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Tellus geochemical survey: comparison of shallow ‘A’ and deeper ‘S’ topsoil data analysed by ICP_{ar}

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Executive Summary

This report summarizes the comparison of inorganic geochemical data for shallow 'A' and deeper 'S' topsoil samples collected at the same site from locations across Ireland. The report is published along with the digital map series available as a separate download. Samples were collected as part of the Tellus geochemical survey programme of Geological Survey, Ireland. This report describes processing and interpretation of selected data acquired for shallow and deeper topsoil, denoted sample type 'A' and 'S', respectively. Summaries of sample collection, preparation and laboratory analysis are provided. Further information on survey design, quality control (QC) and quality assurance can be accessed through dedicated QC reports published separately.

In this report, data for selected elements (P, Pb, Sn, V, Zn, Ca) are shown for samples collected at 9918 sites in the northern region of Ireland and analysed by ICP MS following *aqua regia* digestion. Sample sites are distributed at a typical density of one site per 4 km^2, and together they represent a variety of geological domains in Ireland.

A comparison of data for the A and S samples show significant, if typically subtle differences between the two. The degree of observed difference between A and S samples varies according to the individual element and overall soil composition, which is largely controlled by the nature of the bedrock and the proportion of organic matter in the soil. Anthropogenic inputs to soil can also be recognized and the variation between A and S data can provide further evidence for their source.

This report is an initial examination of the variation in composition between A and S topsoil samples collected for the Tellus programme. The variations observed for a selection of samples reflect different influences on the composition of topsoil, including bedrock composition, organic matter content and anthropogenic activities. More detailed evaluation of the recorded variations in composition between the A and S topsoil data should enhance understanding of the processes that affect topsoil composition in Ireland. This preliminary examination demonstrates the value of collecting and analysing topsoil samples from different horizons in the soil profile.

All data and publications are freely available at www.gsi.ie/tellus.

Acknowledgements

Geological Survey Ireland and the Tellus geochemistry team gratefully acknowledge all contributors and contractors for their efforts towards this report and accompanying data and publications. The Tellus survey would like to acknowledge the efforts of all project partners, contractors and especially field samplers, and the kind co-operation of all landowners and stakeholders.

Disclaimer

Although every effort has been made to ensure the accuracy of the material contained in this report, complete accuracy cannot be guaranteed. Neither Geological Survey Ireland nor the authors accept any responsibility whatsoever for loss or damage occasioned, or claimed to have been occasioned, in part or in full as a consequence of any person acting or refraining from acting, as a result of a matter contained in this report.

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Table of contents

List of Figures

List of Tables

Introduction

Shallow and deeper topsoil samples are two of four sample media analysed by the Tellus program. Both topsoil horizons are analysed for major, minor and trace elements by two multi-element techniques, (i) XRFS and (ii) ICP following *aqua regia* digestion.

The analytical data received from the laboratory are first scrutinized for quality and then further processed by the Tellus team to produce a variety of outputs such as: numerical data sets, statistical summaries, map series, exploratory data sets as well as scientific outputs aimed at answering specific question, to inform policymaking or foster scientific collaboration between other agencies, education institutions and individual researchers.

As part of these efforts, this report aims to examine the degree of difference in composition between shallow (A) and deeper (S) topsoil across the northern part of Ireland. Only ICP data are considered, as XRFS data are available only for part of the study area. We employed interpolation techniques to produce ratio maps for selected elements. We also use Principal Component Analysis (PCA) to evaluate differences between both data sets as whole.

Six elements were selected for investigation: phosphorus (P), lead (Pb), tin (Sn), vanadium (V), zinc (Zn) and calcium (Ca). There was some evidence from previous reviews of Tellus data to suggest that in topsoil the first three elements may include an anthropogenic component. If so, then examination of the ratio of A and S topsoil might provide further evidence. Preliminary comparison of V in both A and S topsoil information suggested near-identical composition, and this was felt to be worth further examination. Zinc is an element that is of mineral exploration significance in the Irish midlands but is quite widely distributed and not easily related to mineralization. Finally, Ca is a major component of limestone bedrock that underlies much of the midlands region and of the topsoil derived from it. It was included in the A v S comparison to examine whether its concentration in topsoil could be related to geological or anthropogenic processes.

The A/S ratios have been mapped using raw, untransformed data and normalized data. The normalized data comprises concentration data for each element in each sample divided by the corresponding Al concentration. Al was chosen as it is a natural element of aluminosilicate minerals found in soils and does not generally have an anthropogenic source. Normalizing the data to Al should thus help to smooth out differences related to intrinsic composition of soils and help identify anthropogenic inputs.

Shallow and deeper topsoil sampling, preparation and analysis

Survey design, sample locations and preparation

The survey design is a semi ad-hoc one based on a predefined fishnet grid to create cells of 2 km by 2 km, based on even easting and northing lines on the national projection co-ordinate system Irish National Grid (Geographic Coordinate System: GCS_TM65). For this study only samples analysed and reported by Tellus via ICP_{ar} with valid results for both 'A' and 'S' horizons were included and thus total number of data points in this report might differ from total number of collected samples reported in the respective QC reports.

From each site two composite samples are collected from two depth intervals by a handheld auger:

- Shallow topsoil, horizon 'A' from depth 0.05 - 0.2 m
- Deeper topsoil, horizon 'S' from depth 0.35 – 0.5 m

In the field collected samples were placed in dedicated sample bags, sorted and pre-dried at 30°C to remove excess moisture. Sample batches were delivered from field bases to GSI where they were checked and prepared for shipment to preparatory lab. Pre analysis preparation involved steps such as: drying, disaggregation, milling and sorting to receive pulverized material consisting of 95% of particles below <32 µm. Samples were then split into aliquots for their respective analysis and sent to analytical laboratory.

Further details on the field sampling logistics, procedures, and outcomes as well as detail sample preparation can be accessed through dedicated QC reports published on the Tellus pages of the GSI website www.gsi.ie and www.tellus.ie.

Soil sample analysis

Soil samples discussed in this report were chemically analysed by the following method:

- Multi-element analysis for a range of major, minor and trace elements by ICP MS following *aqua regia* digestion ("ICP_{ar}").

Two laboratories provided analytical services for ICP analysis: SGS Minerals Services (Toronto, Canada) for the samples from the Tellus Border area and ALS Minerals Ltd. ('OMAC' Loughrea, Ireland) for the remaining areas.

Details of soil analysis conditions, concentration units, methods, lower limits of detection (LLD), upper calibration limits (UCL), lower calibration limits (LCL) and method uncertainties are available in dedicated QC reports published on GSI website (see References). Note that for the purpose of creation of continuous interpolated maps LLDs were levelled upwards for element data reported with two different LLDs.

Interpolation

Each single variable map and residual map is derived from a naïve interpolation method, Inverse Distance Weighting (IDW). The interpolation predicts new values as an inverse distance weighted average of surrounding observations, *i.e.* a predicted value will be more similar to nearby observations than to distant observations, and will not extrapolate beyond the chosen search radius range of observed values. The interpolation makes no assumptions about the vector of relationships between data points. The IDW function determines the value of a raster surface (grid cell) using a linear weighted combination set of sample points (Childs, 2004). The weighting is based on the distance of an input (sample data) point from the output cell location, therefore the greater the distance the less influence the cell has on the output value. The interpolated mapping parameters used to create map presented in this study are given in Table 1.

Interpolation type	Search radius (m)	Fixed/variable	Power distance exponent	Number of points	Output cell size (m)	Best viewed at maximum scale
Inverse distance weighted (IDW)	2000	Variable	2	8	250	1:200,000

Table 1 Tellus geochemical map series interpolation mapping parameters

The inverse distance weighted (IDW) interpolation was performed on all geochemical data (at a regional scale). These parameters were selected to account for the typical inter-sample distances across the whole survey area. Interpolated mapped images have been generated for the dataset on a *regional scale*, therefore they are not suitable to evaluate the predicted distribution at a localised scale. It is acknowledged that alternative and geostatistical interpolation techniques might be equally or more useful depending on the application and scale of use of these data.

All raster grids and interpolated maps were generated using this geodatabase in ArcGIS™ PRO 2.9.1 with Spatial Analyst toolbox. Each raster grid was symbolised in ArcMap™ and attributed to coloured classifications to match the non-parametric statistics calculated for the entire data set. Tukey boxplots were generated using iOGAS software package.

A and S Comparison: element ratios

Introduction

Data for A and S topsoil samples were merged, and the A/S ratio calculated for each element for each site. In addition, the concentration of each element for each A and S sample was normalized to its Al concentration, i.e. each element concentration was divided by its respective Al concentration to generate a new normalized element concentration. The ratios of the normalized A and S concentrations were then calculated to produce normalized A/S element ratios.

The mineral and organic matter components of soil samples can vary significantly both in amount and composition. These unknown variables can make direct comparison of the chemical composition of different soil samples potentially problematic. Normalization to an element that is considered conservative can help reduce the uncertainty arising from these unknown variables, particularly among soil samples that have a broadly similar composition, e.g. those overlying similar bedrock. For this study, Al was selected as it is a major component of silicate minerals that comprise a significant part of the clastic rocks underlying much of the region.

Not all bedrock in the region contains Al-rich minerals, limestone being an obvious example. Hence, while normalization is a potentially useful aid to comparing soil samples that share a similar origin or chemical influence, e.g. similar bedrock source, it may have limited relevance when comparing soil samples across the whole region under review, given the significantly different bedrock composition found and the presence of soils with significant organic matter content.

For both the raw and normalized data, the A/S ratios were interpolated using inverse distance weighting to produce maps showing the variation in A/S across the region. Six elements were selected for inclusion in this report as an illustration of the observed variation in composition between A and S topsoil. Phosphorus (P), lead (Pb) and tin (Sn) are elements that have been noted in previous Tellus work as likely to have an anthropogenic component and, as such, may potentially display differences between A and S topsoil. Vanadium (V) was selected as an example of an element that on examination appeared to show little variation between A and S samples. Zinc (Zn) is an important component of mineral deposits in Ireland but there appear to be multiple controls on its distribution in topsoil. It was selected to assess if Investigation of the variation in A and S topsoil composition might provide further information on these controls. Calcium (Ca) was selected as an example of a major element that is of particular significance in the midlands where the soil composition is strongly influenced by limestone bedrock.

Phosphorus (P)

Background

Figures 1 and 2 show the distribution of phosphorus (P) in shallow (A) and deeper (S) topsoil. The overall distribution is very similar in both and does not show any specific correlation with bedrock geology. Higher P values are recorded over the midlands and elsewhere where mineral soils predominate, while lower values, e.g., in the west and northwest, generally coincide with organic-rich peaty soils.

Figure 3 displays the P data for deeper (S) topsoil classified by land use (Corine 2018). Soil from land used for agriculture, especially arable land and pasture, typically has the highest recorded P concentrations while mineral-poor substrates, such as peat bogs, moors and heathland, beach sand and soils in coniferous forests, have notably lower P concentrations. This suggests that anthropogenic factors, particularly those related to agriculture, such as fertilizer application, are an important control on the distribution of P in topsoil. This suggestion is supported by Figure 4, which displays the upper 10th percentile of P data (A soils) overlaid on areas of pasture and arable land. The highest P concentrations are largely constrained within the mapped boundaries of arable and pasture land.

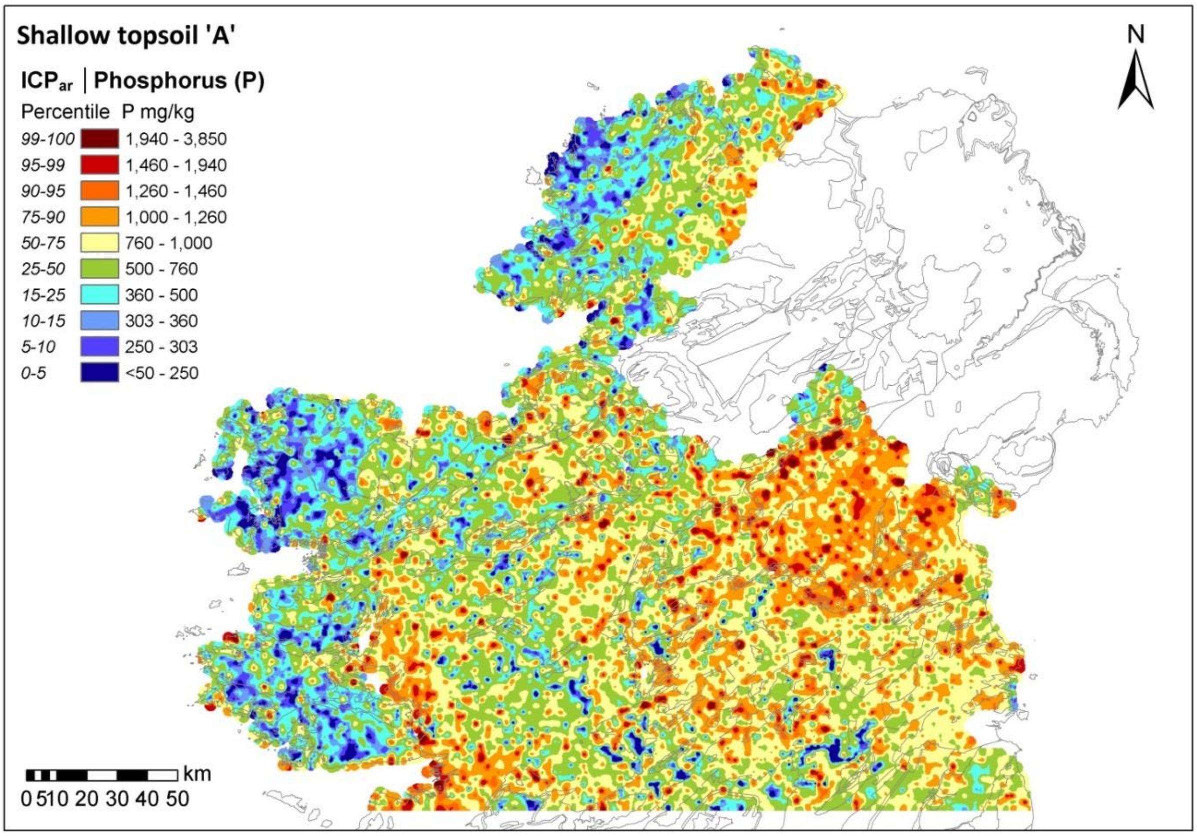

Figure 1 Distribution of P in shallow (A) topsoil.

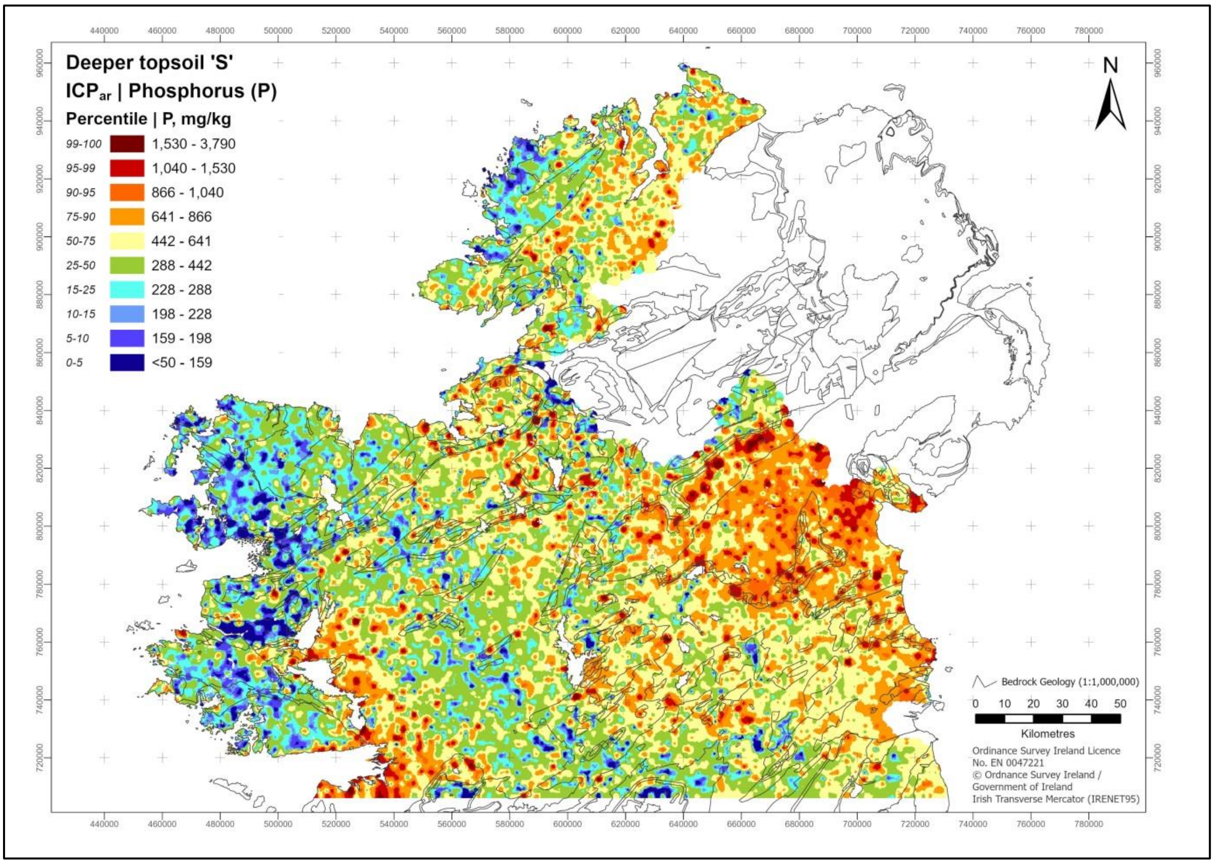

Figure 2 Distribution of P in deeper (S) topsoil.

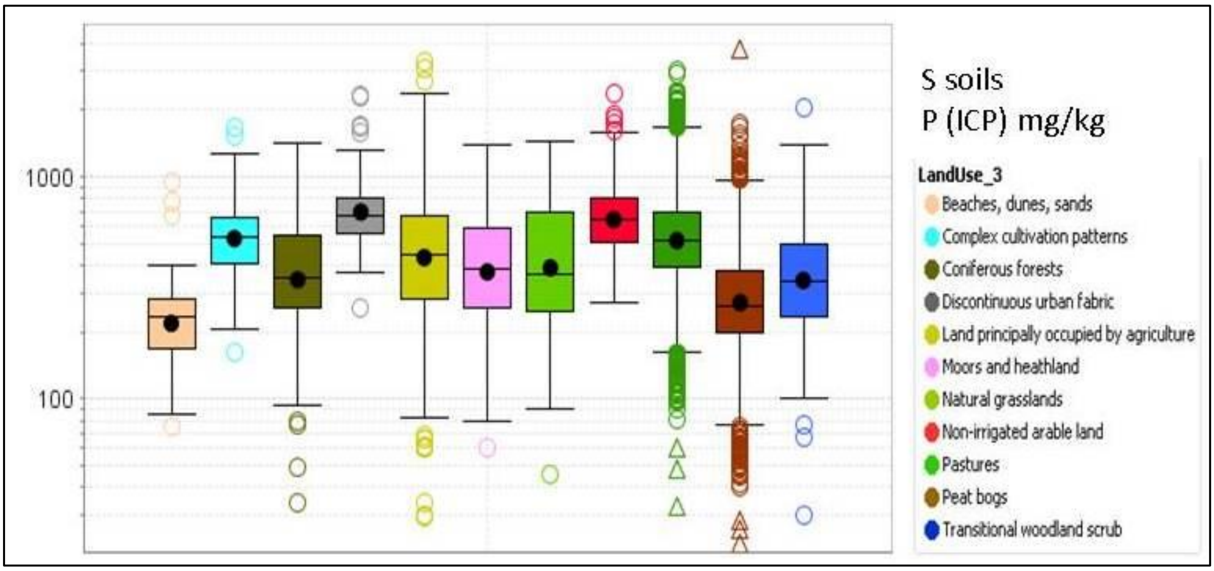

Figure 3 Tukey boxplots of P in deeper (S) topsoil, classified by land use (Corine 2018)

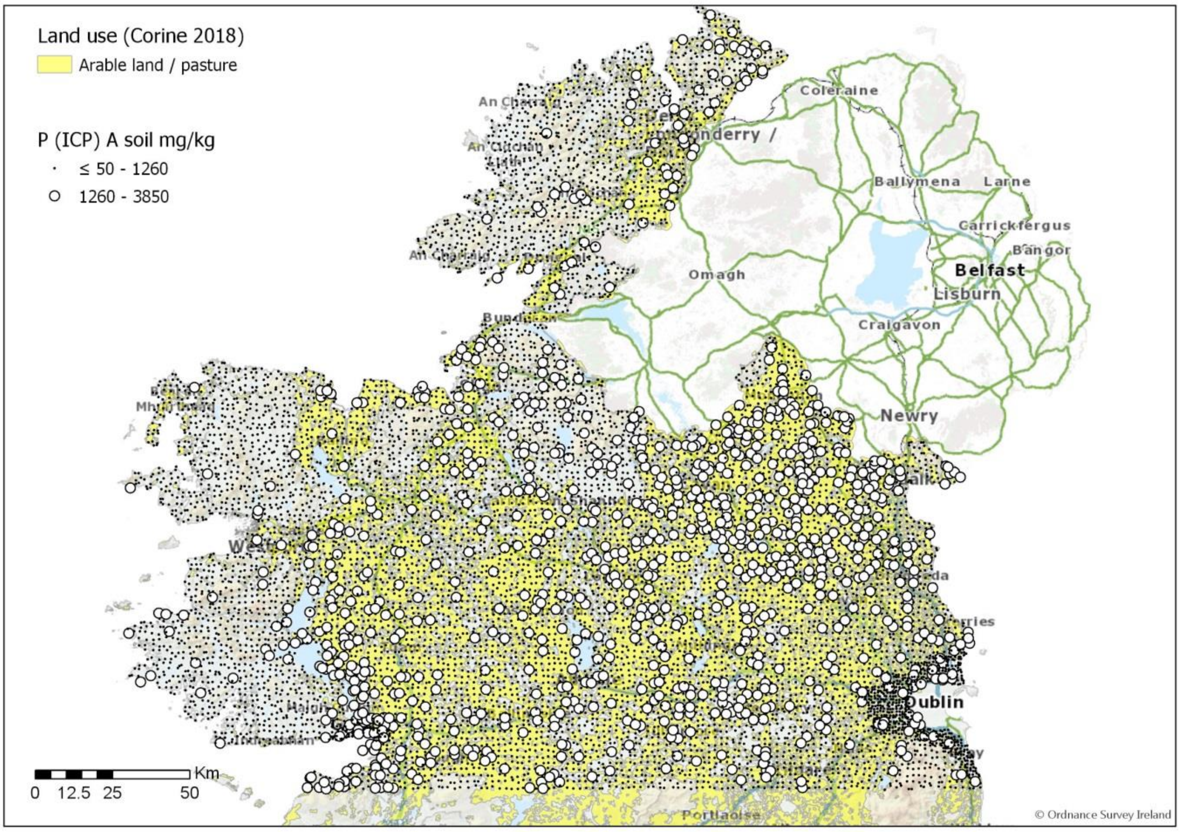

Figure 4 Pasture and arable land (Corine 2018) with phosphorus ICP point data displayed at 90th percentile cut-off

Phosphorus in A and S topsoil

Comparison of A and S soil ICP data for phosphorus, whether raw or normalized to Al, shows relative enrichment of P in the A soils (Figure 5, Table 2). Mapping of the data for the ratio of A to S shows that the concentration of P in A soils exceeds that recorded in S soils (Figure 6 and 7) over most of the study area. Normalization of the P concentrations to the Al concentration (Figure 7) does not alter the overall picture greatly, albeit the A/S ratio increases significantly in a largely proportionate way across the region. In part this occurs because A soils tend to have a higher organic content than S soils and a correspondingly lower Al content (Table 3). Normalizing A and S soils to their respective Al concentrations thus tends to increase the A/S ratio when compared to non-normalized data.

