# Geological Survey Ireland

# Lithium in stream sediments in southeast Ireland: AAS geochemical data for samples collected in the period 1986 – 1990.

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## 1. Background

In 1984 GSI commenced a regional stream sediment survey programme that continued into the early 1990s. The bulk of the programme focused on the Caledonides of southeast Ireland where over 2,000 samples, including field duplicates and follow-up high-density samples, were collected from 1986 to 1990. Analysis of trace elements in the sediments was carried out using two methods, instrumental neutron activation analysis (INAA) and atomic absorption spectroscopy (AAS). The resulting database of analyses of samples from 1884 unique sample sites was available for purchase for a period in the 1990s and it formed the basis of a number of publications (e.g. O'Connor and Reimann 1993, O'Connor and Gallagher 1995). The excess physical samples were retained as part of GSI's geochemical sample archive.

In 2014 the archive samples were reanalysed as part of the Tellus programme, using XRFS for major and trace analyses and fire assay with ICP-MS for Au, Pt and Pd. These analyses expanded the range of reported elements and provided improved detection limits for many elements, notably Au. However, a significant omission from the subsequently reported data is lithium (Li), which cannot be measured by XRFS. Lithium is a geochemically important element in southeast Ireland because of the occurrence there of Li pegmatites, potential ores for this critical element. In this context, and given that GSI is unlikely to carry out further analyses on these sediment samples in the near future, the original stream sediment Li data are now made available.

## 2. Data structure

The data are presented in spreadsheet form. Table 1 lists the data fields.

| Field name | Description |
|---|---|
| GSI_ID | Original GSI sample ID. The first two numerals refer to the year of collection. |
| Sample_ID | Corresponding Tellus sample ID. |
| Easting | Irish National Grid easting coordinate |
| Northing | Irish National Grid northing coordinate |
| X_ITM | Easting ITM coordinate |
| Y_ITM | Northing ITM coordinate |
| Li_AAS | Reported Li concentration by AAS (ppm or mg/kg) |

**Table 1: Summary of stream sediment Li database.**

## 3. Sample coordinates

Samples were originally collected and geo-located in the field using 1:25,000 basemaps produced in GSI by photo-reduction of 1:10,560 maps. Subsequently GSI adopted a digital basemap. The original field maps were used in 2015 to digitize the sample site locations onto the digital basemap.

## 4. Available sample data

The original geochemical database for southeast Ireland stream sediments was compiled in the early 1990s after completion of sampling in 1990. It included data for 1884 unique sites, sampled over the Caledonides at a density of approximately one site per 3 $km^2$. Lithium data for a further 22 samples collected in 1988 near several Li pegmatite deposits are also included in this data release, giving Li data for a total of 1906 samples. In the archive of these 1906 samples sufficient material was available for 1860 to be reanalysed in 2014-2015 as part of the Tellus programme and their Tellus sample IDs are included in the database. Tellus XRFS and FA-ICP data are also available for these samples. Tellus sample IDs are included for 1860 samples for which multielement data were published in 2019. These data can downloaded as part of the Tellus stream sediment data download (Knights *et al*. 2020) available at www.gsi.ie.

## 5. Geochemical analysis

Samples were analysed for Li by Atomic Absorption Spectrophotometry (AAS). 0.5 g of each sample was digested with 5 ml 49% HF and 3 ml 70% $HCl0_4$ to dryness. The residue was dissolved by warming with 5 ml conc. HCl and quantitatively transferred to a 25ml volumetric flask. 2.5 ml each of 1% w/v $NH_4$ (as $NH_4$ Cl) and 1% w/v (as $LaCl_3$) were added and the solution then made up to 25ml with water and mixed well. All elements were determined on PU 7000 and PE 5000 series instruments at the former Mercury Analytical Ltd. (Ireland). The equipment was calibrated using commercial liquid standards. The reported lower limit of detection (LLD) for Li was 1 ppm (mg/kg). No data were reported as being below the LLD. All results were read and are reported to the nearest ppm.

