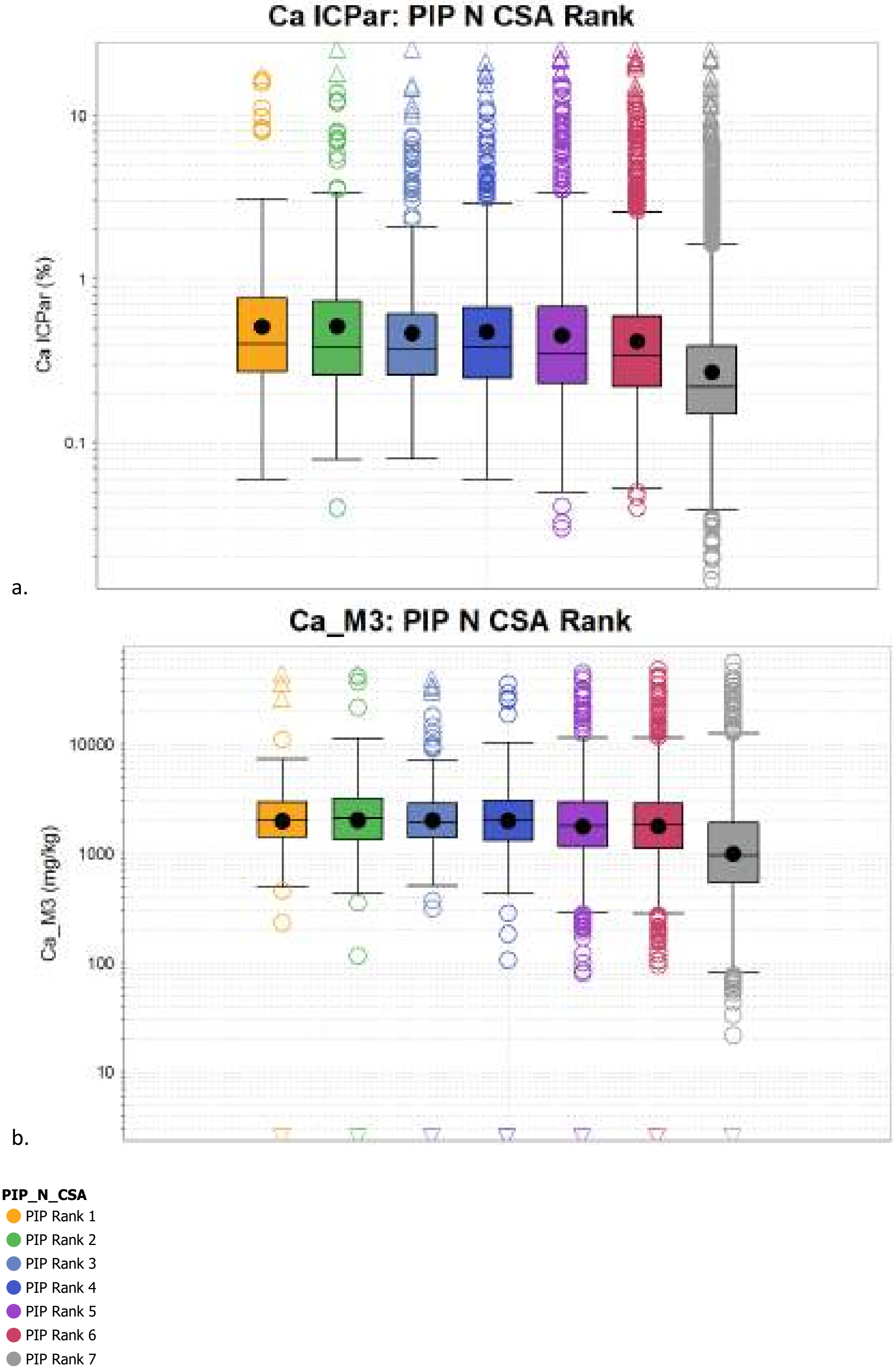


Figure 425: a. Ca ICPar: PIP N CSA rank, b. Ca M3: PIP N CSA rank

11. Conclusions

The Terra Soil project has analysed almost 10,000 soil samples, originally collected as part of GSI's Tellus Programme, for available nutrients, metals, and trace elements, following digestion by both Mehlich's 3 (Al, Ca, Co, Cu, Fe, K, Mg, Mn, P, S, Zn) and Morgan's (K, P) reagents. Spectroscopic analysis to predict texture class and particle size has also been conducted. The resulting Terra Soil data comprise a unique dataset covering the northern part of Ireland at a spatial resolution far greater than any previous agrichemical soil datasets. This has allowed detailed regional mapping of agrichemical parameters and indices to provide new insights into Ireland's soil fertility, crop and animal health, land drainage, nutrient management and farm economics.

Geochemical assessments were carried out on the Terra Soil and pre-existing Tellus data to provide an overview of the geochemistry of topsoil within the northern half of Ireland, providing a context for a wider understanding the new Terra Soil data. Attributed geochemical data were assessed using exploratory data analysis to examine patterns in the data and assess their likely causes.

In general, Tellus ICP *aqua regia* (ICPar) data demonstrate a strong geogenic signature, at least in areas of mineral soil. Areas predominantly comprising peat soils have a very attenuated geochemical signal, reflecting low absolute concentrations of elements in peat or soils with very high organic matter (OM) content. Geochemical maps generated from ICPar data typically display higher element concentrations in the midlands, where mineral soils predominate, and lower concentrations over blanket bogs in the uplands of Galway, Mayo, Donegal and Wicklow, and some raised bogs in the midlands. Mehlich's 3 (M3) data, despite the much weaker digestion involved, display similar spatial distributions to ICPar data, but only for the elements Al, Ca, Cu, Mn and S. In contrast, the elements Fe, K, Mg, Zn have spatial distributions that are essentially the opposite to those displayed by ICPar data, with relatively high M3 element concentrations present in areas of peatland. This phenomenon clearly reflects the selective nature of the M3 digestion.