Also displayed in Figures 6 and 7 are ICP data for phosphorus in shallow (A) topsoil, shown as points with a cut-off value at the 90^{th} percentile. As shown also in Figure 4, these data emphasize that the highest recorded P concentrations are clustered in the midlands over productive agricultural land. However, the highest recorded P concentrations do not necessarily coincide with the highest A/S values for P, suggesting that factors other than anthropogenic inputs also contribute to the difference in recorded A and S soil P concentrations. Factors could include fixation of P by organic matter. Since A soils typically have a higher organic content than S soils, this process will lead to a relative increase in A/S ratios for P in areas of peat bogs, as suggested in Figure 8.

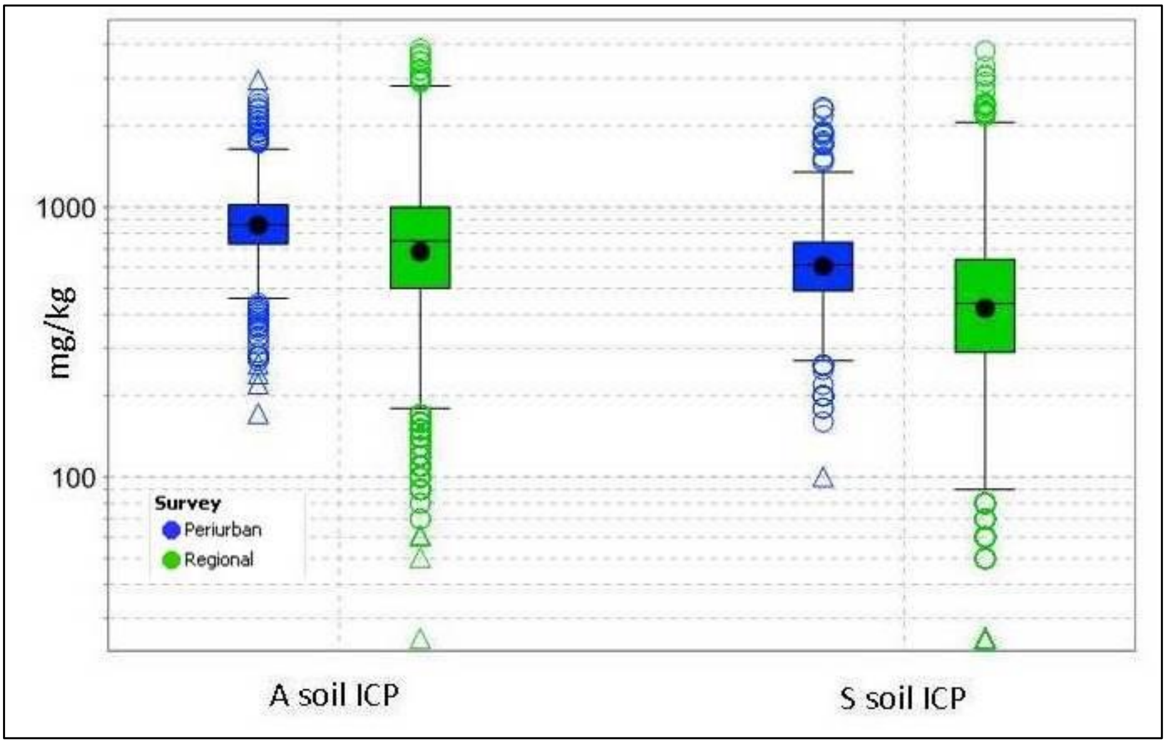

Figure 5 Tukey boxplots of P data (ICP, raw data) for A and S soil, classified by survey type

P (ICP), mg/kg	All data (n=9920)		Regional samples (n=9217)		Periurban samples (n=703)	
	A	S	A	S	A	S
Minimum	<50	<50	<50	<50	170	100
25th percentile	520	293	500	290	730	490
50th percentile	770	450	750	440	860	610
75th percentile	1000	650	1000	640	1020	740
Maximum	3850	3790	3850	3790	2940	2340

Table 2 Summary statistics for phosphorus ICP analyses in A and S topsoil

Al v LOI	LOI %		Al % (ICP)	
	A	S	A	S
Minimum	0.63	0.3	0.005	0.27
25th percentile	9.7	4.5	0.37	0.47
50th percentile	14.6	7.13	0.97	1.13
75th percentile	56.5	34.6	1.42	1.65
Maximum	99.9	100	9.27	7.67

Table 3 Summary statistics for Al and LOI in A and S topsoil

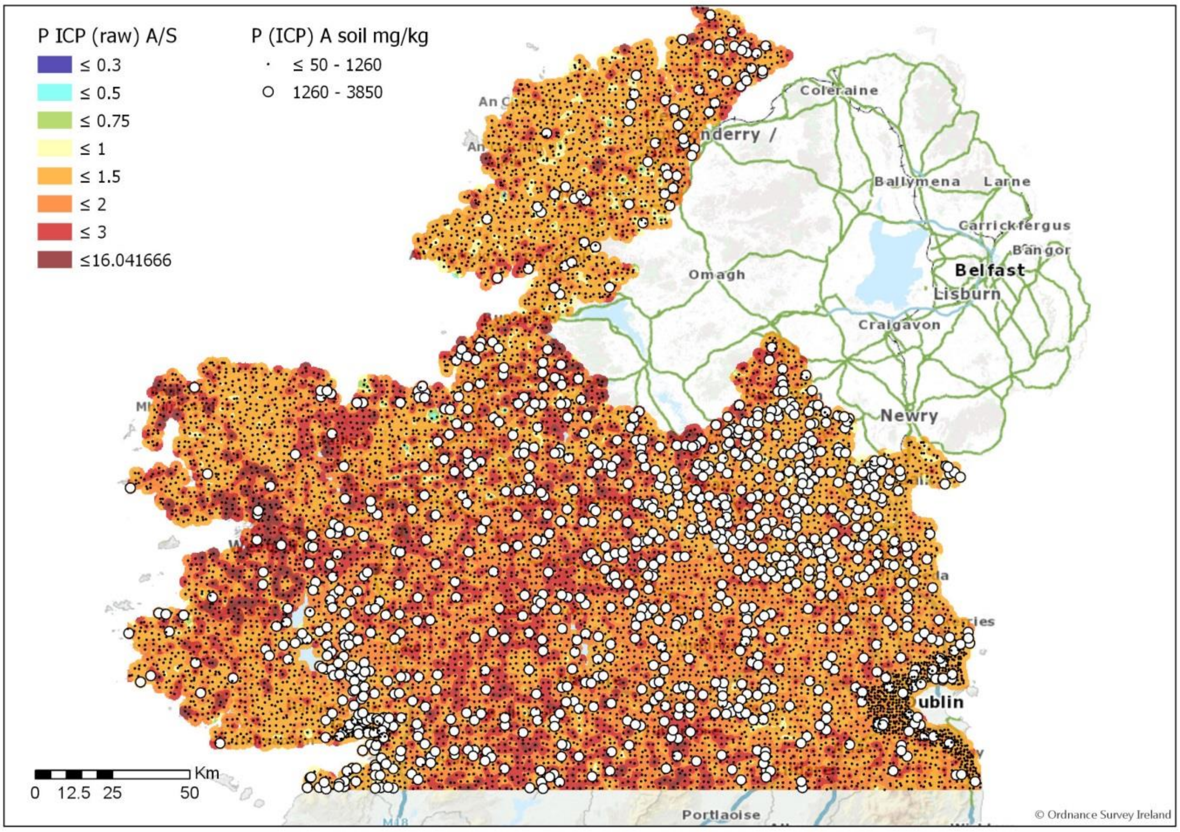

Figure 6 Ratio of P in A and S topsoil (non-normalized raw ICP data); point data displayed at 90th percentile cut-off.

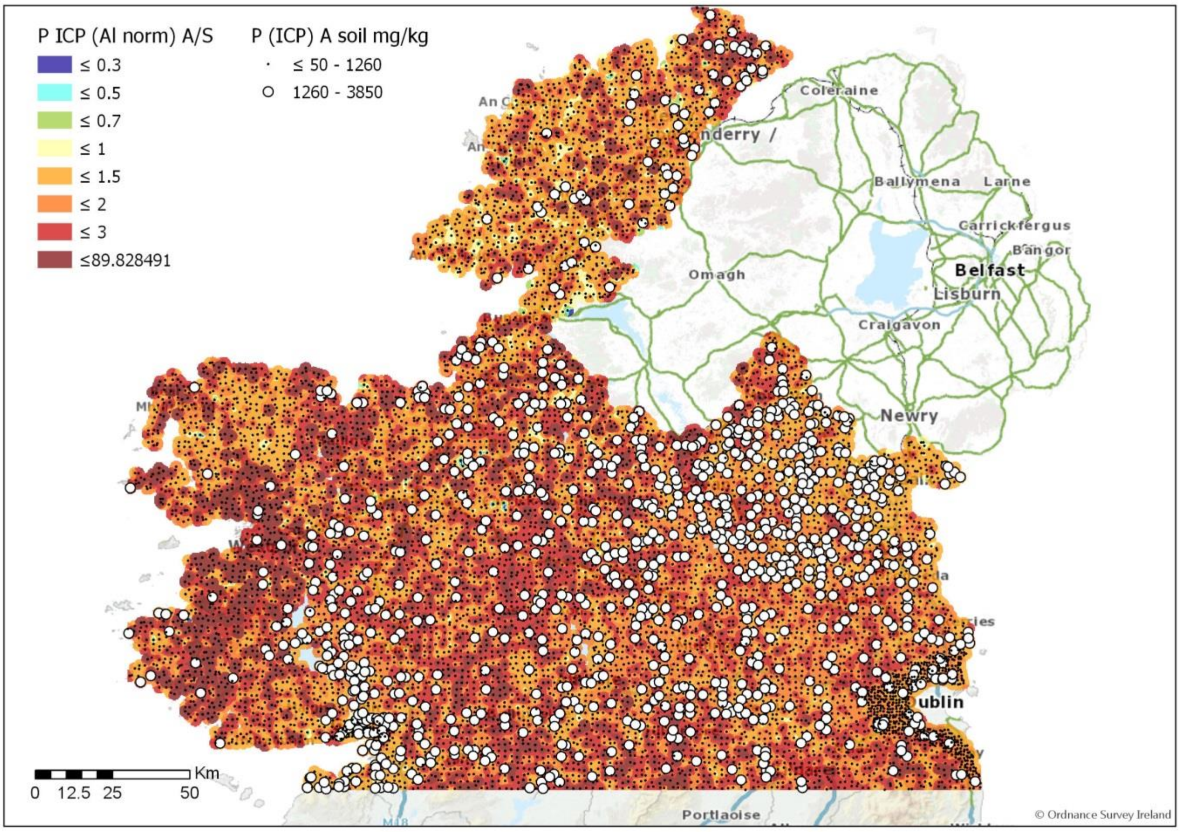

Figure 7 Ratio of P in A and S topsoil (ICP data normalized to Al concentration); point data displayed at 90th percentile cut-off.

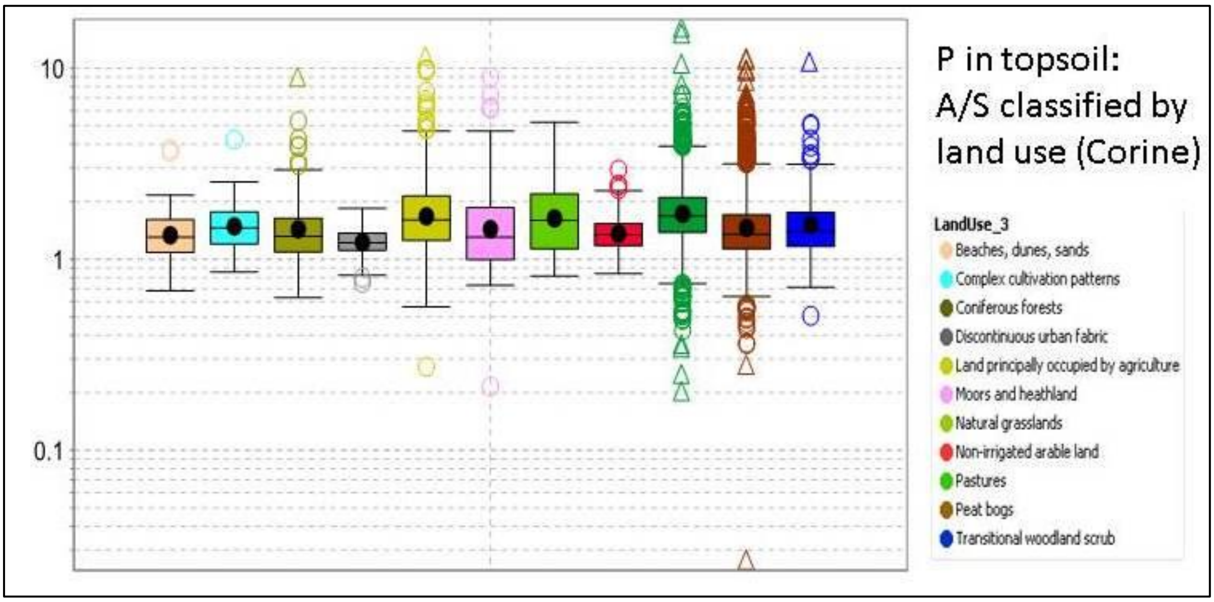

Figure 8 Tukey boxplots of A/S ratio of P in topsoil, classified by land use (Corine 2018)

Summary

Classification of topsoil data according to land use suggests that anthropogenic factors, notably agricultural practices, play a significant role in determining bulk P contents of soil. Recorded phosphorus concentrations in shallower (A) topsoil are generally higher than those for deeper (S) topsoil, across the entire region. Spatial patterns of A/S ratios for P are broadly consistent with the overall distribution of P in the region, suggesting that the excess of P in A soils relative to S soils largely reflects addition of P in fertilizer to the surface of the soil. However, detailed examination of local areas is required to determine the precise controls on A/S ratios in a given location.

Lead (Pb)

Background

Figures 9 and 10 show the distribution of lead (Pb) in shallow (A) and deeper (S) topsoil. The overall distribution is very similar in both. The observed distribution of Pb reflects several distinct controls: bedrock geology, including mineralization, distribution of organic-rich soils, including peat, and anthropogenic factors. Bedrock control is displayed by the generally higher concentrations of Pb observed in regions underlain by clastic and crystalline rocks, such as the Lower Palaeozoic greywacke of the Longford-Down inlier, the Dalradian metasediments of Donegal and the clastic sediments, including shale, of the Lower Carboniferous in the eastern midlands. Mineralization signatures are apparent throughout the region but are especially strong in east Monaghan (minor 19th-century Zn-Pb mines) and southeast Galway (Tynagh mine). The low Pb concentrations observed over much of Connemara, west Mayo, west Donegal and the northwest-southeast-trending "corridor" in east Mayo, Roscommon and east Galway can be related to peat and organic-rich soil, in which the mineral content and absolute Pb concentrations are typically very low. Anthropogenic inputs are most obvious in the Dublin and Galway periurban areas.

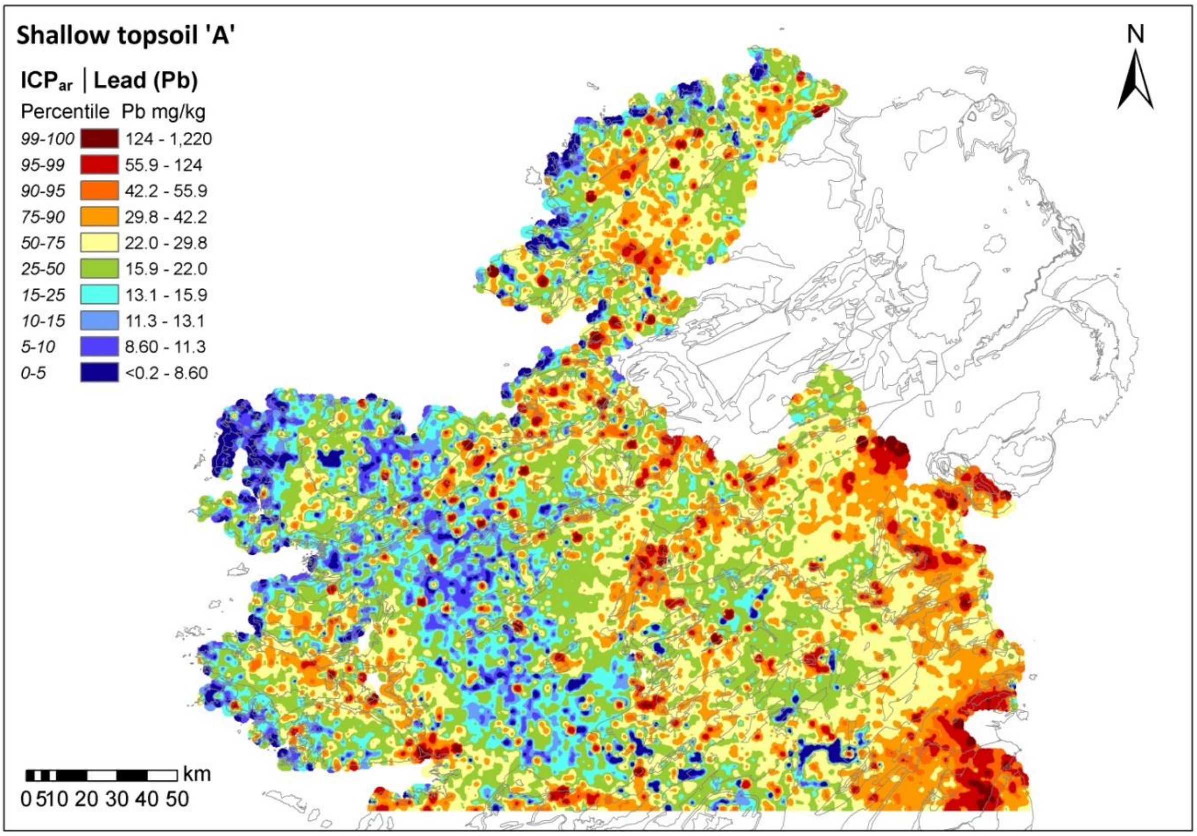

Figure 9 Distribution of Pb in shallower (A) topsoil.

