An Roinn Comhshaoil, Aeráide agus Cumarsáide
Department of the Environment, Climate and Communications

Geological Survey
Suirbhéireacht Gheolaíochta
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Geochemical characterization of the Dublin Boulder Clay

Geological Survey Ireland Report 2022

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Gallagher, V., Lilburn, S., Fitzsimons, M. and Symons, J. (2022) Geochemical Characterization of the Dublin Boulder Clay. Geological Survey Ireland report.

Acknowledgements

The authors wish to thank the following companies that volunteered geochemical data in support of this study: Causeway Geotech Ltd, Geosyntec Consultants, Inc., Malone O'Regan Consulting Engineers, Minerex Environmental Ltd and Verde Environmental Group. The authors gratefully acknowledge Stuart Huskisson (Environmental Protection Agency) and colleagues at Geological Survey Ireland (Ray Scanlon, Sophie O'Connor, Clare Glanville and Michael Sheehy) for their review of this report.

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Executive Summary

Ireland is transitioning to a circular economy – one in which our environment will be protected and restored through sustainable resource use (Dept. of the Environment, Climate and Communications 2021). Previous collaboration between Geological Survey Ireland (GSI) and the Environmental Protection Agency (EPA) established Geochemically Appropriate Levels (GALs) for 8 metals/metalloids in soil for Soil Recovery Facilities (SRFs) (Glennon *et al*. 2020). The project recommended that further study be carried out to geochemically characterize the deep, stiff lodgement tills that predominate across the Greater Dublin area, as this material accounts for a large volume of material being excavated from Dublin and moved to SRFs. The geochemistry of these subsoil deposits, known colloquially as the Dublin Boulder Clay (DBC), is poorly understood but there have been anecdotal reports of anomalously high concentrations of some elements, including molybdenum, antimony and selenium. This follow-on study addresses the question of whether the DBC has anomalous geochemical concentrations compared to surrounding soils and informs its management within the soil waste regime.

This project compiled third-party environmental investigation data, directly from the private sector and from published Environmental Impact Assessment Reports, as well as GSI's National Geotechnical Database. The DBC data have been examined with respect to data quality, data distribution, geospatial patterns and vertical variation and have also been compared with quality-controlled, systematically-collected data available from GSI's Tellus survey. The DBC data are not accompanied by detailed quality control data that would enable a thorough evaluation of their quality. Moreover, several elements, notably Mo, Sb and Se, are reported with a high proportion of data below the limit of analytical detection, further limiting the scope for data interpretation. Nevertheless, the database does allow for generation of basic statistics for several key elements, identification of broad trends in the data, and semi-quantitative/qualitative comparison of the DBC with other datasets.

The analysis suggests possible ranges of concentrations for arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), copper (Cu), molybdenum (Mo), nickel (Ni), lead (Pb), vanadium (V), and zinc (Zn), which give an impression of the geochemical character of the DBC, using different statistical methods. It was not feasible to define such concentration ranges for mercury (Hg), antimony (Sb) or selenium (Se), as the analytical quality of the data for these elements was generally poor. In general, typical element concentration ranges calculated for the DBC are comparable to those estimated for soils in the Greater Dublin region and do not suggest that the DBC has a composition that is intrinsically enriched in the elements of interest. The geochemistry of the DBC, as reflected in the database compiled for this work, most closely resembles regional Tellus soils classified as Irish Sea till (particularly IrSTLs) and till with dominant limestone clast composition. Thus, the DBC composition largely reflects geogenic influence. An example is the relatively high Cd concentrations in the DBC, which reflect the influence of Carboniferous 'Calp' limestone and shale clasts on its geochemistry. Higher quality analytical data than available for this compilation are required to determine if Mo, Sb and Se are present in the DBC in concentrations greater than soils in the surrounding region. Further analyses using the low detection limits typical of modern ICP-MS analysis are necessary if this question is to be successfully addressed.

Recommendations for further study include the collection of high-quality deeper subsoil data for subsoils underlying Dublin, and comparison of Dublin Boulder Clay geochemistry with the forthcoming Tellus urban geochemical survey.

1. Introduction

1.1. Background

Ireland is transitioning to a circular economy – one in which our environment will be protected and restored through sustainable resource use (Dept. of the Environment, Climate and Communications 2021). Collaboration between Geological Survey Ireland (GSI) and the Environmental Protection Agency (EPA) in 2019/20 established appropriate trigger levels for metals for acceptance of uncontaminated soil and stone at waste-licensed Soil Recovery Facilities (SRFs) (Glennon *et al.* 2020). As part of the SRFs study it was assumed that soil and stone with similar geochemistry to that of soil in the vicinity of a given SRF could be admitted to the facility with minimal risk to receptors (down-gradient aquifers). Thus, Geochemically Appropriate Levels (GALs) were established for a range of elements in seven separate domains, reflecting the natural geochemical variation observed in geological materials across Ireland.

The GALs were established on the basis of the National Soil Database (NSDB) (Fay *et al.* 2007), which is a survey of rural topsoil and therefore did not include samples from urban Dublin. It was recommended that further study be carried out to geochemically characterize the deep, stiff lodgement tills that predominate across the Greater Dublin area, as this material accounts for a large volume of material being excavated from Dublin and moved to SRFs. The geochemistry of these subsoil deposits, known colloquially as the Dublin Boulder Clay (DBC), is poorly understood but there have been anecdotal reports of anomalously high concentrations of some elements, including molybdenum, antimony and selenium. This follow-on study addresses the question of whether the DBC has anomalous geochemical concentrations compared to surrounding soils and informs its management within the soil waste regime.

1.2. Aims and Objectives

The aim of this project was to carry out an initial geochemical characterization of the tills of the Greater Dublin area, i.e. the DBC, to develop a better understanding of the chemical composition of these tills and determine whether previous reports of naturally elevated concentrations of some elements in the DBC have any evidential basis.

In order to address this, a desk-based investigation was carried out to:

- Scope the potential for determining ranges of concentrations of naturally-occurring elements in the DBC, representative of the typical geochemical signature of the material, from high-quality third-party subsoil geochemical data.
- Analyse the compiled data to assess whether the DBC is geochemically distinct from neighbouring soil and subsoil deposits.

1.3. Properties of the Dublin Boulder Clay

1.3.1. Quaternary geology

"Dublin Boulder Clay" (DBC) refers colloquially to the stiff-to-very-stiff, deep, poorly-sorted lodgement tills in the Greater Dublin area (Long and Menkiti 2007; Skipper *et al.* 2005; Farrell and Wall 1990). These tills overlie Lower Carboniferous argillaceous limestone bedrock of the Lucan Formation, known as 'Calp' (GSI 1:100,000 bedrock map sheets 13 and 16), and represent the primary superficial deposit in the region. Figure 1 shows the distribution of Quaternary sediments in the Greater Dublin region. The bedrock geology of the region is shown in Figure 2 for reference. The subsoil near the city is predominantly comprised of till derived from limestone. However, a significant geological feature of the city is the buried pre-glacial channel north of the River Liffey. This channel is up to 45 m deep and is infilled by variable, dense and in many cases saturated glaciofluvial gravels. It is not always possible to distinguish these gravels from the till (Long *et al.* 2012).