## 6. Quality Control

The available data for quality control purposes are limited. Mercury Analytical ran an in-house reference material (the long-discontinued Canmet CRM BL-4, reported in the literature as a radioactive ore and a standard for uranium) for each analytical batch. For 21 analyses of this material for which data are available, the mean reported Li concentration was 12.5 ppm. However, no certificates stating the Li concentration of this reference material were discovered during the course of this data compilation.

GSI included an in-house stream sediment reference material with each stream sediment sample batch collected and analysed in the period 1986-1990. This material was subsequently repurposed for the Tellus survey, after re-homogenization and re-milling to Tellus standards. Now named SEIRE, it has been extensively analysed by ICP-MS since 2012 as part of Tellus geochemistry quality control (e.g. Knights *et al.* 2020). Table 2 shows the mean concentration of Li in SEIRE analysed in the 1980s by Mercury Analytical for AAS and in SEIRE and certified reference materials analysed by Tellus since 2012 by ICP-MS following *aqua regia* extraction.

For the certified reference materials, the reported values for ICP-MS analyses are as expected lower than the certified "total" concentrations, since *aqua regia* provides only a partial extraction. In the case of the two stream sediment materials (STSD-1 and STSD-3) the reported values are c. 80% or more of the certified values. Reported concentrations for the till samples are lower (60 – 80 %) relative to the certified concentrations. The difference between the reported concentrations for sediment and till may the different matrices in these reference materials. For the in-house GSI reference material, SEIRE, the mean for Tellus ICP-MS analyses (75.4 ppm) is lower than that for the AAS analyses carried out by Mercury Analytical (81 ppm), again as expected since the AAS analyses followed a near-total extraction using strong acids.

The results of Tellus analyses of certified reference materials indicate that the ICP-MS (*aqua regia*) analyses yield reasonable results for Li, particularly for sediments. The results reported for AAS analyses carried out on SEIRE by Mercury Analytical are comparable to those reported by Tellus for the same material following ICP-MS (*aqua regia*) analyses.

| Reference material | Certified "total" (ppm) | Tellus ICP-MS (*aqua regia*) (mean, ppm) (2012-2020) | n | AAS (mean, ppm) n = 101 (1986-1990) |
|---|---|---|---|---|
| **SEIRE (sediment)** | - | 75.4 | 28 | 82.4 |
| **Canmet STSD-1** | 11 | 8.8 | 59 | - |
| **Canmet STSD-3** | 23 | 19.5 | 60 | - |
| **Canmet TILL-1** | 15 | 9.5 | 59 | - |
| **Canmet TILL-2** | 47 | 34.7 | 59 | - |
| **Canmet TILL-3** | 21 | 16.6 | 56 | - |
| **Canmet TILL-4** | 30 | 20.0 | 41 | - |

**Table 2. Compilation of certified and reported concentrations for Li in reference materials analysed as part of GSI regional geochemistry programmes**

## 7. Distribution of Li in stream sediments and rocks in southeast Ireland

The distribution of Li in stream sediments and rocks in southeast Ireland is illustrated by reference to GSI's 1:500,000-scale bedrock geology map of the region (Figures 1 and 2). There is a cluster of strong Li anomalies over the Northern pluton and the southern end of the Tullow pluton (Figure 3). Many samples from streams draining the Blackstairs and Lugnaquillia plutons also have Li contents exceeding the 75 percentile value of 68 ppm. There are very few positive Li anomalies (> 95$^{th}$ percentile, 135 ppm) outside the boundaries of the Leinster Granite. Stream sediments overlying most of the areas underlain by Lower Palaeozoic metasedimentary and metavolcanic rocks typically have intermediate Li concentrations (25$^{th}$ – 75$^{th}$ percentile, 36 – 68 ppm), although the former generally have significantly more Li than the latter. Sediments in streams draining the Cambrian Bray and Cahore Groups and Silurian Kilcullen Group in west Wicklow samples have strikingly low Li contents, as have samples underlain by the Croghan Kinshelagh-Annagh Hill granite-dolerite complex. Sediments overlying the Tullow pluton as a whole have lower concentrations, reflecting very low values over the western half of the pluton, where the thick overburden comprises tills dominated by limestone clasts. Concentrations of stream sediment Li anomalies along the eastern margin of the southern part of Tullow pluton are found downstream of the Seskinnamadra and Coolasnaghta Li pegmatite occurrences (Figure 1). The Monaughrim, Moylisha and Stranakelly Li pegmatites also have attendant stream sediment signatures, although these are more muted than those further south. Only at Aclare, where the largest known Li pegmatite occurs, has no Li stream sediment anomaly been found, in keeping with previous findings (Steiger 1977). Tantalum (Ta), which occurs in the mineral columbite-tantalite, reported from Li pegmatites in southeast Ireland, is also well correlated with Li in the southeastern part of the Tullow pluton in the vicinity of Li pegmatite occurrences (Figure 4).