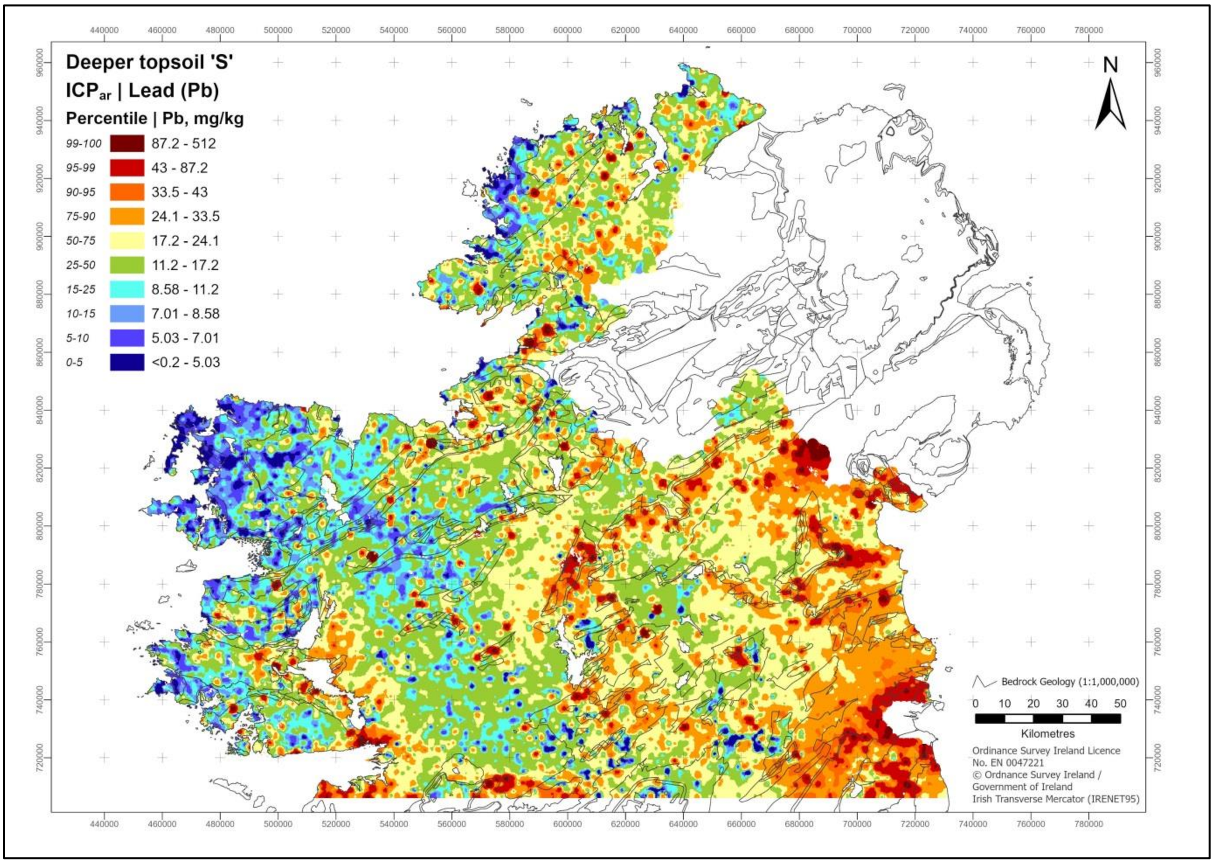

Figure 10 Distribution of Pb in deeper (S) topsoil.

Figure 11 displays boxplots of the Pb data for S topsoil classified by land use (Corine 2018). Soil samples from land classed as discontinuous urban fabric have notably higher Pb than other classes, which, except for beach sands, have broadly similar interquartile ranges of Pb concentrations. The high Pb in the discontinuous urban fabric class is largely consistent with the distribution observed on the map (Figure 9), where the highest Pb tends to correspond to the urban areas around Dublin and Galway. The low Pb concentrations mapped in the west and northwest are reflected in the large number of negative outliers observed for the peat classification.

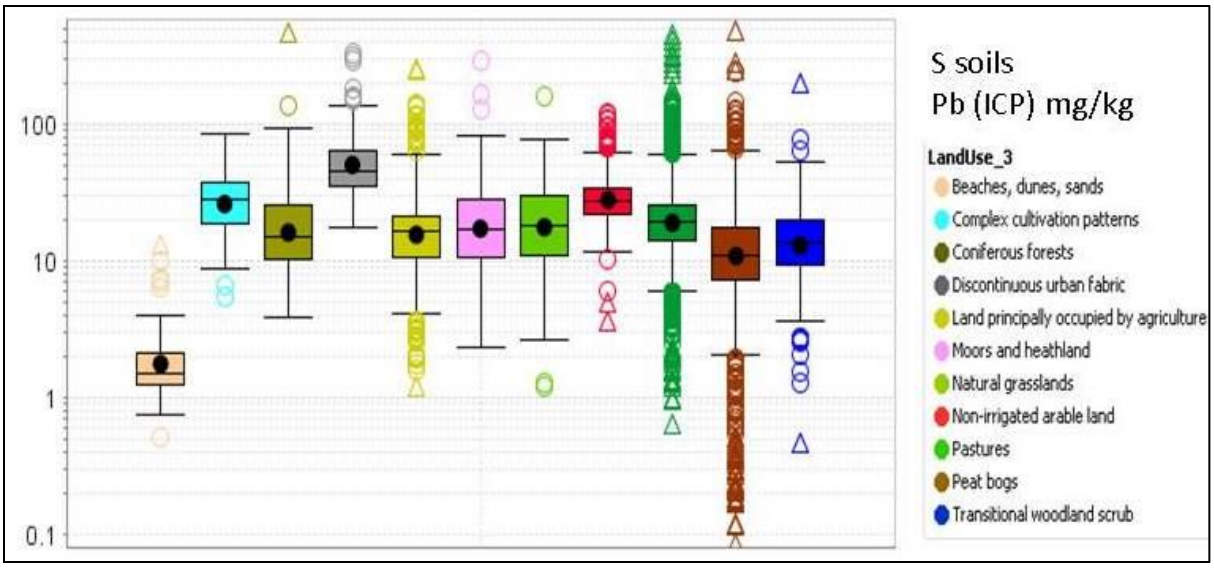

Figure 11 Tukey boxplots of Pb in deeper (S) topsoil, classified by land use (Corine 2018)

Lead in A and S topsoil

Comparison of A and S soil ICP data for lead, whether raw or normalized to Al, shows a small relative enrichment of Pb in the A soils (Figure 12, Table 4). Mapping of the data for the ratio of A to S shows that the concentration of Pb in A soils exceeds that recorded in S soils (Figures 13 and 14) over most of the study area.

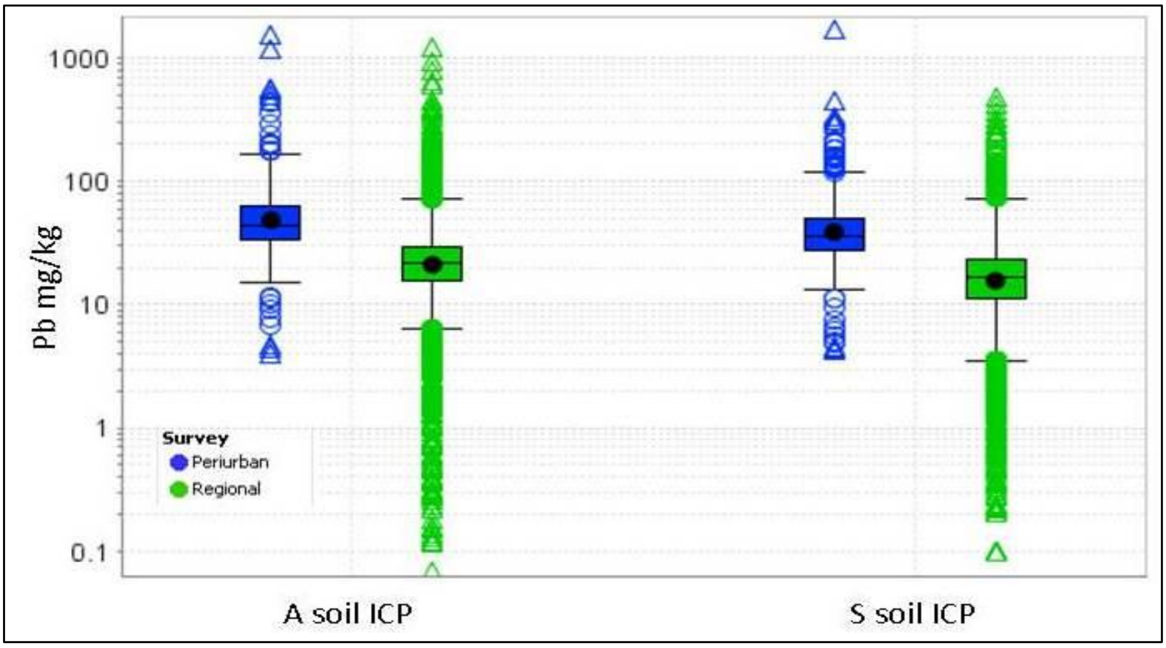

Figure 12 Tukey boxplots of Pb data (ICP raw data) for A and S topsoil, classified by survey type

Normalization of the Pb concentrations to the Al concentration (Figure 14) does not alter the overall picture greatly, albeit the A/S ratio is increased significantly, in a largely proportionate way, across the region. In part this occurs because A soils tend to have a higher organic content than S soils and a correspondingly lower Al content (Table 4). Normalizing A and S soils to their respective Al concentrations thus tends to increase the A/S ratio when compared to non-normalized data. Common to both raw and normalized data distributions is the observation that areas dominated by organic-rich soils and peat, notably blanket bog, have the highest A/S ratios for Pb.

Pb (ICP), mg/kg	All data (n=9920)		Regional samples (n=9217)		Periurban samples (n=703)	
	A	S	A	S	A	S
Minimum	0.068	0.1	0.068	0.1	3.96	4.28
25th percentile	16.2	11.5	15.8	11.05	33.5	27.6
50th percentile	22.6	17.8	21.8	17.0	44.1	36.1
75th percentile	31.3	25.4	29.1	23.6	63.8	49.8
Maximum	1540	1715	1230	485	1540	1715

Table 4 Summary statistics for Pb ICP analyses in A and S topsoil

This is apparent in Figures 13 and 14 in west Galway, northwest Mayo, west Donegal and the Dublin-Wicklow mountains. This suggests that fixation of metals by organic matter may play a significant role in determining Pb concentrations in at least some soils. Figure 15 shows boxplots of the A/S ratio for Pb classified by land use (Corine 2018).

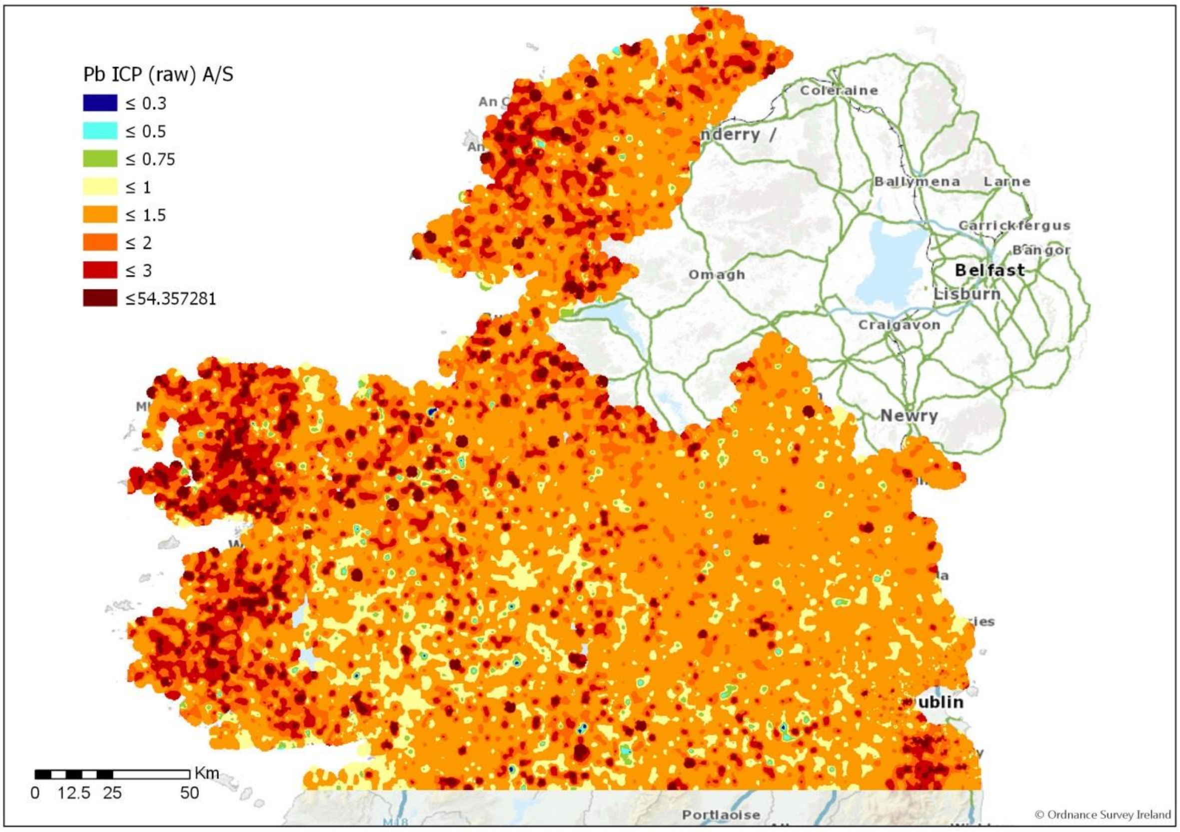

Figure 13 Ratio of Pb in A and S topsoil (non-normalized raw ICP data).

These appear to confirm the association between areas dominated by peat and higher Pb concentrations in shallow topsoil compared to deeper topsoil. The A/S ratios for Pb are generally highest in areas where topsoil has significant organic matter content, such as peat bogs, moorland, and woodland. They are lowest in areas of pasture, arable land, and discontinuous urban fabric where topsoil is typically mineral-rich with limited organic matter content, so that fixation by organic matter is likely to be of limited importance.

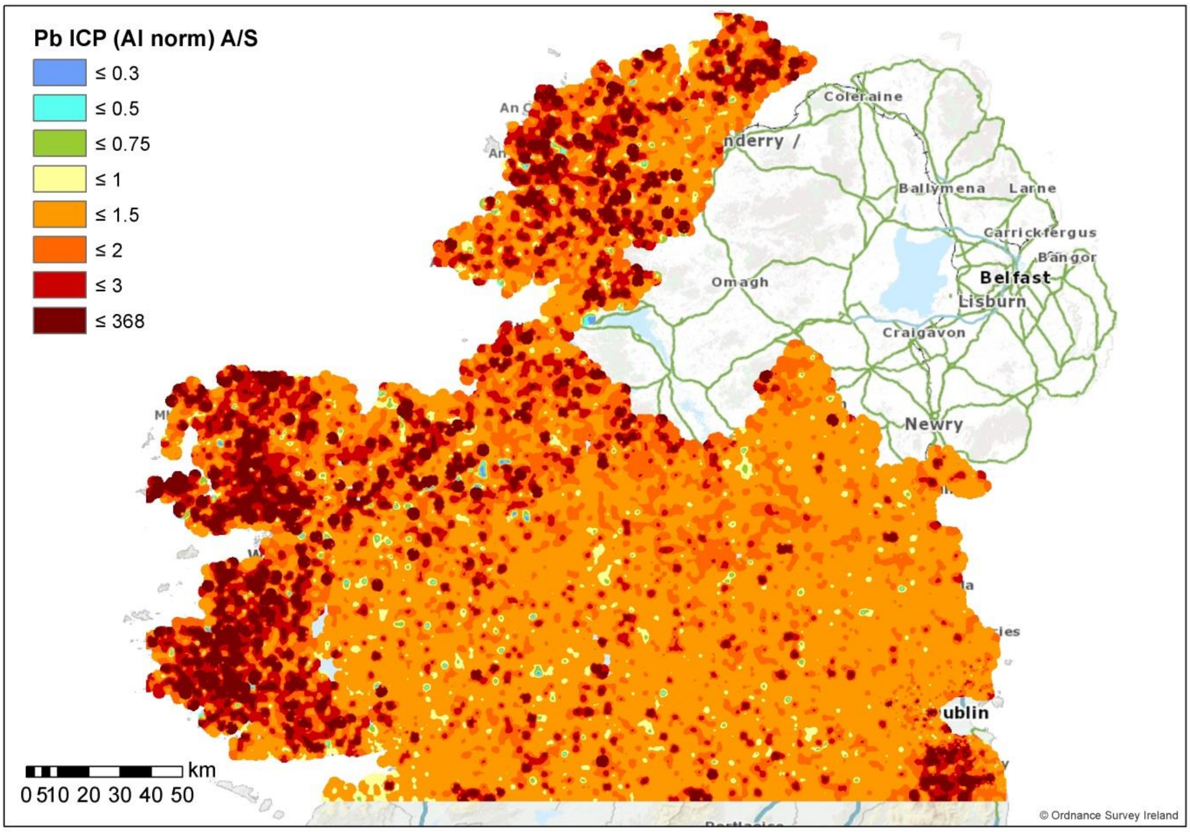

Figure 14 Ratio of Pb in A and S topsoil (ICP data normalized to Al concentration).

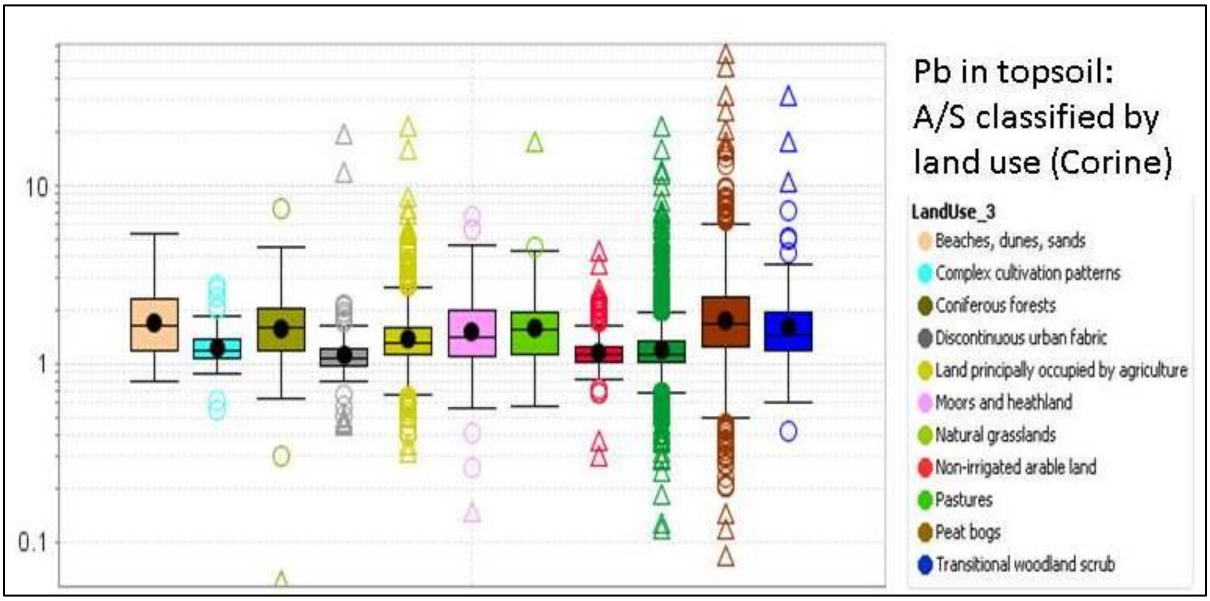

Figure 15 Tukey boxplots of A/S ratio of Pb in topsoil, classified by land use (Corine 2018).

Thus, in areas dominated by mineral soil, e.g. the periurban areas of Dublin and Galway, topsoil in which the Pb concentration is significantly higher in the upper part of the soil profile is more likely to reflect diffuse anthropogenic contamination.

Summary

Comparison of shallow and deeper topsoil Pb data indicate that shallower topsoil typically has a higher concentration of Pb than deeper topsoil. In part this may be ascribed to fixation of Pb by organic matter, which is generally more abundant in shallower topsoil. In areas where soil is mineral-rich, diffuse anthropogenic contamination may play be responsible for the observed difference between shallow and deeper topsoil, especially in periurban areas.

Tin (Sn)

Background

Figures 16 and 17 show the distribution of tin (Sn) in shallow (A) and deeper (S) topsoil. The overall distribution is very similar in both. It broadly reflects bedrock geology in that high Sn concentrations typically occur over areas of clastic or crystalline bedrock, such as the Longford-Down Inlier and Dalradian metasediments of east Donegal. High Sn is also a feature of topsoil in the Dublin and Galway periurban areas – in the former, Sn concentrations are highest in areas closest to the city. More generally, high Sn concentration in topsoil is associated with towns and villages throughout the study area, giving rise to point ("bull's eye") anomalies. The presence of peat or organic-rich soil also exerts a considerable influence of the observed distribution: areas of low Sn in northwest Mayo, west Donegal, Connemara and in the northwest-southeast Mayo-Roscommon-Galway corridor of the west midlands coincide with areas of blanket and raised bogs.

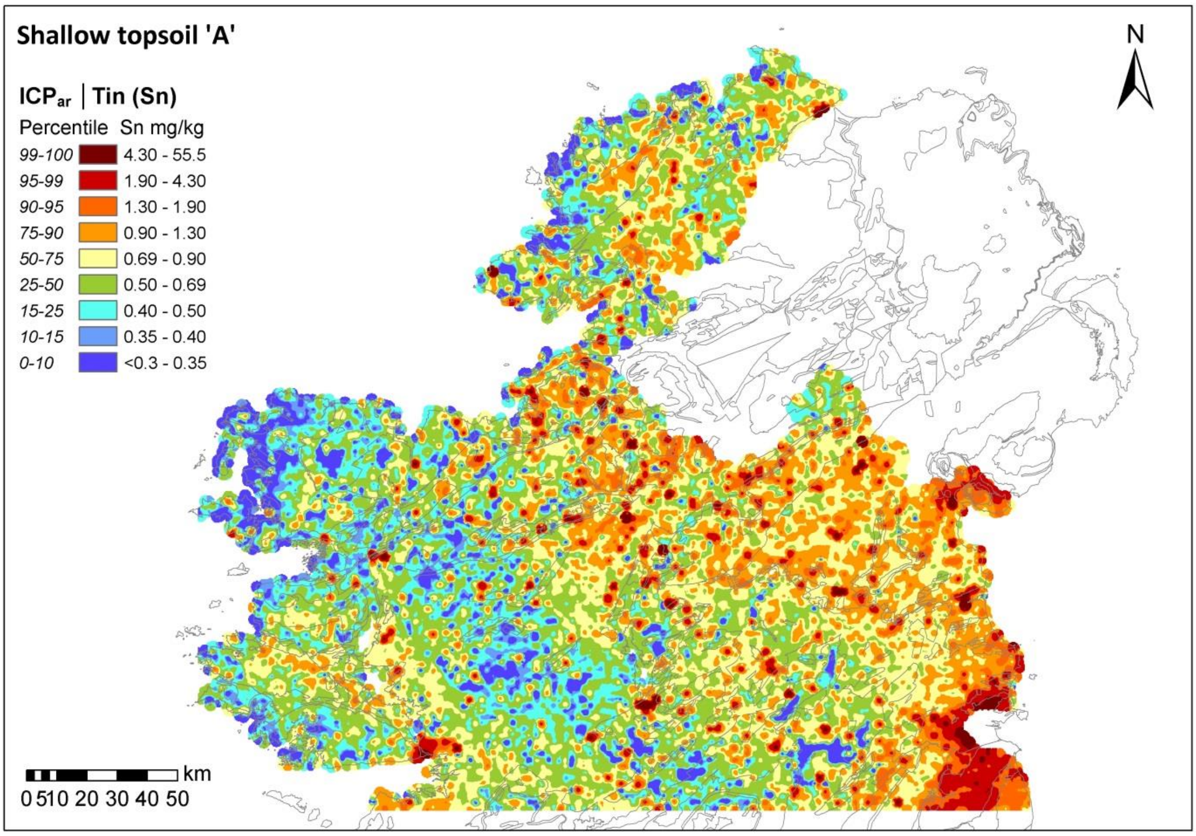

Figure 16 Distribution of Sn in shallower (A) topsoil

Figure 18 displays the Sn data for S topsoil classified by land use (Corine 2018). Soil samples from land classed as discontinuous urban fabric have notably higher Sn than other classes. The high Sn in the discontinuous urban fabric class is largely consistent with the distribution observed on the map (Figures 16 and 17), where the highest Sn tends to correspond to the urban areas around Dublin and Galway, with numerous positive Sn anomalies also associated with towns and villages. The low Sn concentrations mapped in the west and northwest are reflected in the lower median concentration and the large number of negative outliers observed for the peat classification.