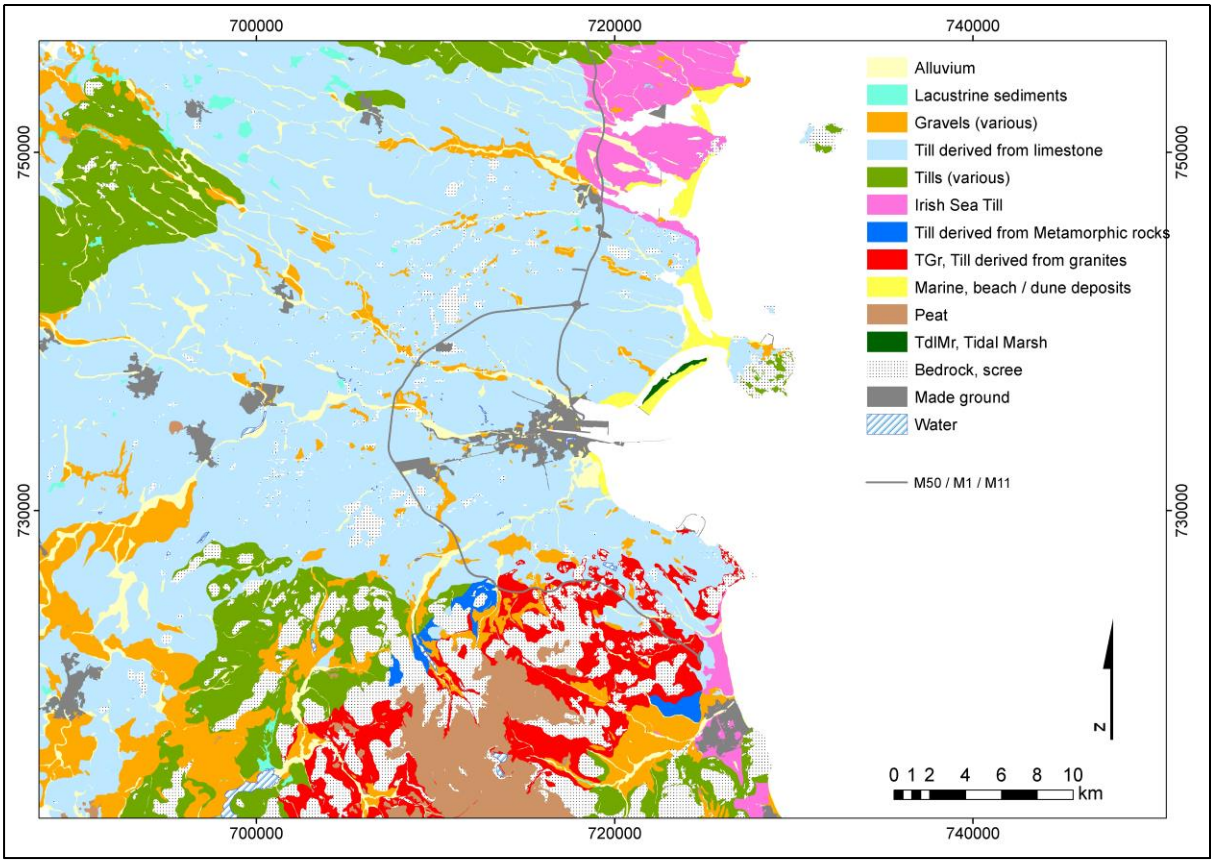


Figure 1 Quaternary sediments map of Greater Dublin area (simplified from Geological Survey Ireland 2022a).

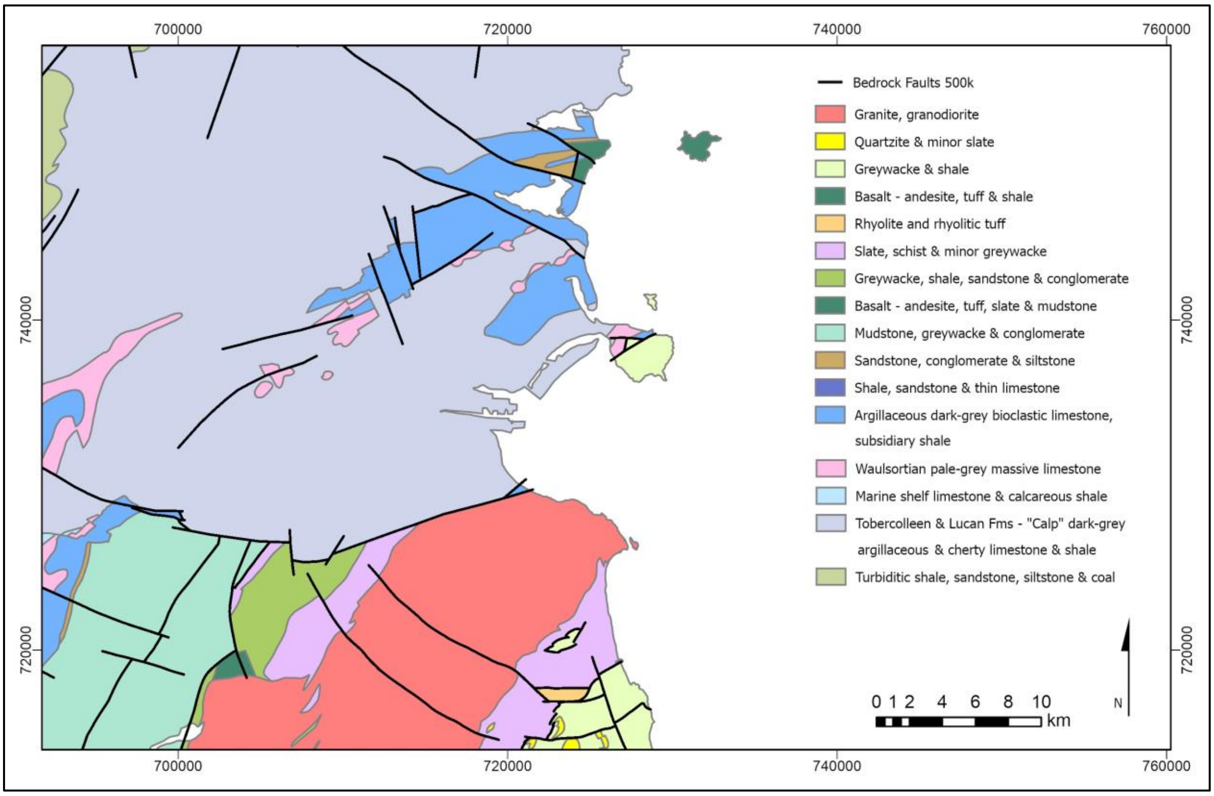


Figure 2 Bedrock geology map of Greater Dublin area (based on Geological Survey Ireland 2022b).

1.3.2. Physical/geotechnical properties

The work of Skipper *et al.* 2005 demonstrates the complexity of the DBC by identifying a range of discontinuities, lithological variability, glacio-tectonic rafting and the presence of large water-bearing units linked with the stratigraphy. The DBC is known to have a very low organic content and relatively high fines content, resulting in low permeability and increased stiffness and strength compared to other tills documented in the literature (Farrell 2016; Long and Menkiti 2007). Lenses of more permeable granular material are observed. In some units the gravel lenses and cobble lines constitute a network that appears to be hydraulically interconnected in some areas and hydraulically isolated elsewhere (Long and Menkiti 2007). Deep excavations for infrastructure projects such as the North Cut and Cover Section of the Dublin Port Tunnel have enabled the identification of four distinct units within the DBC, at least in the port area, namely the Upper Brown Boulder Clay, Upper Black Boulder Clay, Lower Brown Boulder Clay and the Lower Black Boulder Clay (Skipper *et al.* 2005).

Upper Brown Boulder Clay (UBrBC):

The uppermost unit, the UBrBc, has been observed to depths of 3 m below ground level (bgl) at the Dublin Port Tunnel North Cut and Cover Site. The UBrBC predates a brown podzol and has pockets of overlying loess suggesting its development in a period of climate warming following deposition of the underlying Upper Black Boulder Clay (UBkBC). It is a “stiff to very stiff, yellowish brown, slightly sandy slightly gravelly SILT/CLAY with some cobbles” (Skipper *et al.* 2005). The UBrBC has a similar particle size distribution to the UBkBC and it has been suggested that it is a weathering/oxidation product of the latter (Farrell 2016).

Upper Black Boulder Clay (UBkBC):

Deposits of “very stiff, dark grey to black, slightly gravelly slightly sandy CLAY with some cobbles” were found to be between 4.5 and 11.5 m thick at the Dublin Port Tunnel site (Skipper *et al.* 2005). A glaciotectonized contact was observed between this unit and the underlying Lower Brown Boulder Clay (LBrBC). Lenses contained granular material comprising up to 90% Carboniferous Limestone.

Lower Brown Boulder Clay (LBrBC):

This unit was found to be noticeably siltier and lighter in colour than adjacent UBkBC and LBkBC units (Skipper *et al.* 2005). Long and Menkiti (2007) referred to this units as a “5-9 m thick, hard, brown silty clay with gravel, cobbles and boulders.” The LBrBC contains a range of clasts, some originating in northeast Northern Ireland and Scotland along with which the presence of shell material suggests an Irish Sea glacial origin (Skipper *et al.* 2005).

Lower Black Boulder Clay (LBkBC):

The final unit is a highly fractured and sheared, 2-4 m thick, “hard, slightly sandy, gravelly clay with an abundance of boulders” (Long and Menkiti 2007). At the Dublin Port site, Skipper *et al.* (2005) noted a glaciotectonized basal contact with Carboniferous Limestone which appeared vulnerable to rafting.

1.3.3. Chemical properties of the Dublin Boulder Clay

The geochemistry of the Dublin Boulder Clay has not been systematically investigated in the literature, nor has Geological Survey Ireland systematically collected/mapped information on the geochemistry of the Dublin Boulder Clay. This study therefore relies on third-party data collected from a number of sources described below.

2. Methodology

2.1. Data Compilation

2.1.1. National Geotechnical Database

Geological Survey Ireland's National Geotechnical Database (Geological Survey Ireland 2022c) was searched systematically (approximately 5% of records) for digitized soil chemical testing data, avoiding sites on reclaimed land in the Dublin Port area and those in which testing was carried out primarily on marine sediments. Of the 100 site investigations examined, the vast majority dates from between 1960 and 1990; and only one site contained detailed inorganic chemical data for till or boulder clay useful for this study. Data for this site (n = 2) have been included in the study. However, given the low availability of detailed inorganic chemical data contained in the Geotechnical database, no further searching was carried out.