Data from rock samples are broadly consistent with stream sediment data (Figure 5), in that most of the observed high Li concentrations have been recorded in Leinster Granite samples whereas samples from clastic sedimentary units such as the Bray and Kilcullen Groups have relatively low Li concentrations. The necessarily selective and geographically restricted nature of rock sampling makes more detailed comparison between these datasets difficult. What seems clear from both stream sediment geochemistry and lithogeochemistry data is that the Leinster Granite is the major bedrock repository of Li in southeast Ireland. The Northern pluton rock samples have a median concentration of 235 ppm Li and those of the Tullow pluton a median of 288 ppm. The four Blackstairs pluton samples range from 85 to 333 ppm Li. The Tullow pluton data are significant in the light of the low Li concentrations recorded in stream sediments over the western half of this pluton, reinforcing the view that stream sediments here do not sample the granite so much as its overburden, some of which has been derived from the Carboniferous terrain to the west. The median Li content of minor granitoids, including the Ballinglen microtonalites, is 43 ppm, close to the crustal clark value for granites. The Croghan Kinshelagh granite has a very low median Li content of 6 ppm, consistent with the cluster of low stream sediment values centred on this pluton.

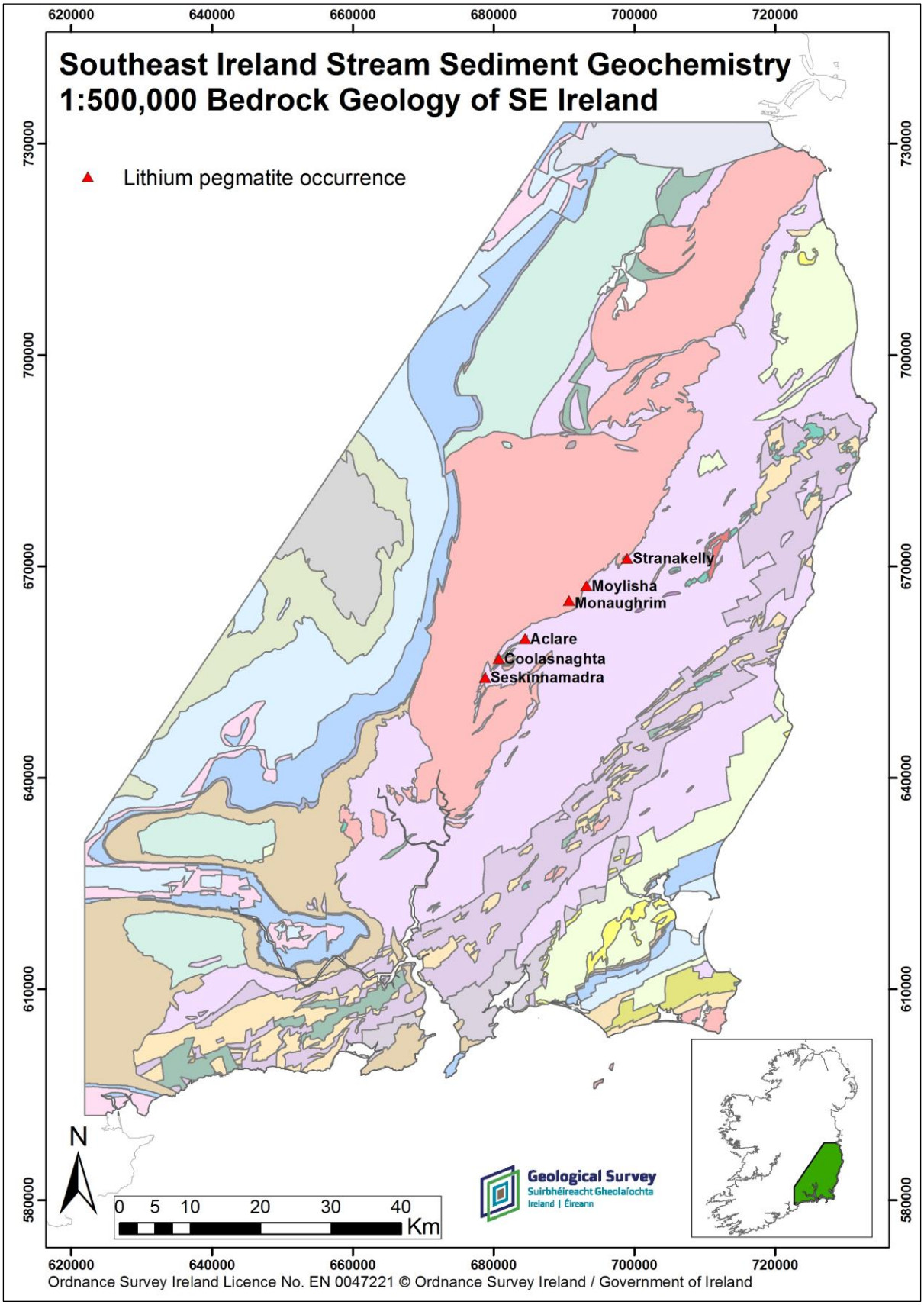


**Figure 1. Bedrock geology of southeast Ireland (1:500,000 scale) with location of Li pegmatite occurrences mentioned in text (See Figure 5 for legend)**