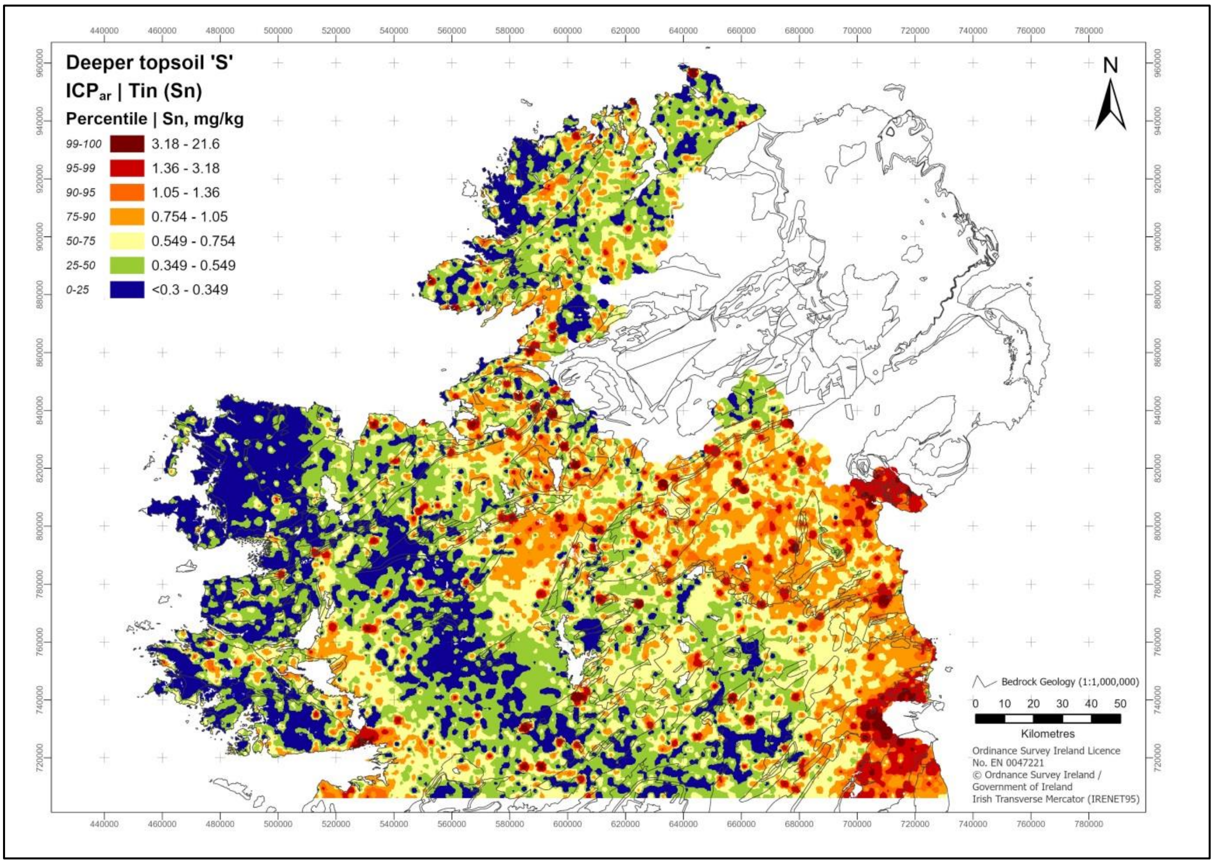

Figure 17 Distribution of Sn in deeper (S) topsoil

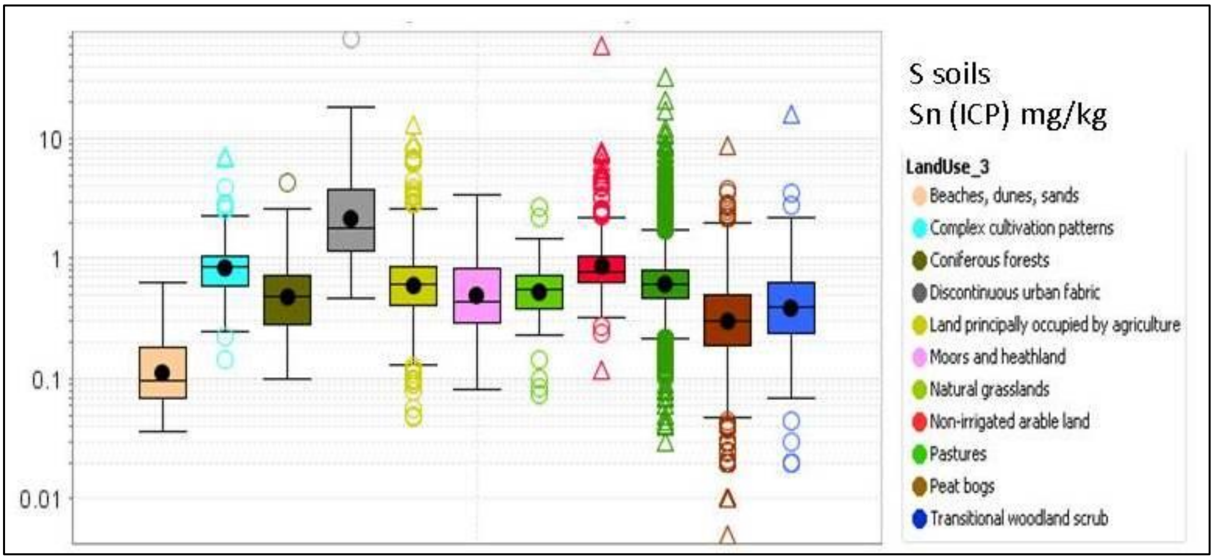

Figure 18 Tukey boxplots of Sn in deeper (S) topsoil, classified by land use (Corine 2018)

Tin in A and S topsoil

Comparison of A and S topsoil ICP data for tin, whether raw or normalized to Al, indicates a small relative enrichment of Sn in the A soils (Figure 19, Table 5). Mapping of the raw data for the ratio of A to S shows that the concentration of Sn in A soils exceeds that recorded in S soils (Figure 20) over most of the study area. Normalization of the Sn concentrations to the Al concentration (Figure 21) does not alter the overall picture greatly, albeit the A/S ratio is increased significantly, in a largely proportionate way, across the region. In part this appears to reflect the fact that A soils tend to have a higher organic content than S soils and a correspondingly lower Al content (Table 3). Normalizing A and S soils to their respective Al concentrations thus tends to increase the A/S ratio when compared to non-normalized data. Common to both raw and normalized data distributions is the observation that areas dominated by organic-rich soils and peat, notably blanket bog, have the highest A/S ratios for Sn. This is apparent in Figures 20 and 21 in west Galway, northwest Mayo, west Donegal and the Dublin-Wicklow mountains. This suggests that fixation of metals by organic matter may play a significant role in determining Sn concentrations at least in some soils. Figure 22 shows boxplots of the A/S ratio for Sn classified by land use (Corine 2018).

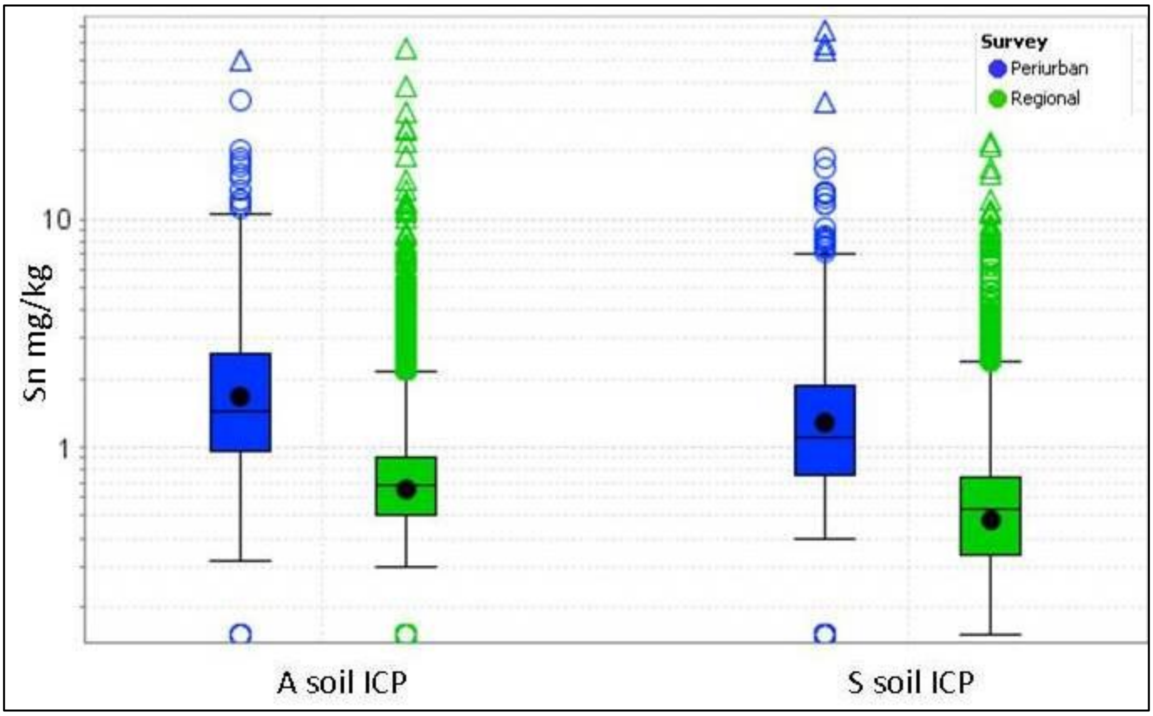

Figure 19 Tukey boxplots of Sn data (ICP raw data) for A and S topsoil, classified by survey type

Sn (ICP), mg/kg	All data (n=9920)		Regional samples (n=9217)		Periurban samples (n=703)	
	A	S	A	S	A	S
Minimum	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
25th percentile	0.50	0.36	0.50	0.34	0.97	0.76
50th percentile	0.70	0.56	0.68	0.54	1.43	1.10
75th percentile	0.95	0.78	0.90	0.74	2.56	1.87
Maximum	55.5	67.1	55.5	21.6	49.9	67.1

Table 5 Summary statistics for Sn ICP analyses in A and S topsoil

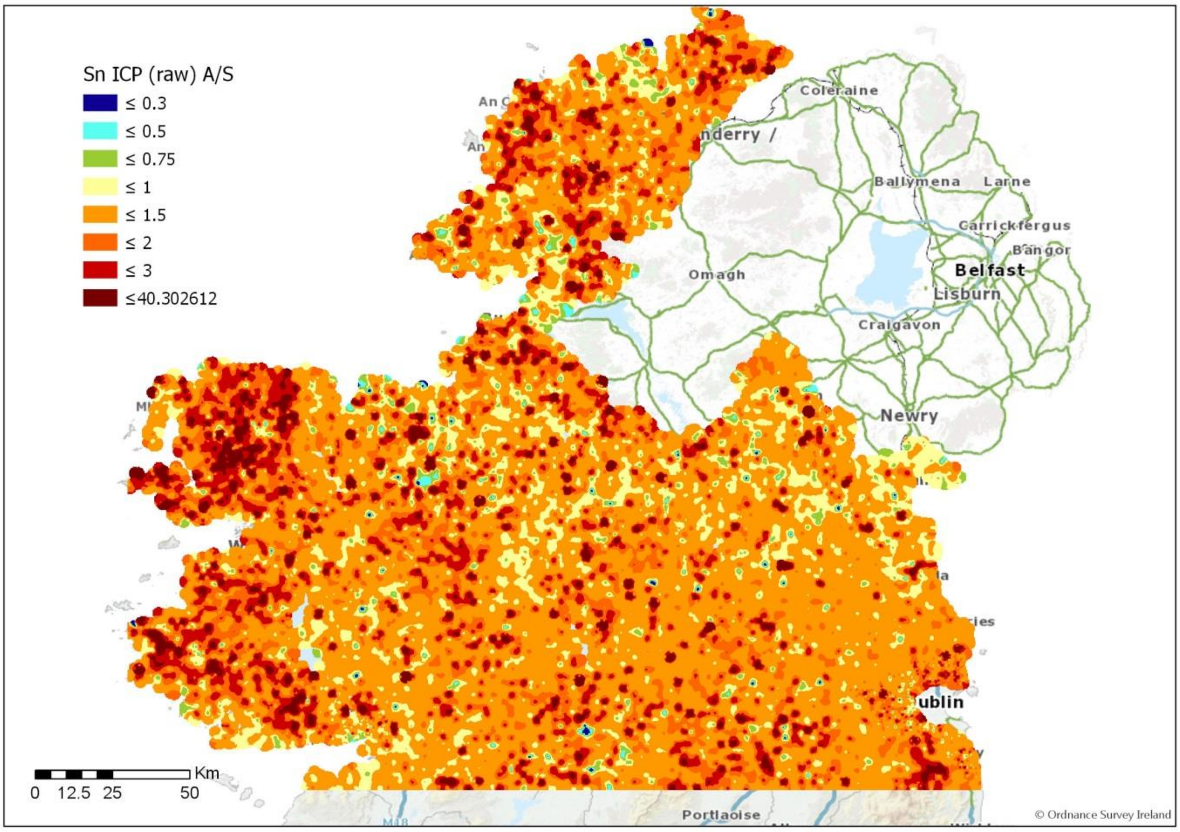

Figure 20 Ratio of Sn in A and S topsoil (non-normalized raw ICP data).

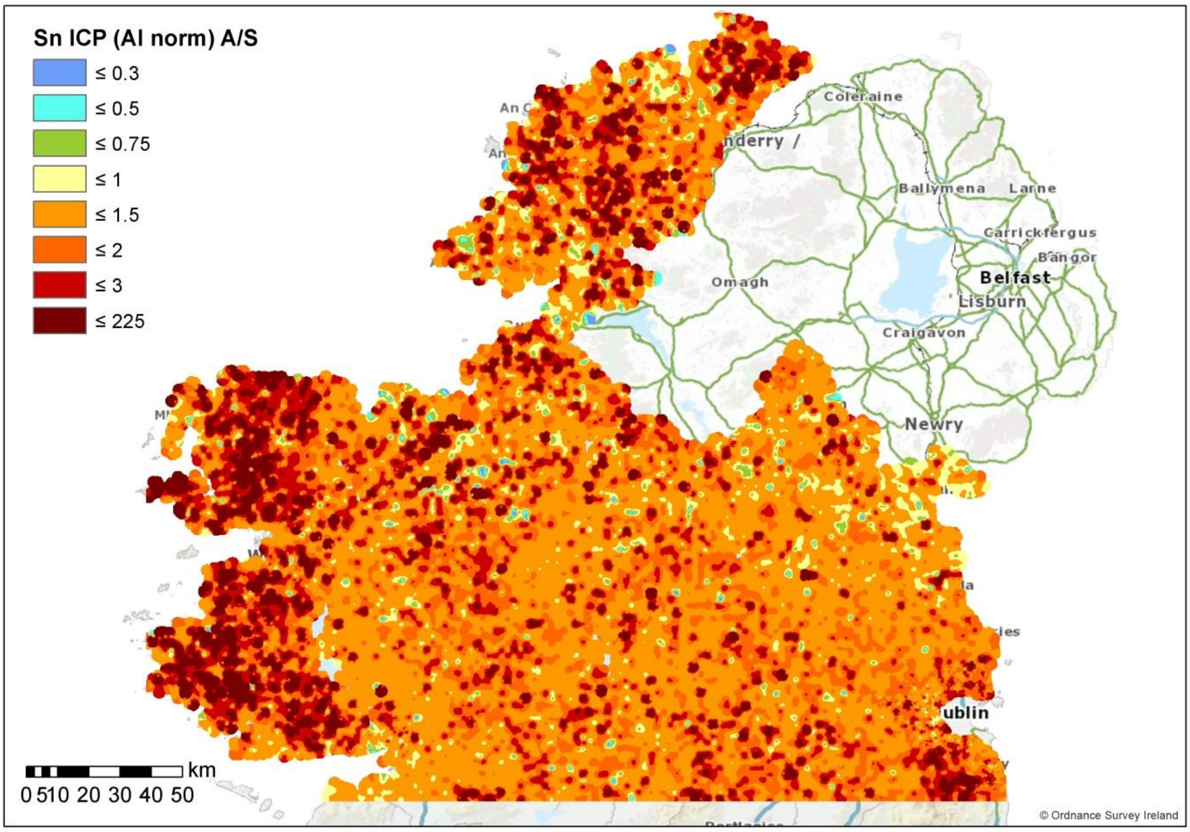

Figure 21 Ratio of Sn in A and S topsoil (ICP data normalized to Al concentration).

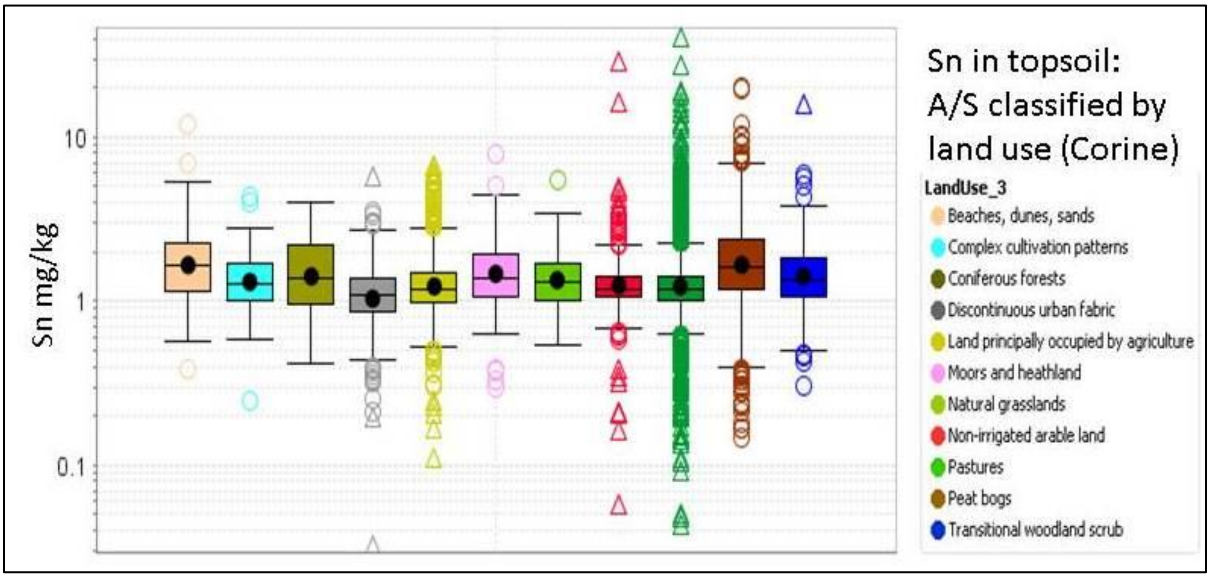

Figure 22 Tukey boxplots of A/S ratio of Sn in topsoil, classified by land use (Corine 2018).

These appear to confirm the association between areas dominated by peat and higher Sn concentrations in shallow topsoil compared to deeper topsoil. The A/S ratios for Sn are generally highest in areas where topsoil has significant organic matter content, such as peat bogs, moorland, and woodland. They are lowest in areas of pasture, arable land, and discontinuous urban fabric where topsoil is typically mineral-rich with limited organic matter content, so that fixation by organic matter is likely to be of limited importance. Thus, in areas dominated by mineral soil, e.g. the periurban areas of Dublin and Galway, topsoil in which the Sn concentration is significantly higher in the upper part of the soil profile is more likely to reflect diffuse anthropogenic contamination.

Summary

Comparison of shallow and deeper topsoil Sn data indicate that shallower topsoil typically has a higher concentration of Sn than deeper topsoil. In part this may be ascribed to fixation of Sn by organic matter, which is generally more abundant in shallower topsoil. In areas where soil is mineral-rich, diffuse anthropogenic contamination may play be responsible for the observed difference between shallow and deeper topsoil, especially in periurban areas.