2.1.2. Private sector data

Environmental consultancies, geotechnical site investigation companies and soil waste management companies were invited to supply inorganic chemical data on the Dublin Boulder Clay, according to the following criteria:

- Quality-controlled, georeferenced geochemical data on DBC subsoil (preferably uncontaminated, but if this was undetermined, data would be accepted and assessed).
- Data to be accompanied by high-quality borehole/trial-pit observations to verify DBC identification and to record any observations of potential sources of contamination.
- Data to be depth-specific and from > 1 m in depth to minimize potential for anthropogenic contamination.
- Dry-weight elemental determinations (bulk) required with specified preparation, extraction and analytical methods. Leach test data (waste classification) were not required but would be considered in the absence of other data.
- Determinands to include as many as possible of As, Be, Cu, Cd, Cr, Hg, Mo, Sb, Sn, Se, Pb, V, Zn.
- Results to be reported in Excel form if possible but other data formats acceptable.

A total of 174 chemical analyses of borehole and trial pit material were received from Causeway Geotech Ltd, Geosyntec Consultants, Inc., Malone O'Regan Consulting Engineers, Minerex Environmental Ltd and Verde Environmental Group. The analysis was carried out using the Inductively Coupled Plasma (ICP) mass spectroscopy (MS) or Optical Emission Spectrometry (OES) analytical techniques, post acid/Aqua Regia digestion. Data were supplied in Excel (.xlsx) or PDF (.pdf) form and included most of the elements specified in the original criteria, with the exception of Sn. The data were added to a database (spreadsheet) containing, in the order as listed, the following columns, where applicable:

Sample_ID, Easting (ITM), Northing (ITM), Depth start (m), Depth end (m), pH, TOC/LOI/OM (mg/kg or %), As_mg/kg, Cd_mg/kg, Cr_mg/kg, Mo_mg/kg, Sb_mg/kg, Cu_mg/kg, Hg_mg/kg, Ni_mg/kg, Pb_mg/kg, Se_mg/kg, V_mg/kg, Zn_mg/kg, Ba_mg/kg, Be_mg/kg, B_mg/kg (Water Soluble), Cr_mg/kg (Hexavalent), Analytical method, Digestion method, Units, Layer Description, Comments and Data Source (borehole/trial pit number and document title).

Values below the laboratory method Lower Limit of Detection, reported as "< LLD" where "LLD" was a specific numerical value, were replaced with "- LLD" and any missing data ("N/A") were replaced with "-99" as placeholders. Site maps were georeferenced in a GIS and the locations of boreholes and pits were digitized. The co-ordinates of each borehole and pit, in Irish Transverse Mercator (ITM) format, were added to the database. An additional sheet in the database was created containing the laboratory LLDs for each element.

DBC was targeted but chemical data for made ground and non-boulder clay units observed and sampled in the same borehole/trial pit were included in the database for comparison with DBC.

2.1.3. Data from EIS/EIAR

Environmental Impact Assessment Reports (EIARs) and Environmental Impact Statements (EISs) pertaining to developments in the Greater Dublin area were retrieved from the following sources:

- An Bord Pleanála: https://www.pleanala.ie/publicaccess/EIAR-NIS/
  All records available, i.e. those for the period 09/06/21 – 28/06/21, were consulted. The specified dates refer to the listing on An Bord Pleanála's website but the submissions covered typically refer to submissions made over the preceding years.

- National Paediatric Hospital Development Board – New Children's Hospital: https://www.nchplanning.ie

- Dublin City Planning Application (Map Search): https://mapzone.dublincity.ie/MapZonePlanning/MapZone.aspx?map=PlanningApplication&search=Plan_Ref&tooltip=Plan_Ref
  Projects subject to an EIA were searched for within the "Granted" layer.

- South Dublin County Council: https://www.sdcc.ie/
  Search term: "EIS"

- Department of Housing, Local Government and Heritage EIA Portal: https://housinggovie.maps.arcgis.com/apps/webappviewer/index.html?id=d7d5a3d48f104ecbb206e7e5f84b71f1

- Fingal County Council: https://www.fingal.ie/council/service/planning-applications-environmental-impact-assessment-report

Sites were initially screened for the potential presence of Dublin Boulder Clay using the GSI Quaternary Geology map viewer (Geological Survey Ireland 2022a), "Subsoil Geology" descriptions in the corresponding EIAR/EIS main text under the chapter heading "Land, Soils and Geology"(or similar) and descriptions of the sampled materials in the accompanying borehole/trial pit records. These descriptions were checked against existing information on the DBC as documented in the literature (section 1.3). More descriptive terms than "DBC" were frequently encountered and included "cohesive deposits," "glacial deposits" or "till derived from limestones."

The "Environmental Laboratory"/"Chemical Testing" records were located in the appropriate chapter or appendix of the EIAR/EIS reports and the data suitability was assessed in respect of the specifications outlined above (section 2.1). 305 chemical data points were added to the database as above.

2.1.4. Summary of data collected

Figure 3 shows the spatial distribution of points in the DBC database. A total of 479 observations, 174 from contacted companies and 305 from EIS/EIAR reports, including two from GSI's National Geotechnical Database, were collected, of which 217 were identified as Dublin Boulder Clay, based on descriptions in accompanying borehole logs. Material described as "till", "boulder clay" or "clay" was assumed to be Dublin boulder clay. The database also included 172 made ground, 16 gravel, 2 sand, 10 silt/clay and 1 peat record, as well as 61 records for which no soil type could be assigned. The latter included samples for which the borehole/trial pit logs had no accompanying unit descriptions, samples from units identified as clay but with "possible made ground" included in the description, and from units described as "sandy gravelly clay" that did not match the typical DBC description (e.g. were softer or lighter in colour than would be expected of DBC).

The non-DBC observations were included in the DBC database to provide a context within which the concentrations of elements of interest in the DBC could be assessed and to investigate downhole variations in concentration with depth (section 2.4) through multiple subsurface layers. Where elements typically associated with anthropogenic contamination were present in high concentrations at shallow depths in the DBC, for example, it was useful to compare these concentrations to those present in the overlying made ground to investigate potential sources of the elements.

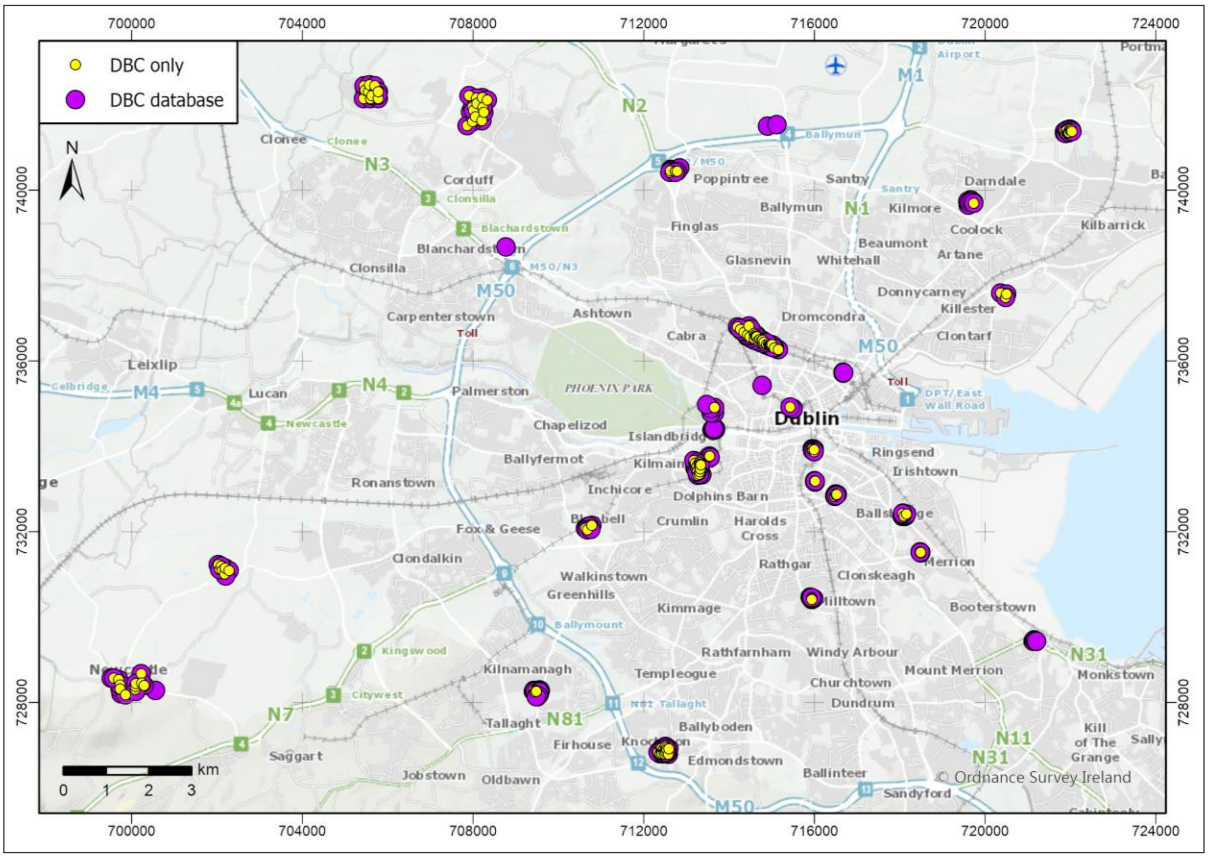


Figure 3 Locations of points in DBC database [ITM co-ordinates].