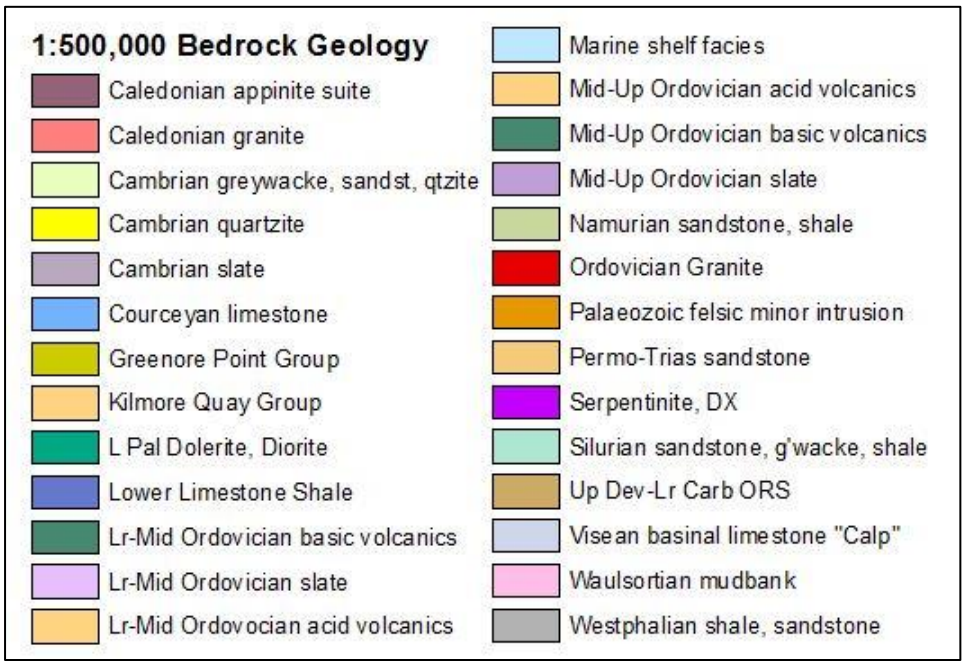


**Figure 2 Legend to Bedrock Geology of southeast Ireland (1:500,000 Scale).**

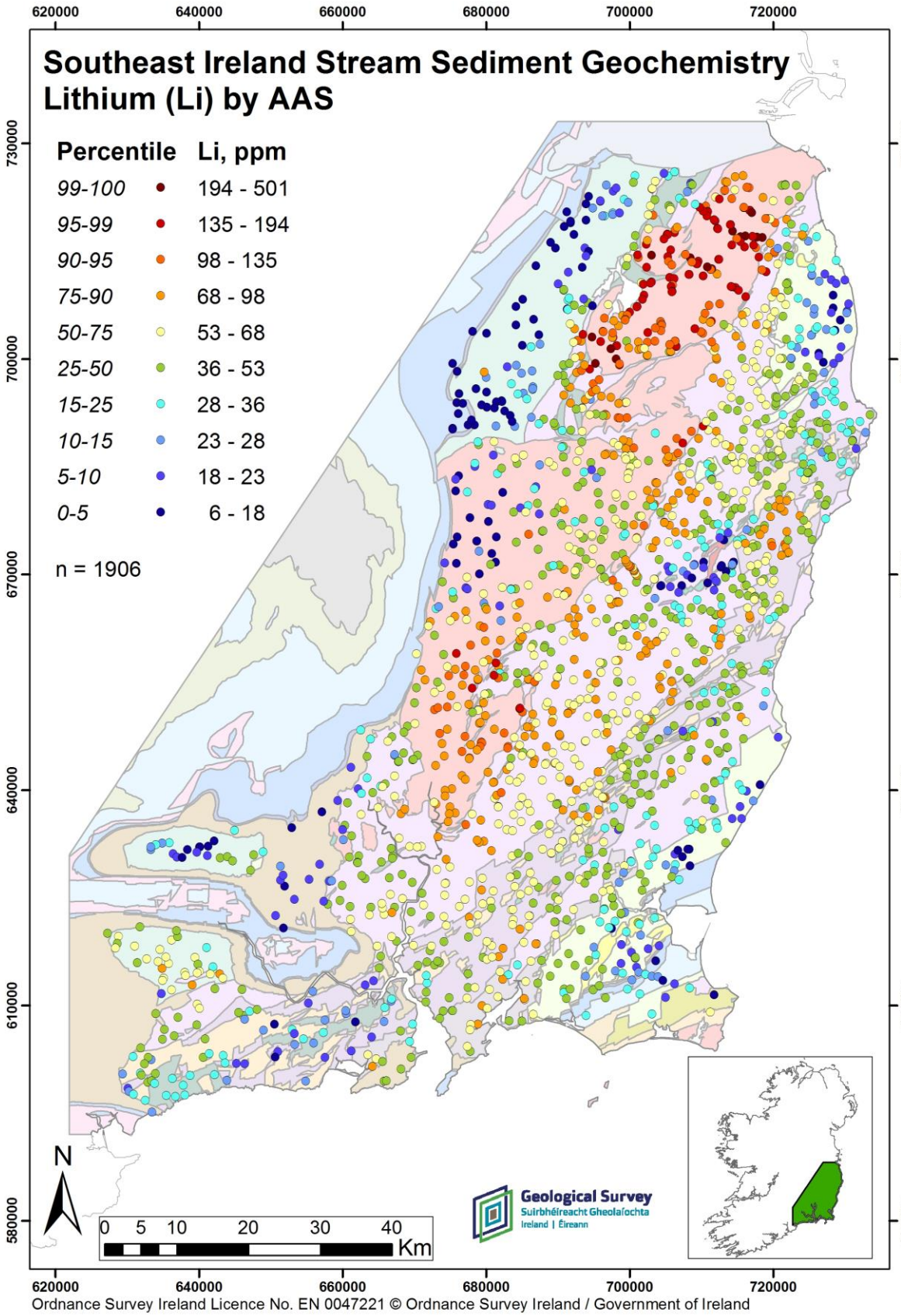


**Figure 3. Distribution of Li in stream sediments in southeast Ireland, on GSI 1:500,000 Bedrock Geology map (see Figures 1 and 2)**