Vanadium (V)

Background

Figures 23 and 24 show the distribution of vanadium in shallow (A) and deeper (S) topsoil. The overall distribution is very similar in both. It displays a clear correlation with bedrock geology. Higher V values are recorded over bedrock dominated by clastic and crystalline rocks, such as the greywacke of the Longford-Down Inlier, the Dalradian metasediments in Donegal, the clastic sequences of the Lower Carboniferous, including the Calp of the Dublin basin. Soils overlying the Lower Palaeozoic sequences in South Mayo, known to be enriched in elements such as Cr and Ni, also display high V concentrations. In contrast, soil underlain by limestone-dominated bedrock in the midlands has moderate to low V concentrations, while areas of raised and blanket bog have very low soil V concentrations. Figure 25 displays the V data for deeper (S) topsoil classified by land use (Corine 2018). The broad distribution of relatively high V soil concentrations in soils overlying clastic rocks (Figures 23 and 24), which typically comprises mineral rather than organic-rich soil, is reflected in the land use classification, with relatively high V in soil on land used for agriculture (pasture, arable land). This also includes most soil in the periurban areas of Dublin and Galway, leading to relatively high V in

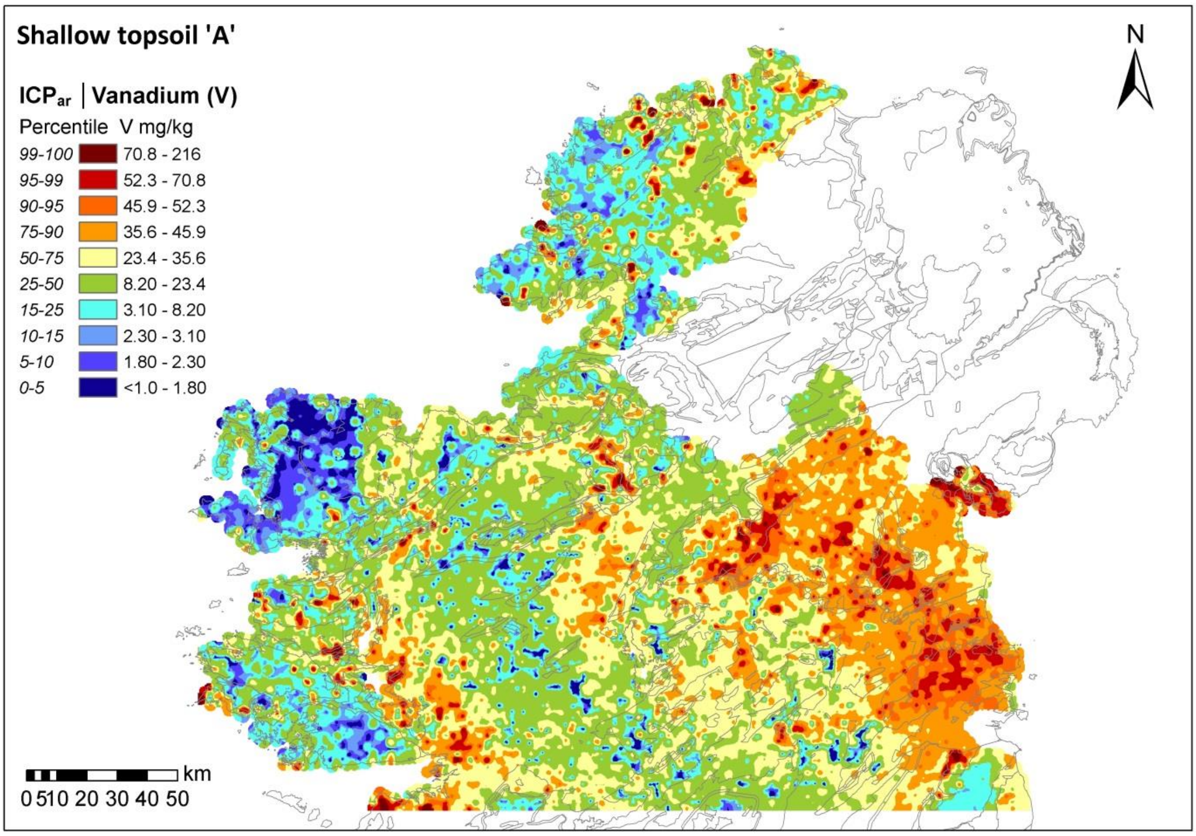

Figure 23 Distribution of V in shallower (A) topsoil

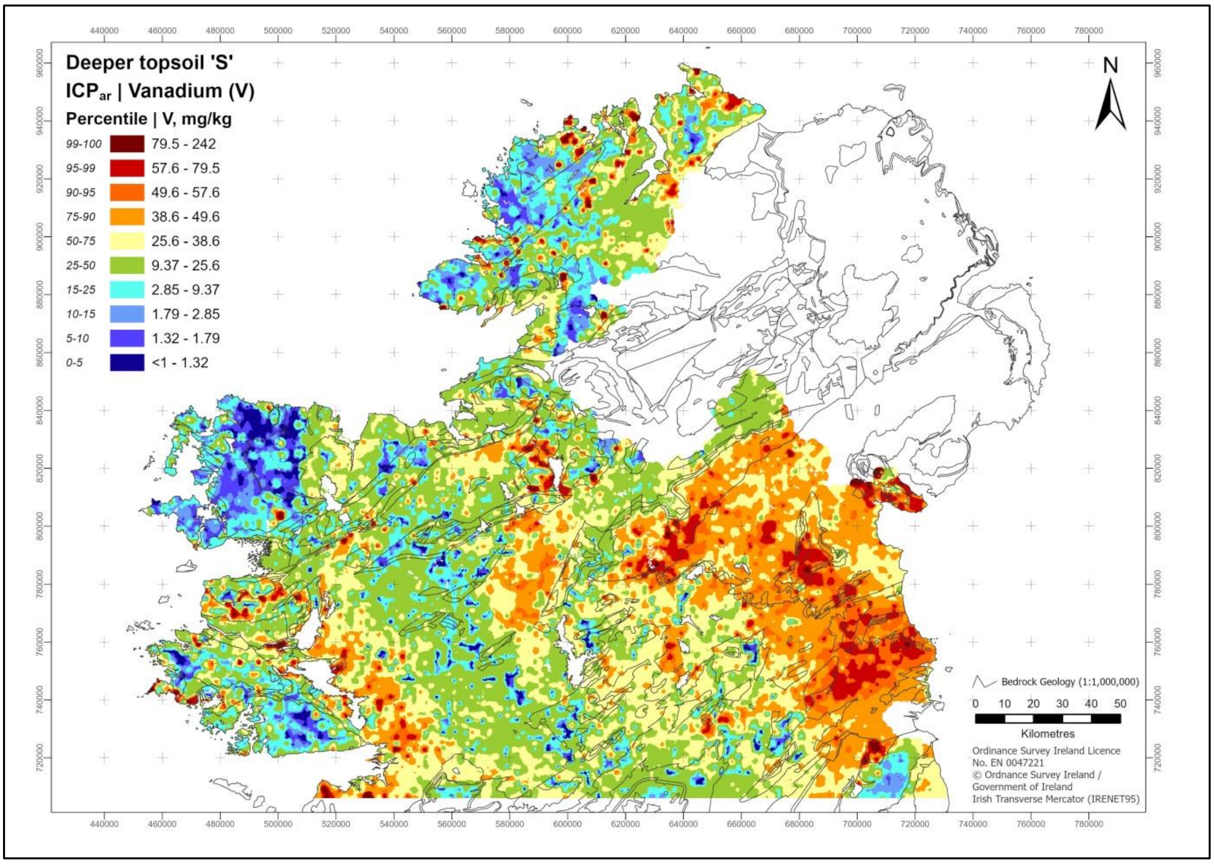

Figure 24 Distribution of V in deeper (S) topsoil

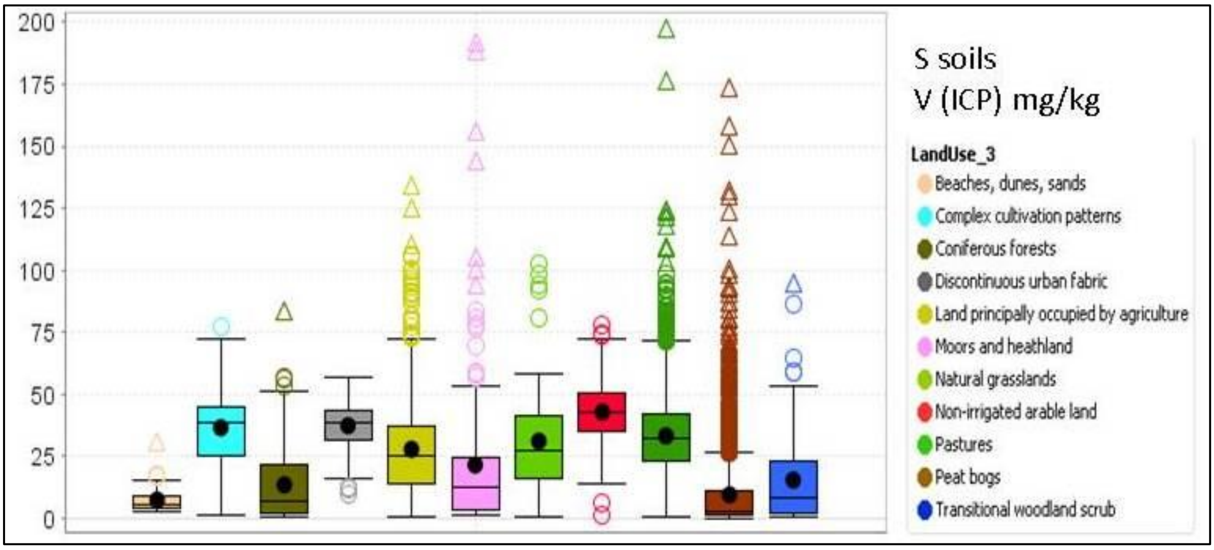

Figure 25 Tukey boxplots of V in deeper (S) topsoil, classified by land use (Corine 2018)

the discontinuous urban fabric land use class. The low V concentrations mapped in areas of peat bogs (uplands in counties Galway, Mayo, Donegal, and Wicklow) are reflected in low V for land use classifications including moorland, peat, and various woodlands.

Vanadium in A and S topsoil

Comparison of A and S soil ICP data for V, whether raw of normalized to Al, shows only a slight difference in V concentration between the two soil horizons, with concentrations higher in S soil (Figure 26, Table 6). Mapping of the raw data for the ratio of A to S (Figure 27) reinforces this observation, with large areas of the map classified as just above or below A/S =1. Normalization of the V concentrations to the Al concentration (Figure 28) does not alter the overall picture greatly, albeit the A/S ratio generally increases, in a largely proportionate way across the region. In part this occurs because A soils tend to have higher organic matter content than S soils and a correspondingly lower Al content. Normalizing A and S soils to their respective Al concentrations thus tends to increase the A/S ratio when compared to non-normalized data.

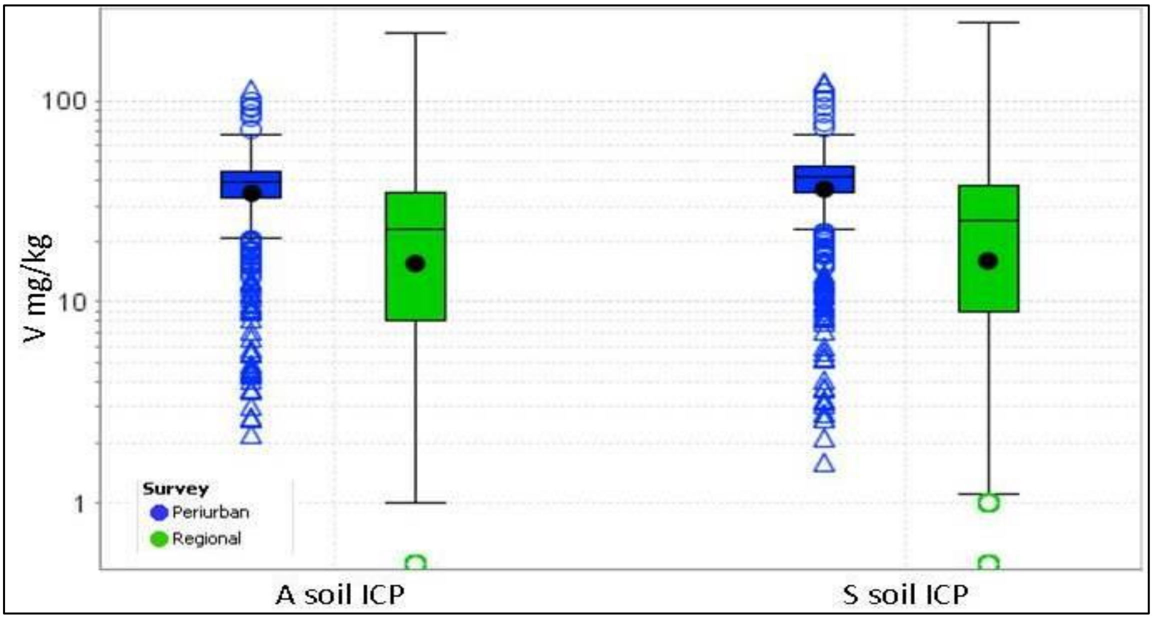

Figure 26 Tukey boxplots of V data (ICP raw data) for A and S topsoil, classified by survey type

Common to both raw and normalized data distributions is the observation that areas dominated by organic-rich soils and peat, notably blanket bog, have the highest A/S ratios for V. This is apparent in Figures 27 and 28 in west Galway, northwest Mayo, west Donegal, and the Dublin-Wicklow mountains. This suggests that fixation of metals by organic matter may play a significant role in determining V concentrations at least in some soils. Figure 29 shows boxplots of the A/S ratio for V classified by land use (Corine 2018). These demonstrate a remarkable consistency across the various land use classes, with all median concentrations near 1 and interquartile ranges displaying very limited range. Nevertheless, the boxplots confirm the association between areas dominated by peat and higher V concentrations in shallow topsoil compared to deeper topsoil.

V (ICP), mg/kg	**All data (n=9920)**		**Regional samples (n=9217)**		**Periurban samples (n=703)**	
	A	**S**	**A**	**S**	**A**	**S**
Minimum	< 1.0	< 1.0	< 1.0	< 1.0	2.2	1.6
25th percentile	9.1	10.4	8	9	32.7	35.1
50th percentile	24.3	26.6	23.0	25.2	39.2	41.6
75th percentile	36.5	39.7	35.0	38.1	44.5	46.9
Maximum	216	242	216	242	115	124

Table 6 Summary statistics for V ICP analyses in A and S topsoil

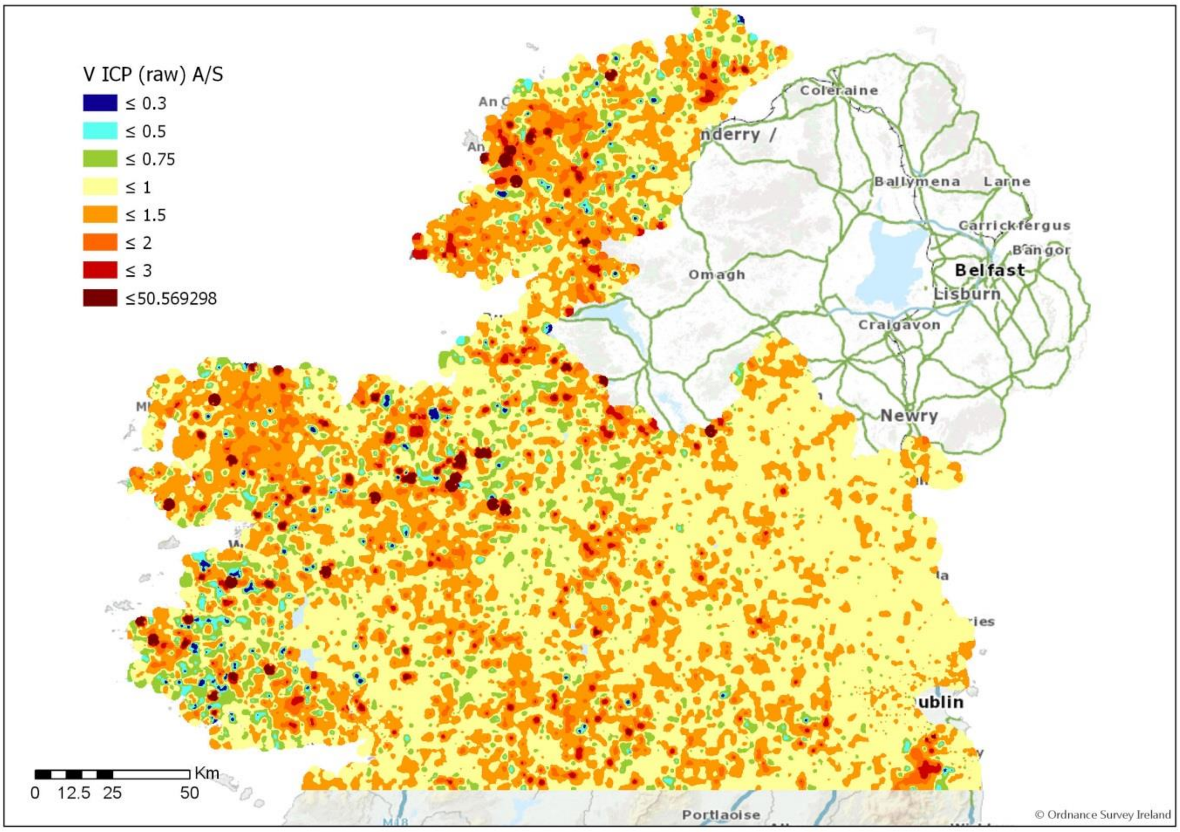

Figure 27 Ratio of V in A and S topsoil (non-normalized raw ICP data)

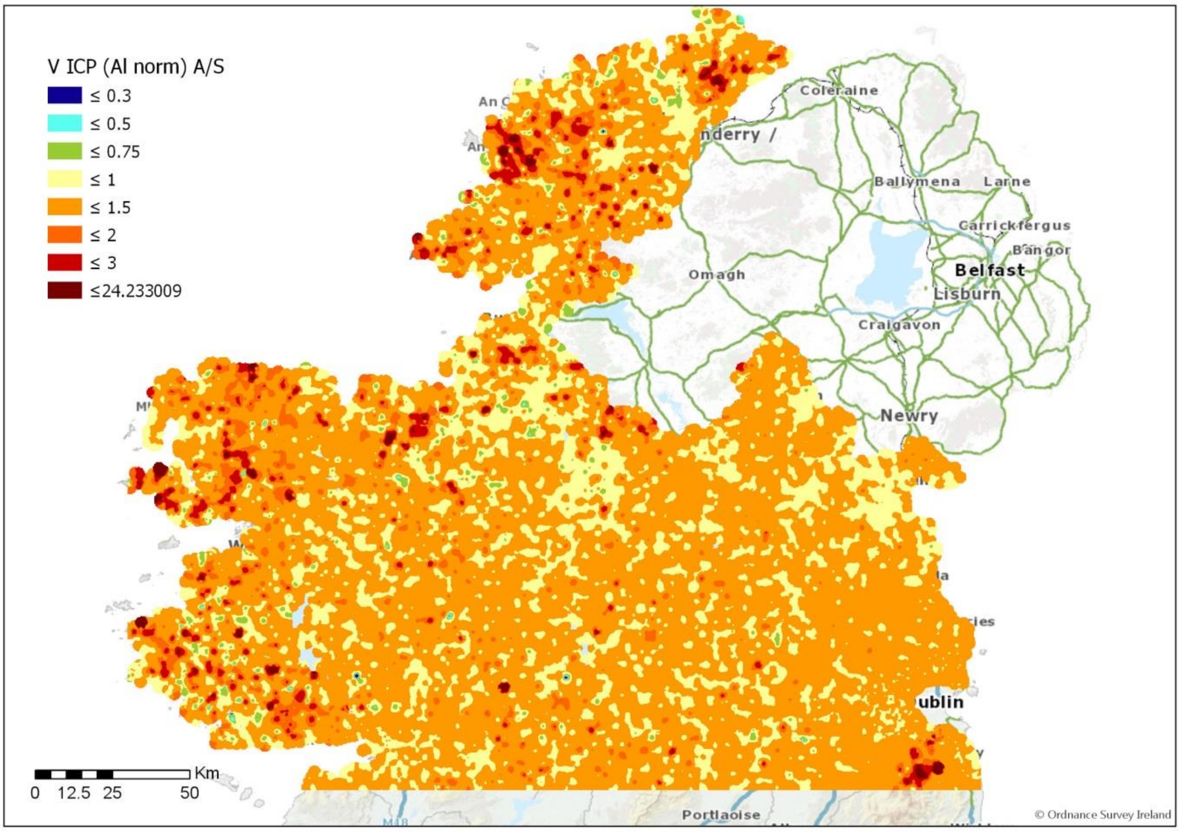

Figure 28 Ratio of V in A and S topsoil (ICP data normalized to Al concentration)

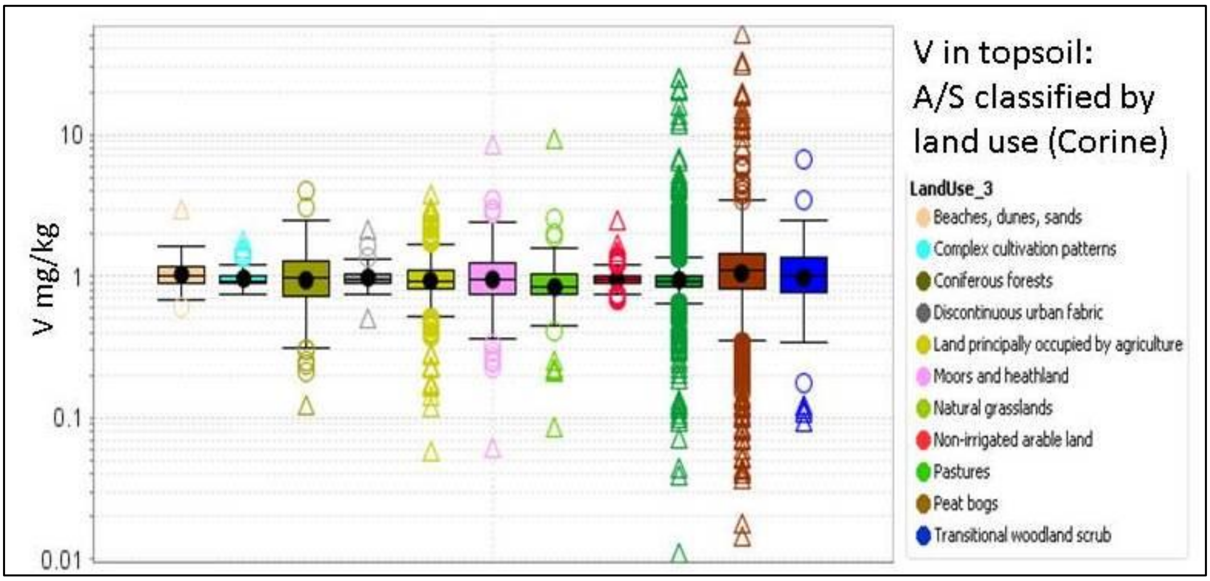

Figure 29 Tukey boxplots of A/S ratio of V in topsoil, classified by land use (Corine 2018)

Summary

The distribution of V in topsoil in the study area reflects strong control by bedrock composition, with highest V concentrations found over bedrock comprising clastic or crystalline rocks. Comparison of shallow and deeper topsoil V data indicates that deeper topsoil typically has a slightly higher concentration of V than shallower topsoil. However, the difference in V concentration between A and S soil is marginal and A/S ratios for various soil types, as expressed by land use classification, are remarkably similar. The only significant difference observed is for the peat land use class, with the concentration of V in shallower topsoil typically exceeding that in deeper topsoil. This may be ascribed to fixation of V by organic matter, which is generally more abundant in shallower topsoil.