2.2. Quality Assessment and Data Preparation

The dataset lacks a systemic quality control scheme, including, for example, field duplicates, analytical replicates and analytical standards/reference materials, that would allow a detailed examination of the quality (accuracy, precision) of the dataset to be carried out. However, lower limits of detection (LLDs) have been examined and treated as follows to prepare data for analysis. Statistical analyses were carried out in iOGAS™ and Microsoft® Excel® (version 14.0.7188.5002 for Microsoft Office Professional Plus 2010). ArcGIS™ Pro (version 2.6.1) was used for mapping and spatial data analysis.

The samples reported in the DBC database were analysed by eight different laboratories and the LLDs for individual elements varied between them (Table 1). To facilitate a quantitative comparison between these datasets and Tellus data, entries in the DBC database for which the concentration of a given element is reported as "< LLD" were censored by replacing "< LLD" with a value equal to 0.5*LLD for analyses conducted at ALS Minerals Ltd. This gave a single set of censored values across all of the datasets. The ALS LLDs and censored values are detailed in Table 2. Missing data (entered as "-99" in the DBC database) were excluded from the analyses.

There is a high proportion of censored values in the DBC for Hg (91%), Sb (41%), Se (14%) and Mo (8%) (Table 3). The high proportions of censored values can be attributed to a detection limit that is high compared to the observed range of the element in question.

Laboratory	ALS Minerals Ltd	ALcontrol Laboratories	Chemtest Ltd	Element Materials Technology	Exova Jones Environmental	Geochem Group Ltd**	Jones Environmental Laboratory	STL CAS (Severn Trent Laboratories Ltd)
As	0.01	0.5	1	0.5	0.5	1	0.5	?
Ba	0.5	1	10	1	1	1	1	?
Cd	0.001	0.5	0.1	0.1	0.1	1	0.1	?
Cr	0.01	1	1	0.5	0.5	1	0.5	?
Cu	0.01	1	0.5	1	1	1	1	?
Hg	0.004	0.3	0.1	0.1	0.1	1	0.1	0.2
Mo	0.01	1	2	0.1	0.1	1	0.1	?
Ni	0.04	1	0.5	0.7	0.7	1	0.7	?
Pb	0.005	1	0.5	5	5	1	5	?
Sb	0.005	1	2*	1*	1*	X	1*	?
Se	0.003	0.5	0.2	1	1	1	1	?
V	0.1	X	5	X	X	X	1*	X
Zn	0.1	1	0.5	5	5	1	5	?

Table 1 Lower Limits of Detection (mg/kg) for elements of interest as analysed in each laboratory.
*** Not accredited; ** Accreditation unknown; X Element not analysed; ? LLD not reported.**

	As	Ba	Cd	Cr	Cu	Hg	Mo	Ni	Pb	Sb	Se	V	Zn
0.5*LLD (ALS)	0.005	0.25	0.0005	0.005	0.005	0.002	0.005	0.02	0.0025	0.0025	0.0015	0.05	0.05

Table 2 Censored values (mg/kg) to replace all data reported as "< LLD," equal to half of the LLD reported by ALS Minerals Ltd.

		As	Ba	Cd	Cr	Cu	Hg	Mo	Ni	Pb	Sb	Se	V	Zn
DBC Database	Total	474	380	474	474	465	465	444	465	474	428	465	79	474
	Censored	6	0	9	0	0	364	34	0	1	144	115	0	0
	% censored	1	0	2	0	0	78	8	0	0.2	34	25	0	0
DBC Only	Total	214	179	214	214	214	214	206	214	214	192	214	40	214
	Censored	1	0	0	0	0	194	16	0	0	78	30	0	0
	% censored	0.5	0	0	0	0	91	8	0	0	41	14	0	0

Table 3 Total number of records collated in the DBC database, and of DBC only, for each element and the number of censored records for each.

2.3. Basic Statistics and Exploratory Data Analysis

Basic summary statistics were calculated for the DBC (Table 4), including % censored values, minimum, maximum, median and several upper range estimators including 90th, 95th, 98th percentiles and the Upper Whisker for most elements. Determination of characteristic concentration ranges is not feasible for some elements in the database, specifically Hg, Sb and Se, for which the data have too many non-detects (Hg, Sb) or the reported concentrations are unreliable (Se) owing to being typically at, or close to, the LLD.

Various exploratory data analysis (EDA) approaches have been taken to establishing geochemical thresholds or background values for soil and other media (e.g. Reimann *et al.* 2005; Ander *et al.* 2013; McIlwaine *et al.* 2014; Reimann *et al.* 2018; Glennon *et al.* 2020), including the 90th, 95th or 98th percentile values, the Upper Whisker value, break values in cumulative frequency plots and even the median value (50th percentile). The Upper Whisker value is calculated as:

75th percentile + (IQR * 1.5)

Where the IQR is the interquartile range, the difference between 75th and 25th percentile values (Figure 4). The Upper Whisker value has been used in Finland to define regional geochemical baseline values, calculated as the upper limit of geochemical variation within the region (Jarva *et al.* 2010). The Upper Whisker value incorporates the bulk of the range of measured concentrations, excluding the upper outliers that may be considered to be anomalous values, perhaps reflecting unusual processes such as anthropogenic contamination. Its value is a function of how the data is distributed and, as a measure of background concentration or a threshold value, it embodies perhaps a more robust approach than selection of an arbitrary percentile value.

In summary, the aim of most of these approaches has been to define threshold values that mark the boundary between "normal" values and unusually high or low values in a dataset. These can be characterized as distinguishing between "background" and "anomalous" values, e.g. as in mineral exploration, or between "usual" and "unusual" values. In statistical terms, most approaches seek to identify a threshold above or below which outliers are present in the dataset.

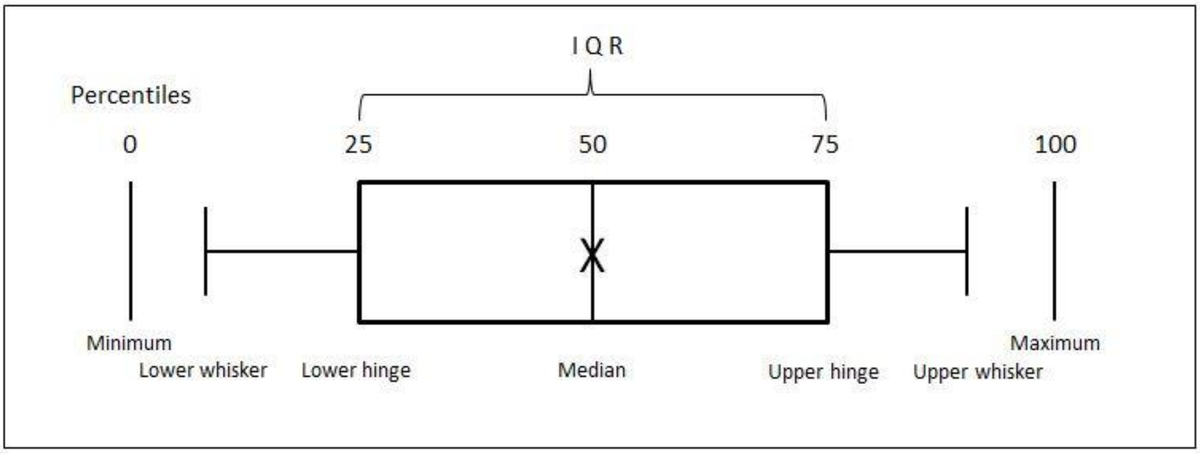


Figure 4 Tukey boxplot

A key consideration when defining threshold values is the purpose to which the values will be put. For example, in the case of identifying possible mineral exploration targets or potentially contaminated sites with a view to remediation, the aim could be to identify only the uppermost outliers, limiting the number of sites to be assessed in line with budgetary and manpower constraints. In such a case, threshold values could be set at a relatively high level. Where the aim is to minimize potential risks to the environment in the context of adopting a conservative approach to environmental protection, lower threshold values may be more appropriate. Where the aim is to define values that are typical of a given medium (soil, water, sediment, rock, etc.) within a specific context, e.g. a region or a geological unit, then the approach is likely to involve defining a threshold above which values are considered to be outliers.