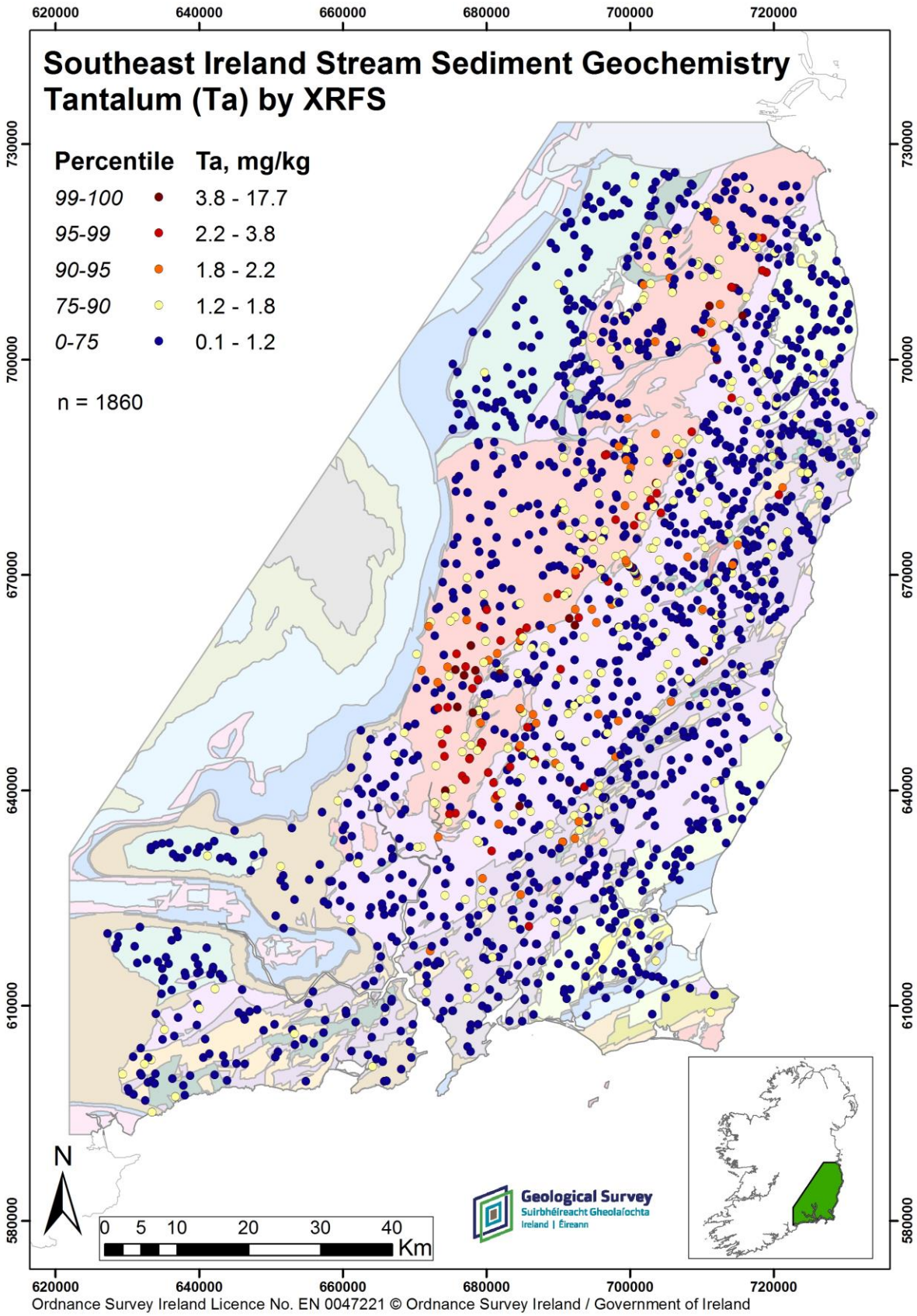


**Figure 2. Distribution of Ta in stream sediments in southeast Ireland, on GSI 1:500,000 Bedrock Geology map (see Figures 1 and 2)**