Zinc (Zn)

Background

Figures 30 and 31 show the distribution of zinc in shallow (A) and deeper (S) topsoil. The overall distribution is very similar in both. It reflects several distinct controls: bedrock geology, including mineralization, distribution of organic-rich soils, including peat, and anthropogenic factors. Bedrock control is displayed by the generally higher concentrations of Zn observed in regions underlain by clastic and crystalline rocks, such as the Lower Palaeozoic greywacke of the Longford-Down inlier, the Dalradian metasediments of Donegal and the clastic sediments, including shale, of the Lower Carboniferous in the eastern midlands. Mineralization signatures are apparent throughout the region but are especially strong in east Monaghan (minor 19th-century Zn-Pb mines) and southeast Galway (Tynagh mine). The low Zn concentrations observed over much of Connemara, west Mayo, west Donegal and the northwest-southeast-trending “corridor” in east Mayo, Roscommon and east Galway can be related to peat and organic-rich soil, in which the mineral content and absolute Zn concentrations are typically very low. Anthropogenic inputs are most obvious in the Dublin and Galway periurban areas.

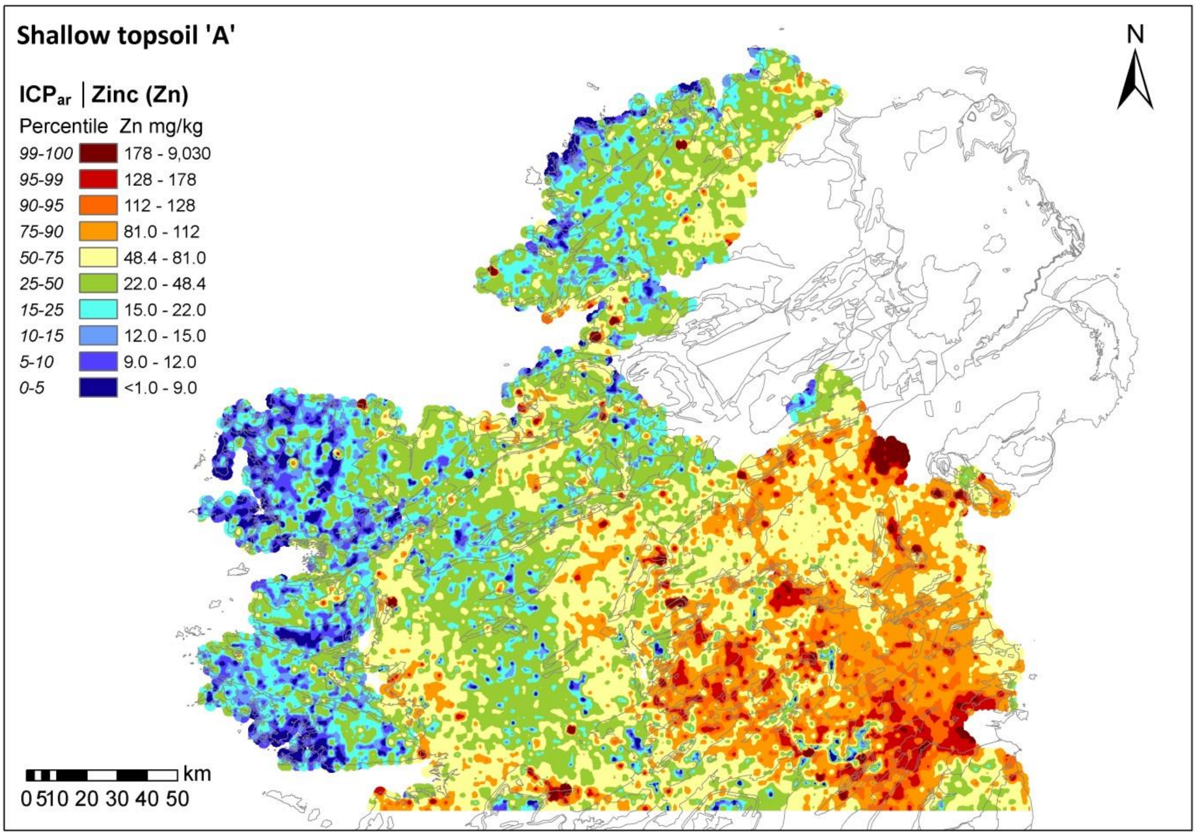

Figure 30 Distribution of Zn in shallower (A) topsoil

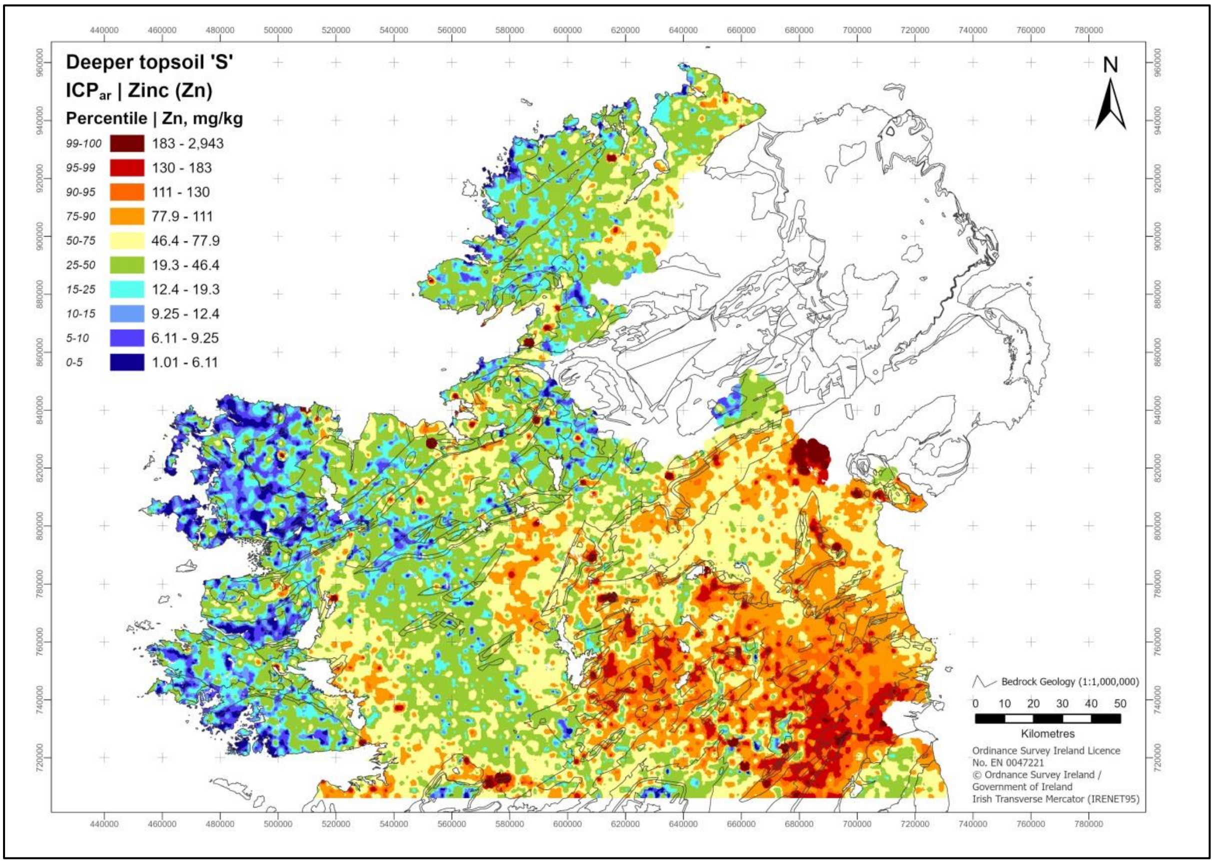

Figure 31 Distribution of Zn in deeper (S) topsoil

Figure 32 displays boxplots of the Zn data for S topsoil classified by land use (Corine 2018). The broad distribution of relatively high Zn soil concentrations in topsoil overlying clastic rocks (Figures 30 and 31), which typically comprises mineral- rather than organic-rich soil, is reflected in the land use classification, with relatively high V in soil on land used for agriculture (pasture, arable land). This also includes most soil in the periurban areas of Dublin and Galway.

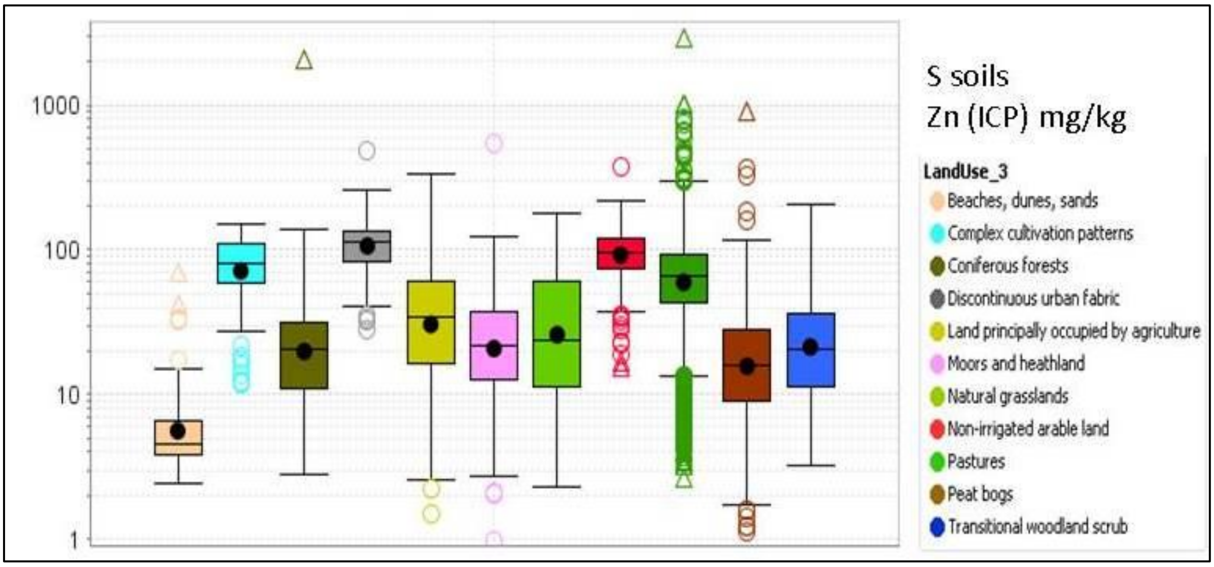

Figure 32 Tukey boxplots of Zn in deeper (S) topsoil, classified by land use (Corine 2018)

The low Zn concentrations mapped in areas of peat bogs (uplands in counties Galway, Mayo, Donegal and Wicklow, parts of the midlands) are reflected in low Zn for land use classifications including moorland, peat and various woodlands.

Zinc in A and S topsoil

Comparison of A and S soil ICP data for Zn, whether raw of normalized to Al, shows only a slight difference in Zn concentration between the two soil horizons, with concentrations higher in A soil (Figure 33, Table 7). Mapping of the raw data for the ratio of A to S (Figure 34) reinforces this observation, with most areas of the map classified as just above or below A/S =1. Normalization of the Zn concentrations to the Al concentration does not alter the overall picture greatly, albeit the A/S ratio generally increases, in a largely proportionate way across the region (Figure 35). In part this occurs because A soils tend to have higher organic matter content than S soils and a correspondingly lower Al content (Table 3).

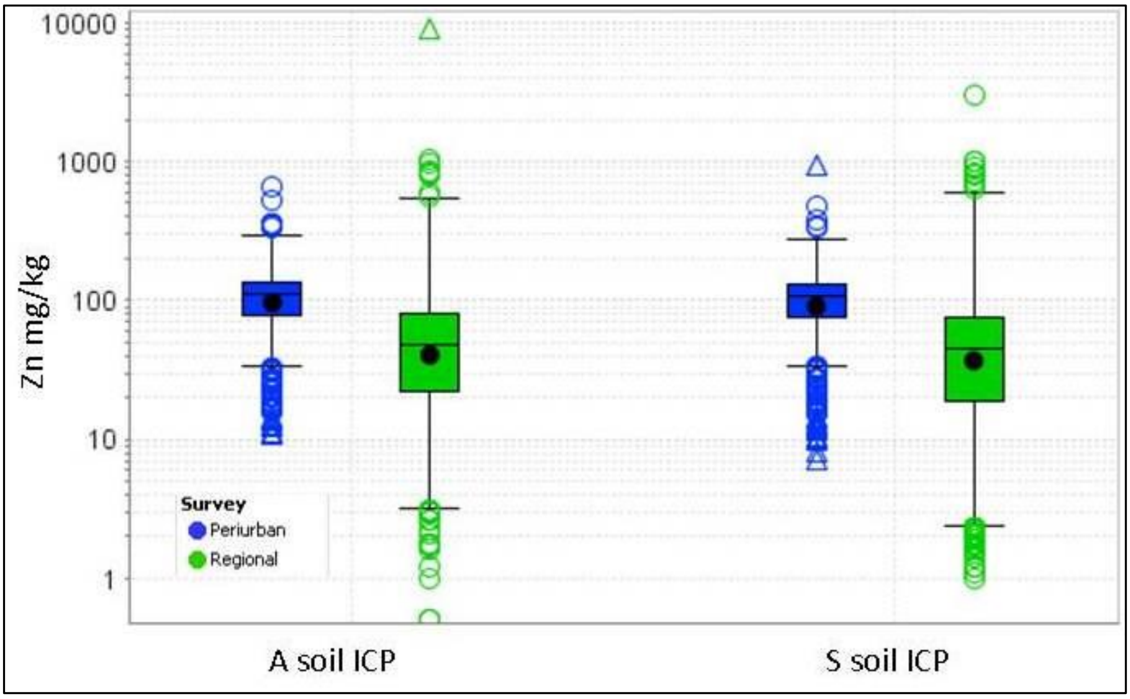

Figure 33 Tukey boxplots of Zn data (ICP raw data) for A and S topsoil, classified by survey type

Zn (ICP), mg/kg	All data (n=9920)		Regional samples (n=9217)		Periurban samples (n=703)	
	A	S	A	S	A	S
Minimum	< 1.0	1.0	< 1.0	1.0	10.9	7.1
25th percentile	23.0	20.2	21.9	19.0	77.1	75.5
50th percentile	51.0	49.3	47.5	45.5	112	108
75th percentile	84.9	81.6	79.4	76.4	134	130
Maximum	9120	2960	9120	2960	660	930

Table 7 Summary statistics for Zn ICP analyses in A and S topsoil

Normalizing A and S soils to their respective Al concentrations thus tends to increase the A/S ratio when compared to non-normalized data. Common to both raw and normalized data distributions is the observation

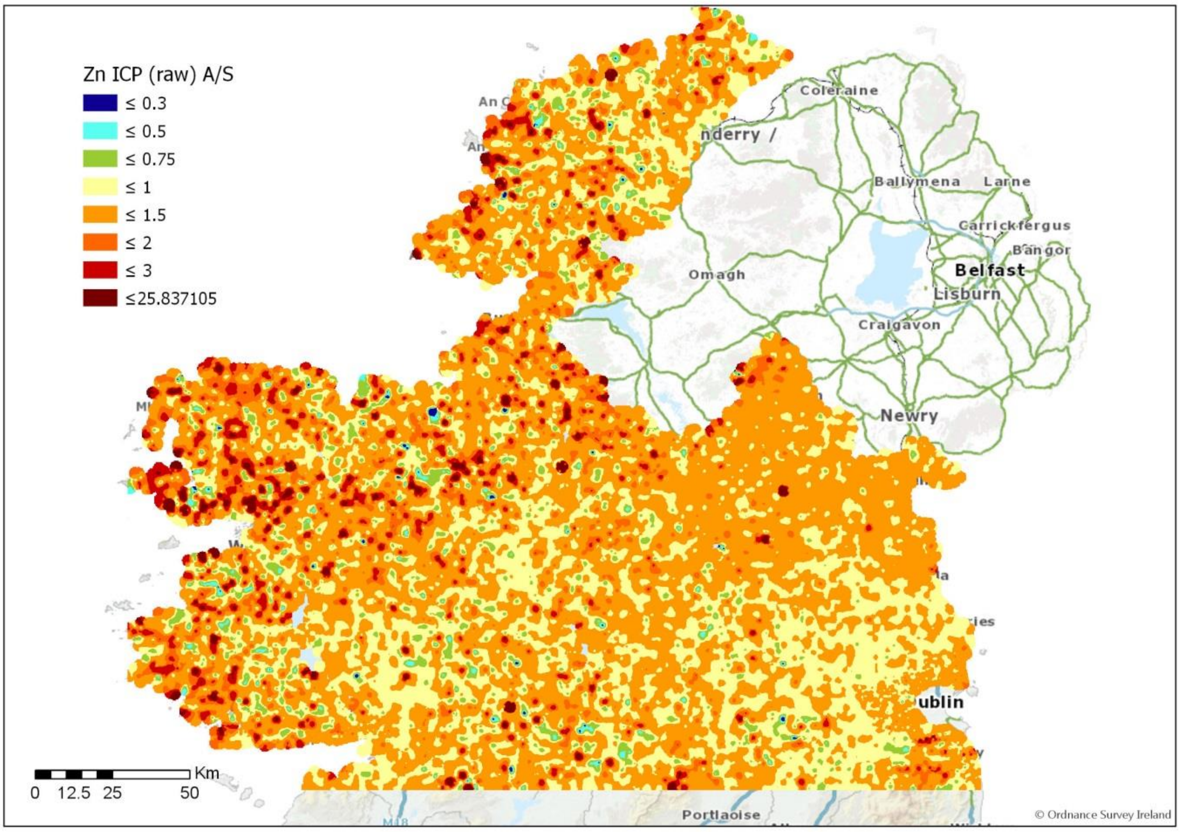

Figure 34 Ratio of Zn in A and S topsoil (non-normalized raw ICP data)

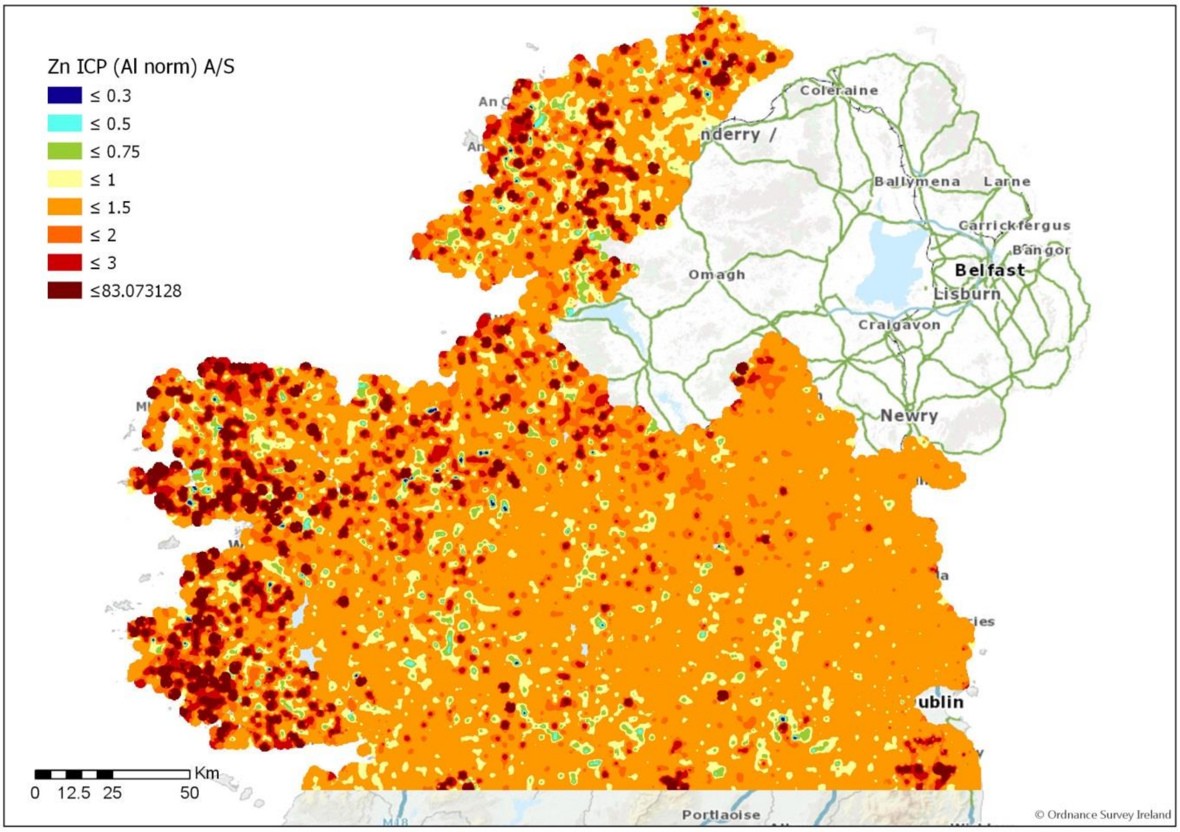

Figure 35 Ratio of Zn in A and S topsoil (ICP data normalized to Al concentration)

that areas dominated by organic-rich soils and peat, both blanket bog in upland areas and raised bog in the midlands, have the highest A/S ratios for Zn. This is apparent in Figures 34 and 35 in west Galway, northwest Mayo, west Donegal, and the Dublin-Wicklow mountains (blanket bog) and in the east Mayo-Roscommon-east Galway "corridor". This suggests that fixation of metals by organic matter may play a significant role in determining Zn concentrations at least in some soils. Figure 36 shows boxplots of the A/S ratio for Zn classified by land use (Corine 2018). As is also the case for vanadium, these demonstrate a remarkable consistency across the various land use classes, with all median concentrations near 1 and interquartile ranges displaying very limited range. An exception is marine sand (beach, dune, etc.) for which the A soil Zn concentration is notably higher, for reasons that are unclear. Otherwise, the boxplots confirm the association between areas dominated by peat or organic-rich soils, such as moorland, and higher Zn concentrations in shallow topsoil compared to deeper topsoil.