Considering the term "Dublin Boulder Clay" is frequently used to describe a poorly-defined, complex material which could comprise several of the individual units described in section 1.3.2., it is not feasible to define a single concentration for a given element that is to be considered the "baseline" or "background" value for that element in the DBC. It is more practicable to determine a range of concentrations for each element that represents the typical geochemical character of the "bulk" material referred to as DBC, while accommodating its inherent compositional diversity.

mg/kg	As	Ba	Cd	Cr	Cu	Hg*	Mo	Ni	Pb	Sb*	Se*	V	Zn
DBC													
n (Total)	214	177	214	214	214	214	206	214	214	192	214	40	214
n (Censored)	1	0	0	0	0	194	16	0	0	78	30	0	0
% Censored	0.5	0	0	0	0	91	8	0	0	41	14	0	0
Min	0.005	30.	0.39	2.90	7.9	0.002	0.005	12.70	5.50	0.0025	0.0015	5.00	29.0
Max	94.00	582	7.70	79.70	108	4.600	11.20	121.00	16,710	37.00	12.00	46.00	541
Median	17.00	76	1.70	28.05	25.0	-	3.60	40.10	22.50	2.00	1.40	24.00	84.0
25 %ile	10.28	52	1.40	17.10	20.0	-	2.60	34.98	16.00	-	-	20.25	67.00
75 %ile	22.00	111	2.32	42.03	32.0	-	4.40	47.60	31.25	-	-	30.00	111.5
90 %ile	27.50	162	2.95	53.60	42.5	-	5.70	64.50	48.0	-	-	37.90	162.0
95 %ile	30.0	213	4.20	60.0	54.2	-	6.50	74.9	89.2	-	-	45.6	200
98 %ile	46.9	290	5.30	71.8	64.8	-	8.50	95.5	219	-	-	46.0	366
Upper whisker	39.6	199	3.70	79.4	50.0	-	7.10	66.5	54.1	-	-	44.6	178

Table 4 Summary statistics for DBC samples. *Estimation of summary statistics and the upper bound of the characteristic concentration ranges is not feasible for some elements due to data quality issues.

2.4. Statistical Comparison of DBC and Tellus Data

Data compiled in the DBC database were merged with Tellus Regional and Periurban Deeper Topsoil 'S' data (ICP-MS/OES analysis following Aqua Regia digestion) to allow concentrations of the elements of interest in the DBC and overlying made ground to be compared to those measured in samples representative of neighbouring soils and materials with different geochemical signatures. The Tellus soil samples were classified by Quaternary parent material and provide a context within which the geochemistry of the DBC may be used to assess its geological and geochemical affinities. It is acknowledged, however, that the Tellus samples were collected from a depth of 0.35 – 0.5 m below ground level (bgl) whereas samples from depths > 1 m bgl were targeted for DBC data, although not all DBC samples are from depths > 1 m. It is also the case that the Tellus data coverage across Greater Dublin is limited to the periurban area (outside of the M50 motorway) while many of the DBC samples were collected from the inner city. All Tellus samples were analysed by ALS Minerals Ltd (Ireland). Tukey boxplots (Tukey 1977) were generated in iOGAS™ to compare the geochemistry of samples identified as DBC to that of made ground and Tellus Regional/Periurban S-soils using a number of classification schemes, detailed below.

Note that in the following, "DBC" refers to units identified as Dublin Boulder Clay based on descriptions in borehole/trial pit logs. "Made" refers to units identified as made ground in borehole/trial pit logs. "DBC database" refers to all data compiled in the database, whether received from companies or extracted from EIARs/EISs, and includes DBC, made ground, silt, clay, sand and gravel units.

In order to investigate the geochemical signature of the DBC, the following classifications were applied to Tellus Regional and Periurban 'S' soils data for comparison with data in the "DBC" and "Made" classes of the DBC database:

- *Quaternary Sediments*

  Generalized Quaternary sediment classes were created from the GSI Quaternary Sediments dataset (Geological Survey Ireland 2022a), by amalgamating individual classes as follows:

  Gravel – GDCSs, GGr, GLPSs, GLPSsS, GLs, GMp.
  Irish Sea Till – IrSTCSsS, IrSTLPSsS, IrSTLs.
  Till – TBi, TCh, TCSs, TCSsCh, TCSsS, TDCSs, TDCSsS, TDSs, TGr, TLCSsS, TLPCSsS, TLPDSs, TLPSs, TLPSsS, TLs, TLSCh, TMp, TNCSSs, TNSSs, TQz.
  Peat – BkPt, Cut, FenPt.

  Amalgamation was carried out to reduce the number of classes and allow generation of manageable comparative plots. The amalgamation was based largely on the nature of the Quaternary sediment – gravel, till or peat – with tills being subdivided into two sub-classes: Irish Sea Tills and other tills. Irish Sea Tills are known to have a distinct clast composition in comparison to other tills in the Dublin region (e.g. Skipper *et al.* 2005) and their chemistry also appears to be distinct (Glennon *et al.* 2020).

  Quaternary Sediment maps of the study area are shown in Figures 1, B.1 and B.2.

- *Quaternary Sediments - Selected tills and peats*

  The following selected till and peat classes from the GSI Quaternary Sediments dataset (GSI 2022a) were examined: IrSTLs, IrSTCSsS, IrSTLPSsS, TLs, TGr, TLPSsS, Cut, BkPt. These classes represent the major Quaternary sediment types found across the Greater Dublin area (Figure 1). Till classes were selected to facilitate a comparison of their chemistry with that of the DBC, which is itself a till, while the peat classes provide context and a common point of reference between the comparative plots of 'selected tills and peats' and those of the above (generalized) quaternary sediment classes.

- *Geochemical (SRF) Domain*

  Domains 1-7 from GSI's Geochemically Appropriate Levels for Soil Recovery Facilities dataset (Glennon *et al.* 2020). A map of the seven geochemical domains is given in Figure B.3 and is also available on GSI's Map Viewer (Geological Survey Ireland 2022d).

- *Database*

Tellus data were classified as either "Tellus Periurban" or "Tellus Regional" for comparison with DBC data. Note that in this instance 'Made' data, i.e. sample points in areas classified as made ground on the Quaternary sediments map, were not included. The survey areas corresponding to these Tellus databases are shown in figure B.4, with the locations of DBC data points included for context.

The following classifications were also applied to data in the DBC database (all data, i.e. not limited to "DBC" and "Made" classes). This information was collected from the original chemical testing reports and borehole/pit logs.

- *Laboratory* (at which chemical testing was conducted)

  Classes: ALcontrol, Chemtest, Element, Exova Jones, Geochem, Jones, STL.

- *Depth (start [m])*

  The start of the sample depth range was used here since not all samples had a defined 'end' or 'bottom' depth. Classes: 0.0 – 0.5 m, 0.5 – 1.0 m, 1.0 – 1.5 m, 1.5 – 2.0 m, 2.0 – 2.5 m, 2.5 – 3.0 m, 3.0 – 5.0 m, 5.0 – 7.0 m, 7.0 – 10.0 m.

2.5. Downhole Plots

Downhole plots (depth below ground level on Y-axis) were created in iOGAS™ for a subset of the DBC database in which at least three samples were taken from the same borehole/trial pit at different depths. The plots include data for DBC, made ground, sand & gravel and silt units (e.g. made ground overlying two DBC samples). Data for 25 boreholes from eight sites were included. The locations of the boreholes/trial pits for which these downhole plots were created are shown in Figure 5.