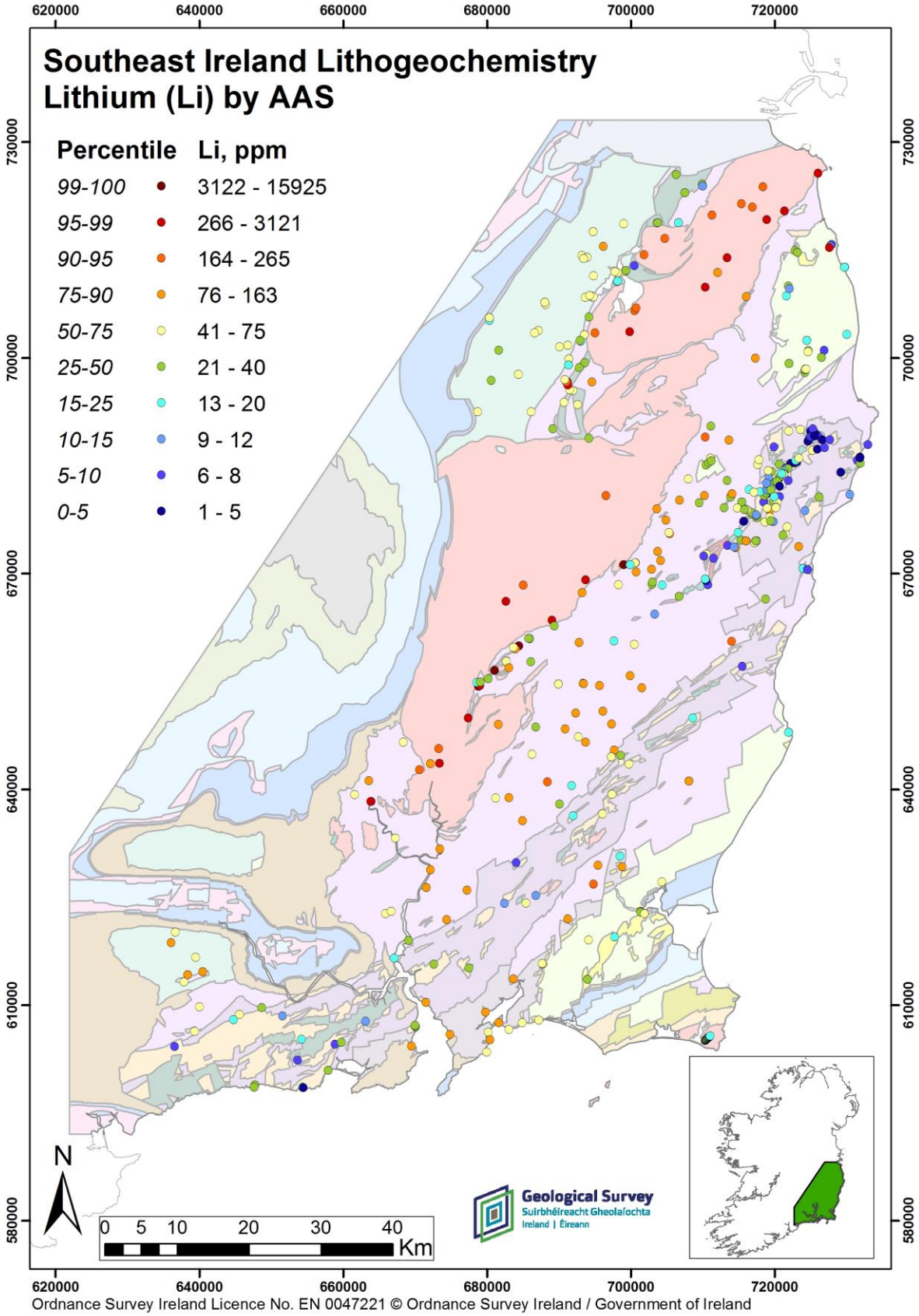


**Figure 3. Distribution of Li in rock samples in southeast Ireland, on GSI 1:500,000 Bedrock Geology map (see Figures 1 and 2)**

## 9. References

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