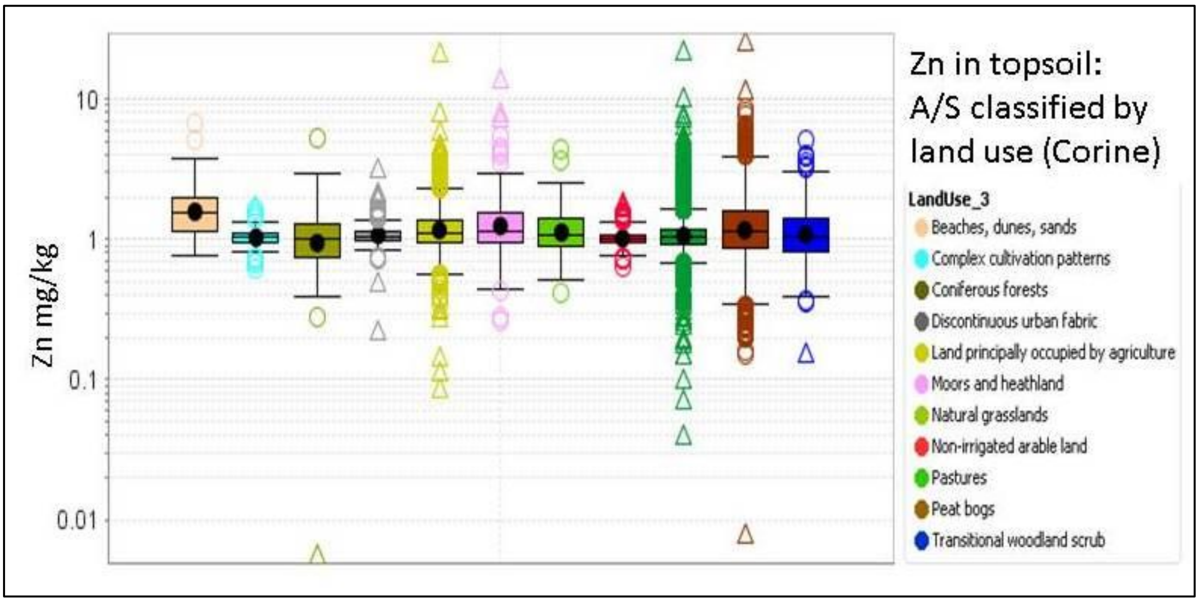

Figure 36 Tukey boxplots of A/S ratio of Zn in topsoil, classified by land use (Corine 2018).

Summary

The distribution of Zn in topsoil in the study area reflects strong control by bedrock composition, with highest Zn concentrations found over bedrock comprising clastic or crystalline rocks as well as known Zn mineralization occurrences. Comparison of shallow and deeper topsoil Zn data indicates that shallower topsoil typically has a slightly higher concentration of Zn than deeper topsoil. However, the difference in Zn concentration between A and S soil is marginal and A/S ratios for various soil types, as expressed by land use classification, are remarkably similar. Apart from marine sand deposits, the only significant difference observed is for the peat / moorland land use classes, with the concentration of Zn in shallower topsoil typically exceeding that in deeper topsoil. This may be ascribed to fixation of Zn by organic matter, which is generally more abundant in shallower topsoil.

Calcium (Ca)

Background

Figures 37 and 38 show the distribution of calcium in shallow (A) and deeper (S) topsoil. The overall distribution is very similar in both. It reflects the bedrock geology, with high-Ca soil found predominantly in the midlands over Lower Carboniferous bedrock. Soil samples with high Ca in small areas around the north and west coasts

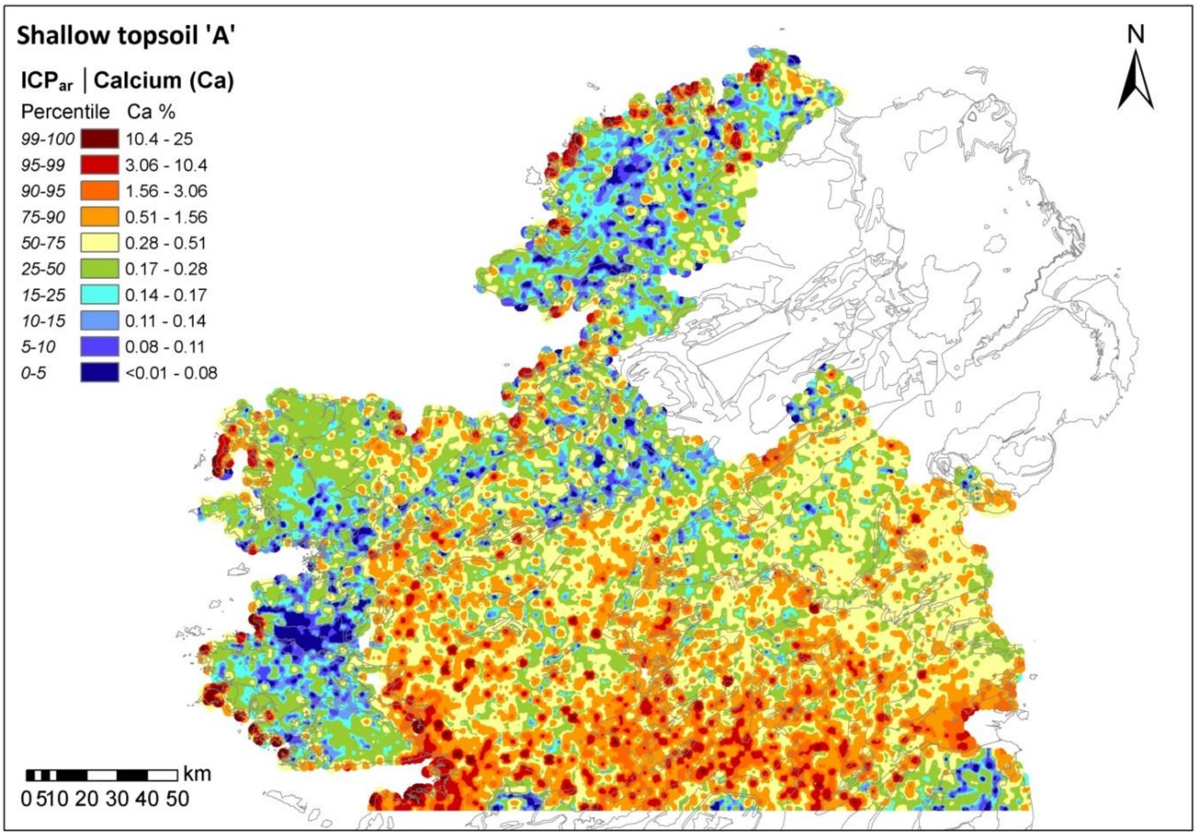

Figure 37 Distribution of Ca in shallower (A) topsoil

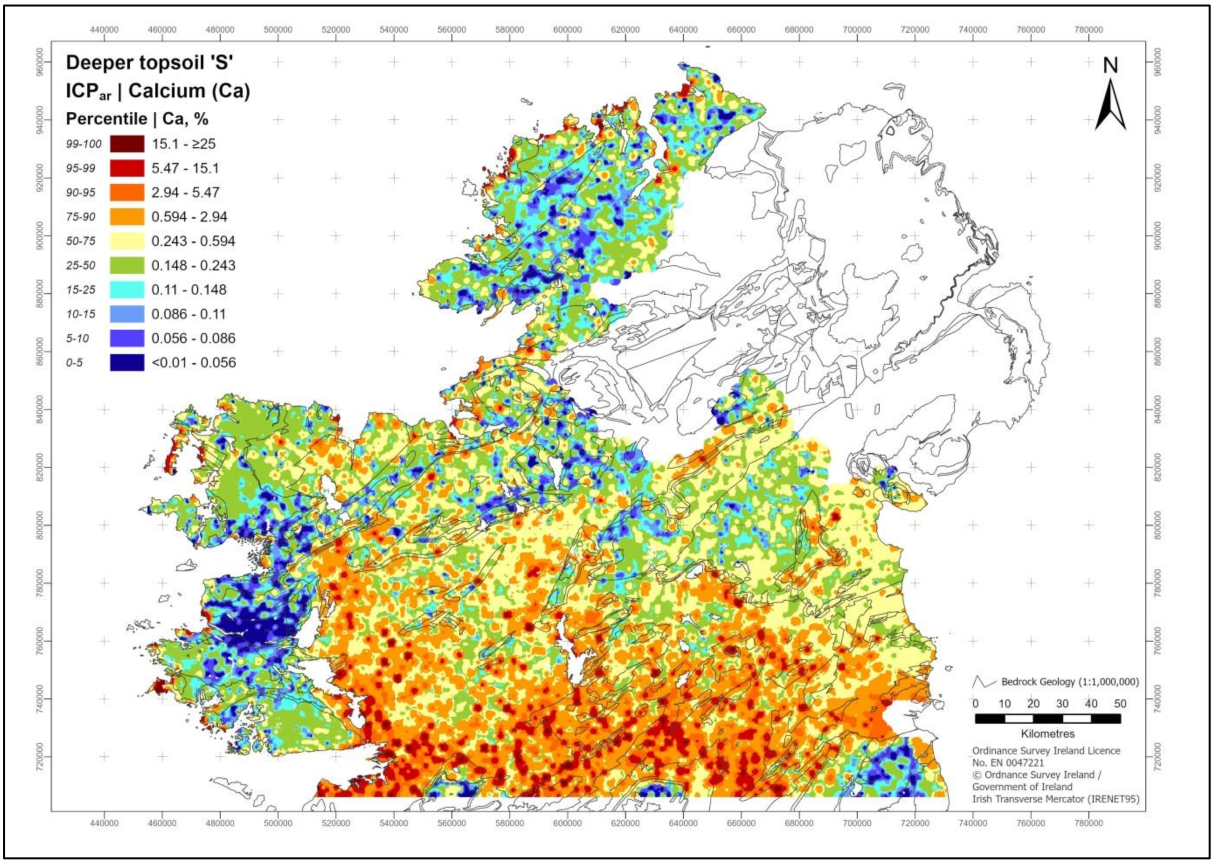

Figure 38 Distribution of Ca in deeper (S) topsoil

were taken from *machairs*, fertile coastal sandy soils rich in shells of marine organisms. The relatively low Ca concentrations observed over much of Connemara, west Mayo, Donegal, Longford-Down and the Wicklow mountains can be related to (i) clastic and crystalline bedrock with low Ca concentrations and (ii) peat and organic-rich soil, in which the mineral content and absolute Ca concentrations are typically very low.

Figure 39 displays boxplots of the Ca data for S topsoil classified by land use (Corine 2018). The broad distribution of relatively high Ca soil concentrations in soils overlying Lower Carboniferous bedrock is reflected in the land use classification, with relatively high Ca in soil on land used for agriculture (pasture, arable land).

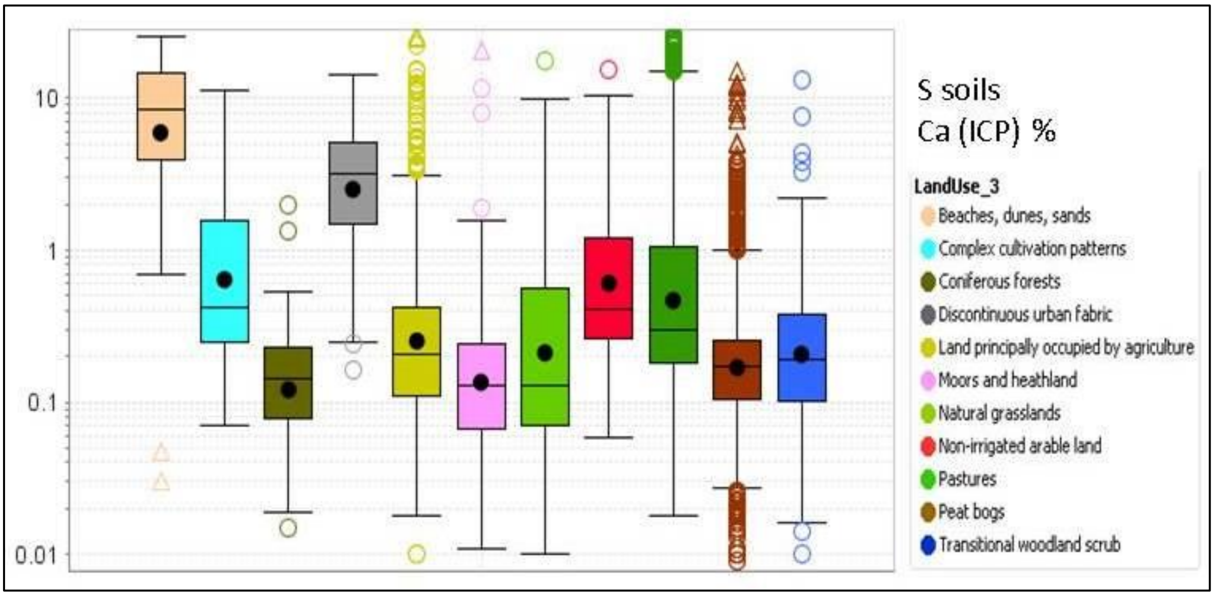

Figure 39 Tukey boxplots of Ca in deeper (S) topsoil, classified by land use (Corine 2018)

This also includes most soil in the periurban areas of Dublin and Galway, which are included within the discontinuous urban fabric class. Soils on beach and dune sands (*machairs*) have the highest Ca concentrations. The relatively low Ca concentrations mapped in areas of peat bogs (uplands in counties Galway, Mayo, Donegal and Wicklow, parts of the midlands) are reflected in relatively low Ca for land use classifications including moorland, peat, and various woodlands.

Calcium in A and S topsoil

Comparison of A and S soil ICP data for Ca, whether raw of normalized to Al, indicates very similar Ca concentrations for both A and S topsoil, albeit regional differences can be observed that appear to reflect bedrock composition and organic matter content. One exception to the general similarity of A and S composition is periurban soil, for which the Ca concentration in S topsoil is 50 % higher than that in A soil (Figure 40, Table 8). Mapping of the raw Ca data for the ratio of Ca in A soil to Ca in S soil shows strong bedrock control of the A/S distribution, with A/S < 1 clearly mapping closely to areas of Lower Carboniferous bedrock (Figure 41). Whether the lower Ca concentration recorded in A soil reflects loss of Ca from the near-surface soil or dilution of the soil Ca concentration by, e.g., organic matter is not clear. The latter has not been observed for other elements so loss of Ca from shallower topsoil must be considered a possibility. The concentration of Ca in A soils exceeds that recorded in S soils where bedrock comprises clastic or crystalline rock or in areas of peat bog. In these areas, the absolute concentration of Ca in topsoil is generally quite low (Figures 37 and 38) and there is greater uncertainty regarding measured A/S ratios. Normalization of the Ca concentration to the Al concentration does not alter the overall picture greatly, albeit the A/S ratio generally increases, in a largely proportionate way across the region (Figure 42). In part this occurs because A soils tend to have higher organic matter content than S soils and a correspondingly lower Al content (Table 3). Normalizing A and S soils to their respective Al concentrations thus tends to increase the A/S ratio when compared to non-normalized data.

Figure 43 shows boxplots of the A/S ratio for Ca classified by land use (Corine 2018). These demonstrate considerable consistency across the various land use classes, with median concentrations fluctuating around 1 and interquartile ranges displaying very limited range. They confirm the association between areas dominated by Ca-rich Lower Carboniferous bedrock and higher Ca concentrations in deeper topsoil compared to shallow topsoil.

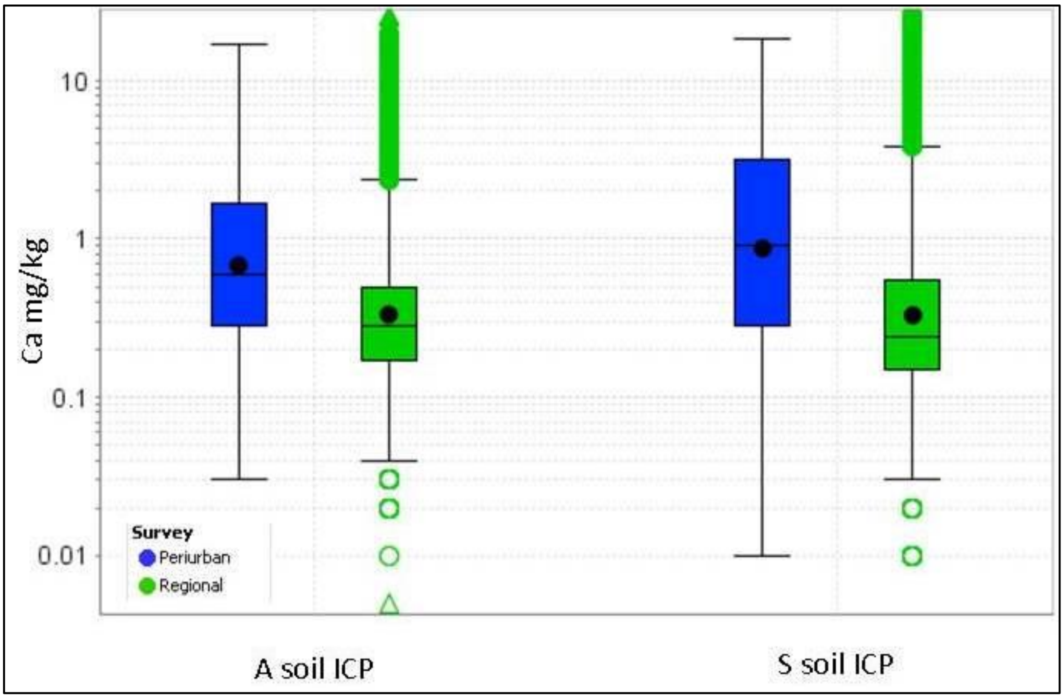

Figure 40 Tukey boxplots of Ca data (ICP raw data) for A and S topsoil, classified by survey type

Ca (ICP), %	All data (n=9920)		Regional samples (n=9217)		Periurban samples (n=703)	
	A	S	A	S	A	S
Minimum	< 0.01	0.01	< 0.01	0.01	0.03	0.01
25th percentile	0.18	0.15	0.17	0.15	0.28	0.28
50th percentile	0.29	0.25	0.28	0.24	0.6	0.92
75th percentile	0.53	0.66	0.49	0.55	1.69	3.18
Maximum	>25	>25	>25	>25	17.0	18.3