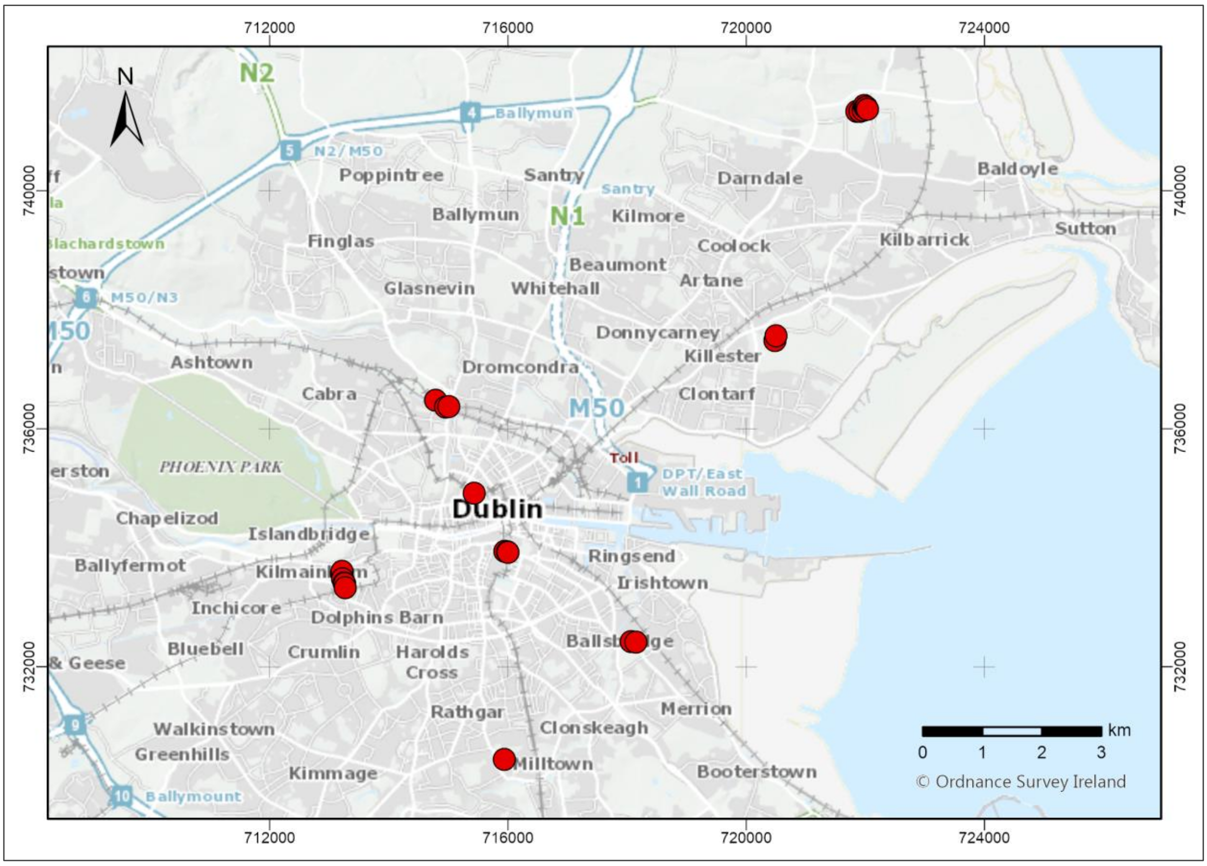


Figure 5 Locations of boreholes/trial pits for which downhole plots were created (red markers). [ITM co-ordinates].

2.6. Spatial Distribution

Data from the DBC database were imported into ArcGIS Pro as XY point data and classified by concentration for each element of interest, and by sample depth, to investigate possible lateral or vertical spatial trends in element levels across the study area. For mapping purposes, sample markers were dispersed where samples were taken at multiple depths from a single borehole/trial pit.

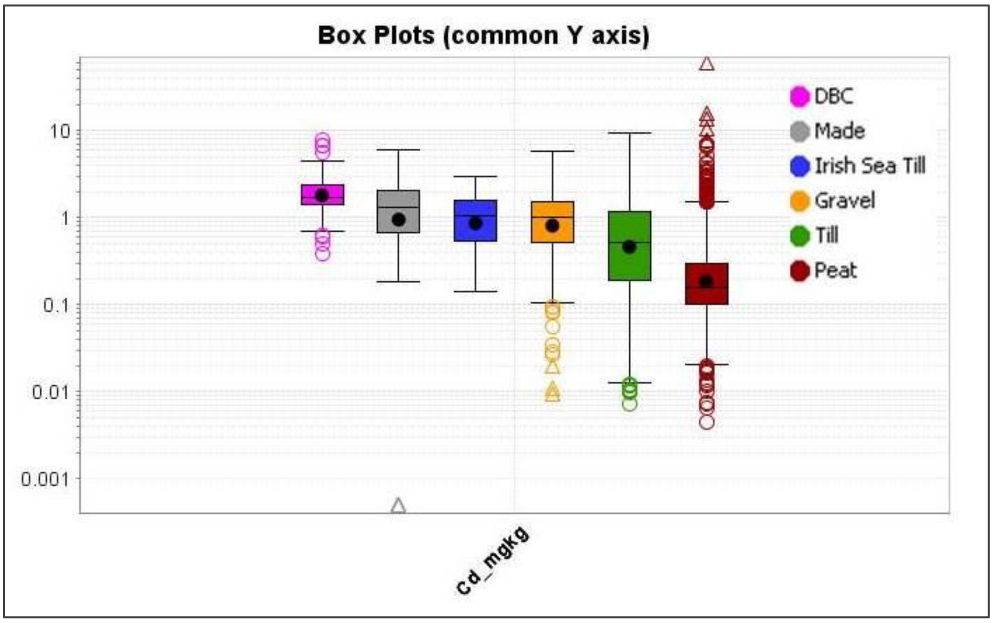
3. Results and Discussion

3.1. DBC and Made Ground v. Tellus Data for Quaternary Sediment Classes

The boxplots in Figures C.1 – C.13 compare concentrations of the elements of interest in the DBC and made ground classes of the DBC database with those in Tellus 'S' topsoil samples classified according to Quaternary sediment (subsoil) type (adapted from GSI Quaternary Sediments database). At a given location, the chemical composition of topsoil typically reflects the composition of subsoils which are in turn influenced by bedrock composition (shown for the Greater Dublin region in Figure 2) (Glennon *et al*. 2020). A comparison of the DBC data and Tellus topsoil data, classified by Quaternary sediment type, was carried out in order to assess potential compositional and geochemical affinities of the DBC. Made ground data were included in the comparison in order to determine whether the chemical composition of this material differs significantly from that of DBC, specifically whether it has higher concentrations of metals that might reflect anthropogenic contamination. EDA was undertaken to investigate the two datasets, principally through plotting boxplots and comparing median concentrations and interquartile ranges of elements across the soil types. The uncertainty associated with the DBC data precludes a more detailed quantitative analysis. Nonetheless some broad trends are apparent.

In general, DBC, made ground and Tellus S soils classed as Irish Sea Till have similar median values and similar, relatively narrow, ranges for many of the reported elements (Figures C.1–C.13). Tellus samples classed as gravel or other till types have similar or slightly lower concentrations. Only in the case of Cd and Mo (Figure 6) does DBC have higher median concentrations than all other soil classes (Table C.1). This may reflect the dominance of limestone clasts in DBC, given the known occurrence of high Cd and Mo concentrations in soils overlying Carboniferous Limestone bedrock, including Calp limestone and shale, in the eastern half of the midlands (Tellus 'S' samples; Figures A.3 and A.7). Similarly, made ground appears to have higher Pb than the rest, likely reflecting anthropogenic contamination associated with urban activities, as observed by Glennon *et al.* (2012). Median concentrations of all elements are typically significantly higher in the DBC than in peat, with the exception of Se, which presumably reflects the ability of organic matter to retain selenium (McGrath and Fleming 2008). Caution is required, however, concerning the reliability of Se data in the DBC database, given the relatively high LLDs reported (Table 2).

For the DBC database, the median and range of reported element concentrations in DBC closely resemble those in made ground samples for As, Ba, Cr, Mo, Ni, Sb and Zn (Figures C.1–C.13), albeit Sb data must be treated with caution given the relatively high LLD and attendant uncertainty. For Cu, Pb and V the concentrations in made ground are somewhat higher than those in DBC, whereas for Cd they are lower. Thus, samples classed as made ground do not appear to be markedly different in chemical composition to those classed as DBC, perhaps suggesting only limited anthropogenic contamination has been captured in these samples. Alternatively, if the chemical composition of made ground samples reflects contamination then the composition of the DBC may also be influenced by contamination.



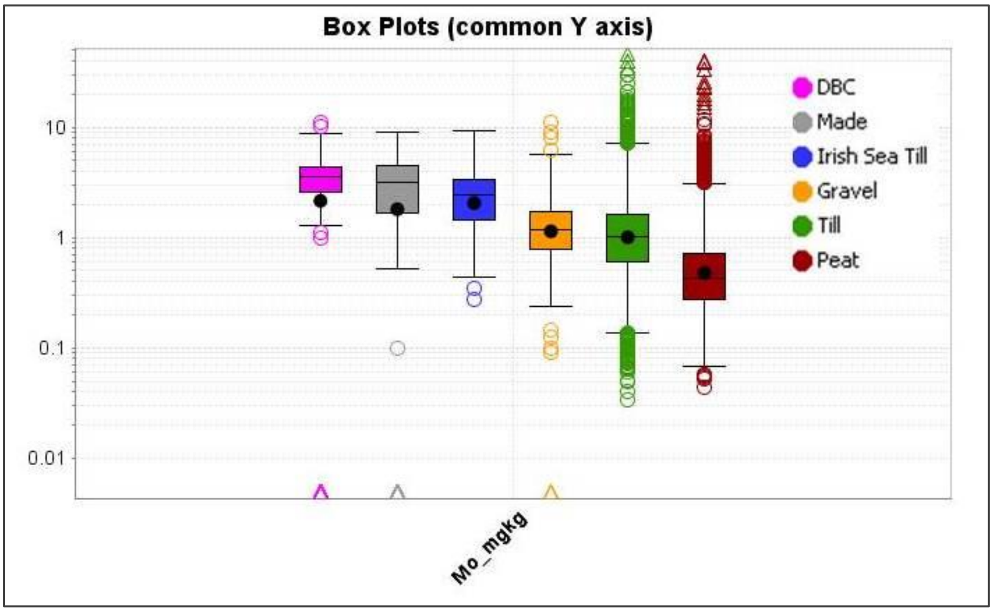


Figure 6 Tukey boxplots for DBC data (DBC and Made) and Tellus samples classified by Quaternary Sediment lithology showing the distribution of Cd (top) and Mo concentrations.