Unlike *aqua regia*, in which element extraction rates are broadly similar for both mineral soils and OM-rich soils, M3 extraction rates appear to depend on the specific element concerned and the amount of OM in the soil. This, for K, Fe, Mg and Zn, the extraction rates in OM-rich soils are substantially higher than for mineral soils, giving rise to measured M3 element concentrations that are higher in areas of peat than in areas of mineral soil. The resulting geochemical maps thus appear as inverses of the corresponding ICPar maps.

The distribution of P as measured by ICPar is broadly similar to other elements, with a significant geogenic signature, mainly linked to mineral soils, and low P over OM-rich soils. However, there is also a strong positive P signature related to tillage farming, especially in north Dublin. The M3 data are broadly similar but the higher extraction rate of P in OM-rich soils means that areas of peatland show some contrast to ICPar data. Morgan's data also display relatively high values over tillage areas and OM-rich soil, but this weak extraction does not reflect the composition of mineral soils to the same degree as M3 does.

Bedrock geology, Quaternary geology and land use display the strongest association with ICPar, Mehlich's 3 and Morgan's data, with distinctive categories of soil displaying specific element compositions. For other soil attributes, a relationship between the attribute and soil chemistry is less readily established or not observed at all. Topography falls within the latter category, with elevation, slope and slope direction exerting no clear influence on soil composition.

Where some relationship appears to be present there is uncertainty as to the degree to which this reflects the specific parameter being assessed or the influence of another, overlapping parameter. An example of this is soil drainage, based on the ISIS soil map, which appears to reflect the OM content of soils. However, the mapped distribution of the "Poor" drainage class largely overlaps that of peat, as displayed on the Quaternary geology map. Soil texture classes (also based on ISIS) partly overlap specific bedrock groups or units and thus, like drainage, this parameter appears to display some correlation with chemical data.