Table 8 Summary statistics for Ca ICP analyses in A and S topsoil

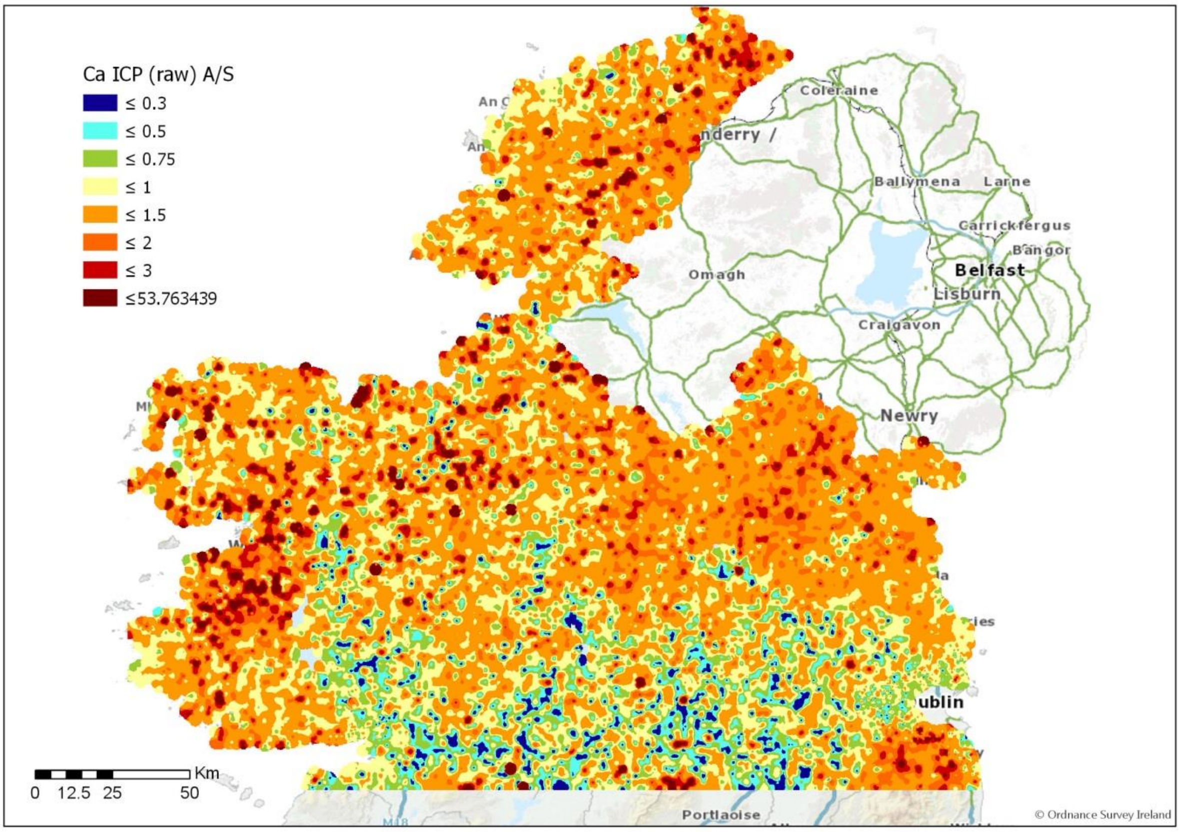

Figure 41 Ratio of Ca in A and S topsoil (non-normalized raw ICP data)

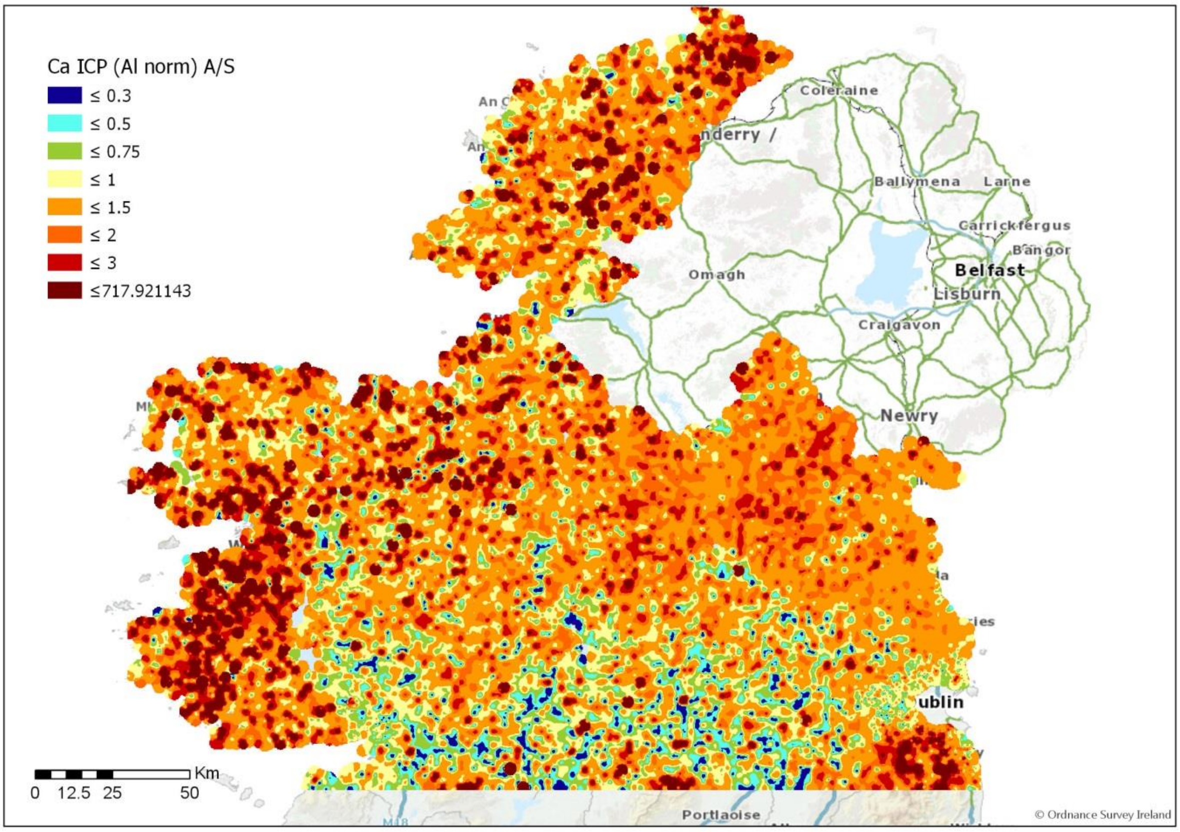

Figure 42 Ratio of Ca in A and S topsoil (ICP data normalized to Al concentration)

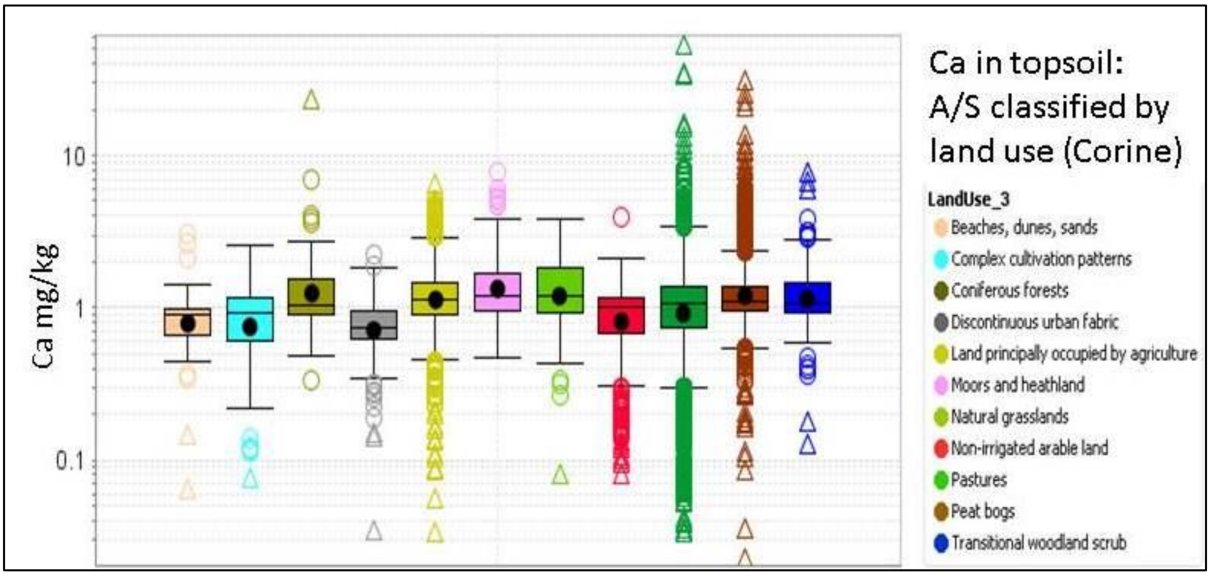

Figure 43 Tukey boxplots of A/S ratio of Ca in topsoil, classified by land use (Corine 2018)

Summary

The distribution of Ca in topsoil in the study area reflects strong control by bedrock composition, with highest Ca concentrations found over bedrock comprising Lower Carboniferous bedrock. *Machair* soils along the north and west coasts have some of the highest recorded soil Ca concentrations. Relatively low Ca characterizes soil overlying clastic or crystalline bedrock. Comparison of shallow and deeper topsoil Ca data indicates that deeper topsoil typically has a slightly higher concentration of Ca than shallow topsoil, although this is considerably more pronounced for periurban soil. The mapped distribution of A/S ratios for Ca reflects strong bedrock control. The A/S ratios for Ca for various soil types, as expressed by land use classification, are generally similar and broadly reflect the bedrock control outlined above.

A and S comparison: geostatistical analysis

Introduction

Multielement geostatistical analysis carried out on the A and S topsoil datasets focused on Principal Component analysis in order to investigate the general relationship between the chemistry of A and S topsoil in the region.

Soil A and Soil S geochemistry were adjusted for values reported at less than the lower limit of detection for the element analyzed. The data were then merged and a centred logratio transform was applied. A principal component analysis based on the covariance structure of the data was applied.

Biplots and maps to the first and seventh principal components were created to illustrate the similarities and differences between the two soil types.

As shown by the eigenvalue screeplot (Figure 44) and the eigenvalues themselves (Table 9), the first four eigevalues account for most of the “structure” in the data, although other components appear to be significant also.

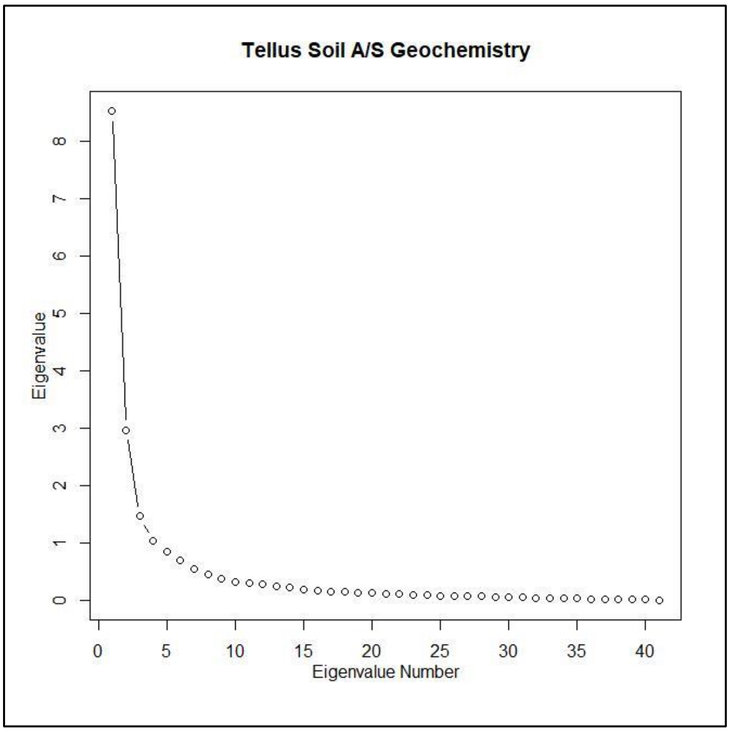

Figure 44 Screeplot of eigenvalues for A and S topsoil

Tellus Soil A/S Geochemistry - All Elements										
	PC1	PC2	PC3	PC4	PC5	PC6	PC7	PC8	PC9	PC10
λ	8.52	2.96	1.46	1.02	0.84	0.68	0.53	0.44	0.37	0.32
λ%	42.4938	14.7631	7.2818	5.0873	4.1895	3.3915	2.6434	2.1945	1.8454	1.596
Σλ%	42.4938	57.2569	64.5387	69.6259	73.8155	77.207	79.8504	82.0449	83.8903	85.4863

Table 9 Eigenvalues for A and S soil data

Principal Component analysis

PC1 and PC2 account for the bulk of the "structure" in the data and, as shown on the biplot of PC1 v PC2 (Figure 45), the chemistry of the two depth profiles are nearly identical. Both the A and S soils display equal distributions across the elements in the biplot. This suggests that the two media are nearly identical in composition.

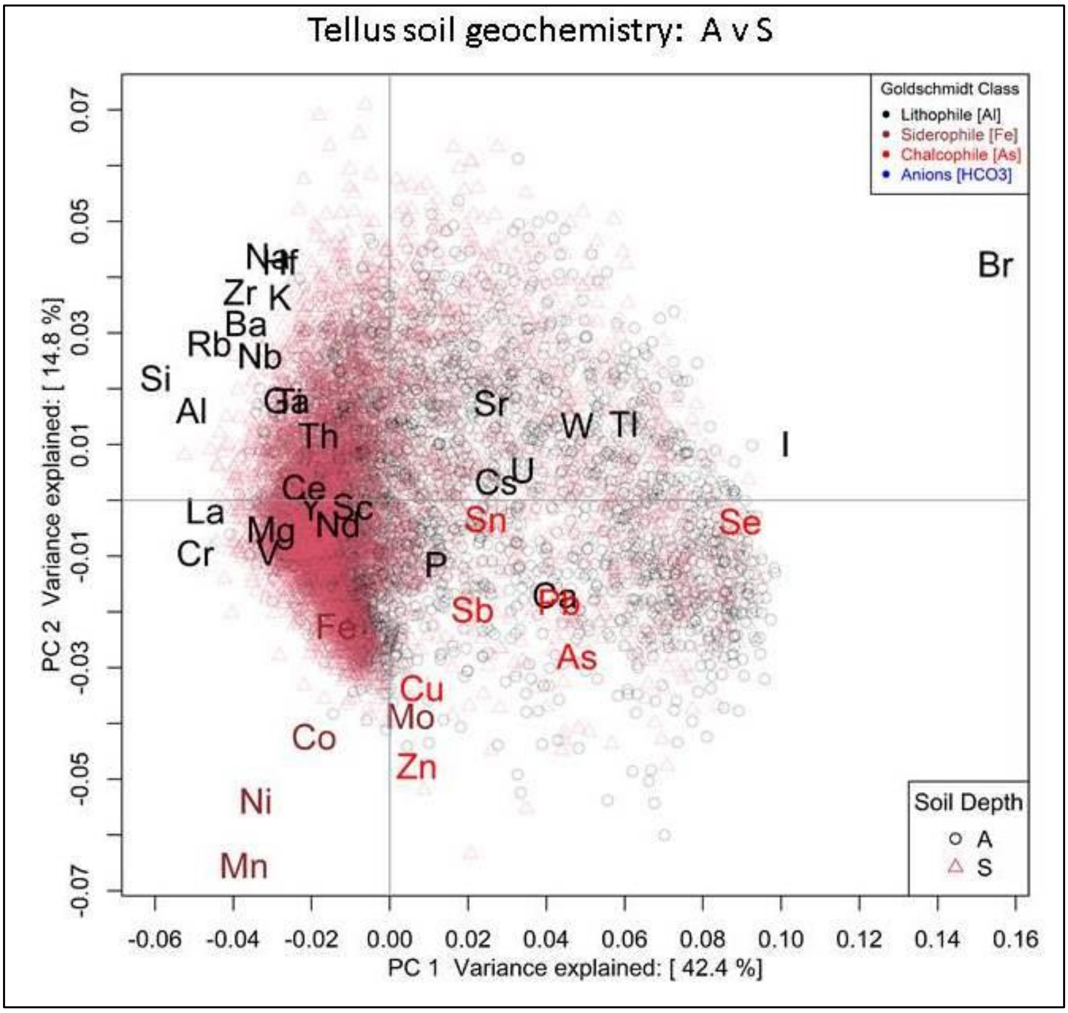

Figure 45 A v S topsoil: PC1 v PC2

In contrast, the biplot of PC6 v PC7 (Figure 46) shows that there is a relative increase in P and Cu along the positive PC7 axis, predominantly associated with A (shallow) topsoil. PC7 accounts for a small component of the data structure (Table 9) and thus reflects a relatively minor process affecting the composition of the topsoil. This process involves relative enrichment of P and Cu in the shallow topsoil and may reflect agricultural inputs, such as fertilizer.

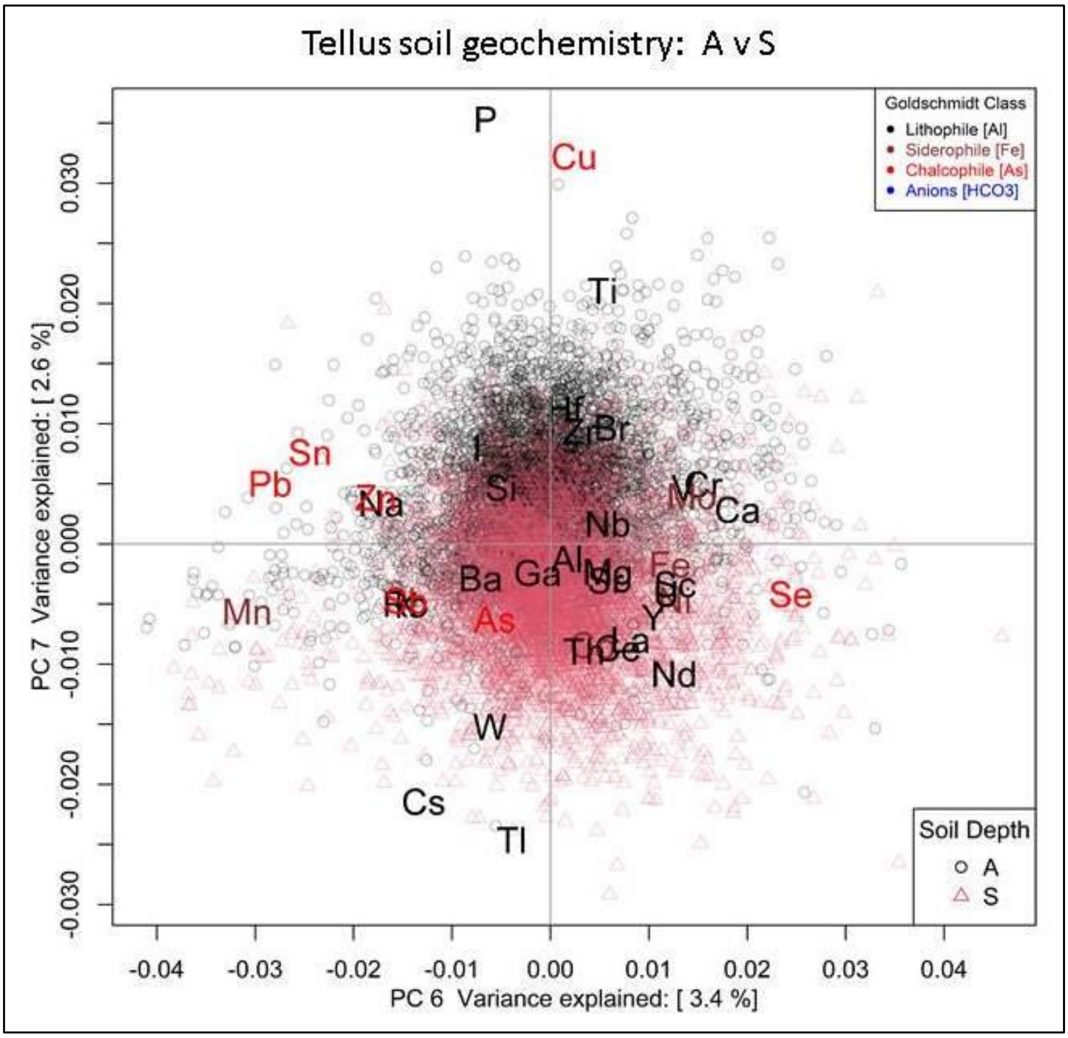

Figure 46 A v S topsoil: PC1 v PC2

Conclusions

Recorded phosphorus (P) concentrations in shallower (A) topsoil are generally higher than those for deeper (S) topsoil, across the entire region. Spatial patterns of A/S ratios for P are broadly consistent with the overall distribution of P in the region, suggesting that the excess of P in A soils relative to S soils largely reflects addition of P in fertilizer to the surface of the soil.

Similarly, shallower topsoil typically has a higher concentration of Pb and Sn than deeper topsoil. In part this may be ascribed to fixation of Pb or Sn by organic matter, which is generally more abundant in shallower topsoil. In areas where soil is mineral-rich, diffuse anthropogenic contamination may be responsible for the observed difference between shallow and deeper topsoil, especially in periurban areas.

In contrast to Pb and Sn, concentrations of V and Zn tend to be higher in deeper rather than shallower topsoil. However, the observed difference between A and S soil is marginal and A/S ratios for various soil types, as expressed by land use classification, are remarkably similar. The only significant difference observed is for the peat / moorland land use class, with the concentration of V and Zn in shallower topsoil typically exceeding that in deeper topsoil, a reversal of the general tendency. This may be ascribed to fixation of these elements by organic matter, which is generally more abundant in shallower topsoil.

Deeper topsoil typically also has a slightly higher concentration of Ca than shallow topsoil, although this is considerably more pronounced for periurban soil. The mapped distribution of A/S ratios for Ca reflects strong bedrock control while the A/S ratios for Ca for various soil types, as expressed by land use classification, are generally similar and also broadly reflect bedrock control.

In summary, a comparison of data for the A and S Tellus topsoil samples shows significant if typically subtle differences between the two. The degree of observed difference between A and S samples varies according to the individual element and overall soil composition, which is largely controlled by the nature of the bedrock and the proportion of organic matter in the soil. Fixation of some elements by organic matter is suggested by the observed difference in A and S concentrations. Metal fixation by organic matter is a significant confounding factor in the use of soil sample geochemistry for mineral exploration – comparison of shallower and deeper topsoil data may suggest approaches for investigating this phenomenon. Anthropogenic inputs to soil can be recognized and the variation between A and S data can provide further evidence for their source.

References

CHILDS, C. 2004. Interpolating surfaces in ArcGIS Spatial Analyst. *ArcUser.* Summer 2004 ed. California, USA:
ESRI.

KNIGHTS, K.V. 2020. Tellus geochemical survey: shallow topsoil data from the border and west of Ireland. Geological Survey Ireland

KNIGHTS, K.V. 2020. Tellus geochemical survey: deeper topsoil data from the border and west of Ireland. Geological Survey Ireland

SZPAK, M.T. 2020. Tellus geochemical survey: shallow topsoil data from the midlands of Ireland. Geological Survey Ireland

SZPAK, M.T. 2020. Tellus geochemical survey: deeper topsoil data from the midlands of Ireland. Geological Survey Ireland