As noted above, DBC samples have a similar range of composition to that of Tellus samples classed as Irish Sea Till (Figure C.1 to C.13), at least for elements As, Cr, Cu, Mo, Ni, Pb and Zn. Tellus samples in other till classes and those classed as gravels tend to have somewhat lower element concentrations. This apparent similarity between DBC and Irish Sea Till is not unexpected given that at least some DBC has been identified as Irish Sea Till (Skipper *et al.* 2005). However, caution is needed when comparing the DBC data to Tellus data, given differences in sampling, analysis, etc., as well as the relatively low number of Tellus samples in some classes. A further complication is that Tellus Periurban samples generally have higher measured concentrations of many elements than the samples collected in rural areas (Tellus Regional samples) (see section 3.3). These differences are well illustrated in Tellus geochemical maps (Figures A.1 to A.13) and boxplots comparing DBC to Tellus Periurban and Regional samples (Figures C.27 to C.39).

Most Hg values reported for the DBC database samples (DBC and made ground classes) are below the LLD. Reported data might suggest that Hg concentrations are higher in made ground than in DBC and also lower in both of these classes compared to Tellus samples. However, the lower reported Hg concentrations in the DBC database may simply reflect improved analysis of Hg for Tellus samples, as reflected in much lower LLDs. In the case of Sb, the range of values in the DBC database classes (DBC and made ground) appears to have been affected by censoring (see Table 3). The LLDs for these data are significantly higher than for Tellus samples, rendering a comparison meaningless, but it is worth noting that Sb concentrations in Tellus samples classed as Irish Sea till are higher than for other Quaternary sediment classes.

3.2. DBC and Made Ground v. Tellus Data for Selected Tills and Peat

The boxplots in Figures C.14 – C.26 compare element concentrations in the DBC and made ground classes of the DBC database with those in Tellus 'S' topsoil samples for selected Quaternary sediment classes. These provide a more detailed comparison between DBC and topsoil classified by the major till types in the northern half of Ireland. They emphasize the similarity in chemical composition of DBC and Irish Sea Tills but there is also considerable overlap between DBC compositions and those for other till classes for many of the elements reported. This is particularly true for tills with a dominant limestone clast composition and tills with a dominant Lower Palaeozoic clast composition – granitic tills tend to have somewhat different compositions, typically with lower element concentrations compared to DBC. As previously noted, reported element concentrations for Tellus topsoil samples classed as peat are generally significantly lower than for DBC or other Quaternary sediment classes.

In detail, the peat and tills with dominant granite clasts (TGr) classes generally exhibit the widest range of concentrations for each element, while the tills with dominant limestone clasts (TLs) and dominant Lower Palaeozoic clasts (TLPSsS), despite covering a larger area geographically, are less varied in their geochemical composition but feature a large number of upper and lower outliers for most elements (Figures C.14 to C.26). Topsoil in the TGr and TLPSsS classes is generally compositionally distinct, with lower concentrations of Ba, Cd, Cr, Mo, Ni and Zn typical of the former and more variable concentrations observed in the latter.

The Tellus topsoil samples classed as tills with a matrix of Irish Sea Basin origin have limited geographic extent (see Figures B.1 and B.2) and correspondingly small sample sizes (e.g. n = 15 for IrSTLs). Their reported geochemistry does not vary greatly. Samples identified as DBC in the DBC database typically have a greater spread of concentrations than Tellus topsoil samples classified as Irish Sea tills but their composition is less variable than that of Tellus topsoil samples classed as limestone till. This latter class comprises all of the Tellus 'S' samples collected from areas of mapped limestone till in the northern half of Ireland (n = 2895). Areas of mapped limestone till occupy a significant portion of the study area (25 %). A closer look at median Cd concentrations in Tellus soils overlying Carboniferous limestone bedrock revealed significant variation within the TLs class. The median Cd concentration in Tellus samples overlying 'Calp' limestone is 1.3 mg/kg whereas those overlying Waulsortian limestone and Visean shelf limestone have median Cd concentrations of 1.0 and 0.54 mg/kg, respectively.

The made ground boxplots generally span a wider range of concentrations than those of the DBC, likely reflecting the highly variable composition of made ground and differing degrees of anthropogenic contamination. As before, the boxplots of Hg, Sb and, to a lesser extent, Se are affected by a large number of censored values.

Similarities between the geochemistry of the DBC and that of limestone till are expected given the prevalence of mapped Carboniferous limestone bedrock and tills derived from limestone across the Greater Dublin area and beyond, and the presence of granular lenses comprising up to 90 % Carboniferous limestone observed within the DBC during deep excavations (Skipper *et al.* 2005). However, element concentrations mirroring those typical of Irish Sea tills and tills derived from Lower Palaeozoic clastic sedimentary rocks are also consistent with the findings of Skipper *et al.* (2005) who reported the presence of shell material and a number of clasts originating from northeast Northern Ireland and Scotland in the LBrBC unit of the DBC.

3.3. DBC v. Tellus Regional and Tellus Periurban Data

The boxplots in Figures C.27 – C.39 compare data for samples identified as DBC with the Tellus Regional and Tellus Periurban data. The DBC and Tellus Periurban samples differ in both depth and location. The mean DBC sample depth ("depth start," i.e. top of sample) is 1.78 m bgl whereas Tellus 'S' samples are collected between 0.35 – 0.5 m bgl. The locations of DBC samples are shown in Figure 3 (yellow markers) - a large proportion of samples was collected within the area bounded by the M50. Tellus Periurban samples on the other hand were collected in the Greater Dublin area outside the M50 (n = 597) and across Galway city (n = 106).

With the exception of V, the Tellus Regional topsoil samples have the lowest median element concentrations of the three classes. Median concentrations of As, Cr, Mo, Sb and Se are highest in the DBC (albeit the data for Sb in DBC should be treated with caution given the relatively high LLD and high proportion of non-detects) while Ba, Cu, Pb, V and Zn concentrations are higher in Tellus Periurban samples than in the DBC. Median Cd and Ni concentrations in the DBC and Tellus Periurban samples are very similar. The proportion of censored Hg values in the DBC is too high to allow useful interpretation of the data. Care is needed when interpreting the data for periurban samples. These samples vary significantly in composition, reflecting variable subsoil and bedrock composition. In the Greater Dublin area, approximately two-thirds of samples are from sites overlying Carboniferous limestone or shale bedrock, with the remainder mostly underlain by granite or Lower Palaeozoic metasediments. As can be seen in Figures A.1 to A.13 these compositional variations can give rise to significant geochemical variation within the Dublin periurban area.

The data do not suggest that DBC samples have significantly higher concentrations of most elements than periurban samples, whereas periurban samples appear to contain higher reported concentrations of Pb, V and Zn. In the case of Mo, relatively low concentrations (median 1.50 mg/kg) of this element occur in the periurban topsoil samples to the south of Dublin city where they overlie bedrock of granite and Lower Palaeozoic metasediments, and include areas of blanket bog (Figure A.7). Periurban samples from areas with Carboniferous limestone bedrock have much higher Mo concentrations (median 3.25 mg/kg), closer to those reported for the DBC.

At least some of the reported element concentrations in periurban samples can be ascribed to diffuse anthropogenic contamination. Geochemical maps show that the highest concentrations of some elements in Dublin periurban samples occur closest to the M50, e.g. Cu, Hg, Pb, Zn (Figures A.5, A.6, A.9, A.13, D.5, D.8, D.11), but DBC data do not appear to suggest that soils within the M50 have higher concentrations of these elements, i.e. DBC samples do not display evidence of greater diffuse anthropogenic contamination than is suggested for periurban samples.

Elevated concentrations of Cu, Pb and Zn in the Tellus Periurban dataset compared to the DBC may be explained by the difference in sample depths. Cu, Pb and Zn are commonly associated with anthropogenic influences such as fossil fuel combustion and metallurgical and chemical industrial activities. SURGE, Geological Survey Ireland's Dublin urban geochemistry project (Glennon *et al.* 2012), found that, along with Hg, these elements were typically enriched in made ground relative to natural soils, with the highest topsoil concentrations observed in the city centre and the port area. The apparent lower median concentrations of these elements in the DBC samples, typically taken from greater depth in the soil profile, may thus reflect their higher concentrations in shallow topsoil and made ground, as may be expected of anthropogenic contaminants in shallow soil that is exposed to pollution sources.

3.4. DBC and Made Ground v. Tellus Data classified by SRF Domain

GSI undertook a geochemical domain-setting exercise as part of the SRF project (Glennon *et al.* 2020), dividing the country into zones or domains based on similar geochemical signature. This was undertaken by classifying the National Soil Database (NSDB) (Fay *et al.* 2007) into domains based on mapped subsoil type and bedrock type, as full national coverage of the higher-resolution Tellus soil data is not yet available. Seven SRF Domains have been defined on the basis of dominant bedrock type or subsoil composition as follows:

1. Domain 1 – Namurian shale and sandstone
2. Domain 2 – Carboniferous limestone and related rocks
3. Domain 3 – Devonian–Carboniferous sandstone and shale
4. Domain 4 – Devonian sandstone and shale
5. Domain 5 – Lower Palaeozoic sandstone, shale and igneous rock
6. Domain 6 – Granitic rock
7. Domain 7 – Schist, quartzite and gneiss

Although the DBC overlies the Lower Carboniferous limestone of the Lucan Formation and the Quaternary deposits across much of the Greater Dublin area are mapped as till derived from limestone, the boxplots for DBC data and Tellus samples classified by SRF Domain (Figures C.40 – C.52) suggest that the concentrations of some of the elements in the DBC, notably Ba, Cr and Cu, also resemble those of the Lower Palaeozoic sandstone, shale and igneous rock of Domain 5. Concentrations of Cd in DBC resemble those in Domain 2 while there is little difference between DBC and Domains 2 and 5 for Pb, Zn and Ni. The same trends can be observed where Tellus data is classified by Quaternary sediment type (Figures C.14 – C.26). As noted above, the DBC is compositionally similar in some respects to Irish Sea Tills – these tills contain a component of Lower Palaeozoic material so the overlap in composition between DBC and Domain 5 is unsurprising. Maps of Tellus geochemistry (Figures A.1 – A.13) display elevated concentrations of these elements in the Lower Palaeozoic rocks north of Dublin. By the same token, the similarity between DBC and Domain 2 for Cd reflects the relatively high Cd concentrations in soils overlying Carboniferous limestone and shale bedrock.

An additional factor to consider is that the SRF Domain classifications do not take account of the peat content of soils. In any SRF Domain, areas of peat are classified according to underlying bedrock. As we have seen in sections 3.1 and 3.2, the concentrations of the elements in peat are usually significantly lower than in the DBC and other mineral soils. Field observations indicate that 22 % of Tellus samples in Domain 2 were identified as peaty soils during collection, compared to 17 % of those in Domain 5. When peaty samples are excluded from the modelling, median Ba, Pb and Zn concentrations in the DBC are most similar to those in Domain 2.

The boxplots also show the Geochemically Appropriate Levels (GALs) for each SRF Domains for those elements included in the SRF analysis (As, Cd, Cr, Cu, Hg, Ni, Pb, Zn). The Dublin region is largely within SRF Domain 2 and, as can be seen from the boxplots, the bulk of reported data for DBC falls below the GAL for each element.

Landfill Waste Acceptance Criteria (WAC) testing (BS EN 12457-2, 10:1 leaching test) results were retrieved, where available, from the data supplied by the private sector and from the EIS/EIAR and geotechnical site investigation reports used to compile the DBC database of soil chemical data, in order to investigate the relationship between WAC exceedances and GAL exceedances. A total of 479 records (samples) were searched, each with leach test results for all of the elements of interest. In total, 83 WAC exceedances for inert landfill were observed, of which 43 were for Se, 16 for Sb, 15 for Hg, 5 for Mo and 2 for As. Two of the Se analyses and two of the Sb analyses also exceeded the WAC for stable, non-reactive hazardous waste in non-hazardous landfill, and one Sb analysis exceeded the WAC for hazardous landfill. Of the 83 leach test results for which an element concentration exceeded the inert WAC, only 17 could be compared to the corresponding solid soil concentration measured in a sample taken from the same borehole/trial pit at the same depth, to determine if the solid soil concentration would exceed the SRF Domain 2 GAL. This is because GALs are not defined for the elements Se, Sb and Mo, in which most of the WAC exceedances are observed. In 14 of the 17 WAC exceedances for which the corresponding GAL exists, the concentrations of the elements in the solid soil sample were below the GAL. It was also noted for all of the samples with leach test (WAC) and solid soil data, i.e. including Se, Sb and Mo, that while in many cases a relatively high solid soil concentration corresponded with a relatively high leach test concentration, this was not true in every case, and incremental increases in the solid concentration did not necessarily correspond to proportional changes in the leaching test concentration, or vice-versa. This result is not unexpected considering WAC testing is carried out on soil samples as they are received (provided at least 95 % of the sample by mass has a grain size < 4 mm; samples may be dried at a temperature no greater than 40 °C only where sieving or crushing of the sample to achieve such grain size is not possible due to its moisture content) and produces a leachate using deionised water in a 10:1 (liquid:solid) ratio (British Standards Institution 2002), whereas solid soil analysis is carried out on samples that have been pre-digested using an acid mixture, typically Aqua Regia.

3.5. DBC Database Classified by Laboratory

The boxplots in figures C.53 – C.65 compare the data for the DBC database classified by the laboratory that conducted the analyses. The range of elements analysed by each laboratory varies so data for all elements are not available for every laboratory. The number of DBC database samples analysed by each laboratory is given in Table 5.

Lab	Alcontrol	Chemtest	Element Materials Technology	Exova Jones Environmental	Geochem Analytical Services	Jones Environmental Laboratory	Severn Trent Laboratories (STL CAS)
n	5	172	43	69	2	187	1

Table 5 Number of samples in the DBC database analysed by each laboratory.

Concentrations of the elements of interest were compared between analytical laboratories to investigate the potential for the laboratory at which the soil samples were analysed to influence or bias the results and consequentially the observed trends or conclusions drawn. Examination of the boxplots does not suggest that any particular laboratory is consistently reporting concentrations that are significantly higher or lower than expected, and differences in laboratory lower limits of detection have not had a major impact on the range of concentrations reported. Aside from these observations, it is difficult to draw conclusions from this investigation for a number of reasons. Firstly, there is a significant disparity between sample sizes corresponding to each of the laboratories, as shown in Table 5, with Alcontrol, Geochem Analytical Services and STL laboratories each analysing ≤ 5 samples, in some cases only for a subset of the elements of interest. Secondly, samples from a given site were analysed together at one laboratory and there were no records of samples from one borehole, trial pit or site being analysed simultaneously in two or more different laboratories for quality control purposes or otherwise. Therefore, we cannot rule out the possibility that the composition of the material analysed in one laboratory differs significantly from that analysed in another.

3.6. DBC Classified by Sample Depth (start [m])

Depth [m bgl]	0 – 0.5	0.5 – 1	1 – 1.5	1.5 – 2	2 – 2.5	2.5 – 3	3 – 5	5 – 7	7 - 10
n	4	48	45	47	23	22	15	9	4

Table 6 Number of DBC samples collected from each range of sample depths. The ranges represent the depths between which the start of the sample intervals lie, as opposed to the sample intervals ('start' and 'end' depths) themselves.

Figures C.66 – C.78 show boxplots of element concentrations in the DBC classified by the depth below ground level (bgl) of the start of the sample interval. Despite the differences in sample size across the depth classes, several elements show a trend of decreasing concentration with increasing depth, namely As, Cu, Ni, Pb and Zn. Of these elements, Cu, Pb and Zn are commonly associated with anthropogenic influences, with elevated soil concentrations found in areas that have a history of heavy industry and human settlement (Glennon *et al.* 2012). Higher concentrations of these metals at shallower depths in the soil profile could be a result of atmospheric deposition as all of these elements can be introduced to the environment through combustion of fossil fuels such as diesel and coal. The GSI Dublin Soil Urban Geochemistry (SURGE) Project (Glennon *et al.* 2012) also found a notable enrichment of Cu, Pb, Zn and Hg in topsoil identified as made ground across the greater Dublin area. The relative enrichment of Cu, Pb and Zn at shallow depths in the DBC profile suggests possible leaching of heavy metals to the boulder clay from overlying made ground.

The data for Hg are inconclusive as over 90 % of the DBC data were reported as being below the detection limit. Sb data is also of limited use given that 40.6 % of all reported DBC data are below the detection limit. Sb data were also largely reported with a low degree of certainty, with typical concentrations of 1 – 3 mg/kg expressed only to the nearest mg/kg. While the boxplots of Ba and Cd could suggest a slight decrease in concentration with increasing depth, this perceived trend relies heavily on the two deepest classes (5 – 7 m bgl and 7 – 10 m bgl), which have small sample sizes of 9 and 4, respectively, limiting the reliability of the statistical treatment.

A series of downhole plots was also created to investigate potential trends in element concentrations with depth within individual boreholes, with the uppermost sample in each borehole being taken from material identified as made ground. No consistent downhole variation in concentration was observed for elements between made ground and DBC. The exceptions were Pb, which was generally higher in the overlying made ground than in the DBC (in 18 out of 24 boreholes).

3.7. Spatial Distribution

Maps showing only DBC data are presented in Figures D.1 – D.11 with sample site markers dispersed so that all values may be seen. These maps are presented for information purposes only. They do not reveal patterns that suggest any consistent spatial control of element concentrations in the study area. Direct comparison with spatial patterns revealed by Tellus maps (Figures A.1 – A.13) is not feasible given the lack of QC information to allow levelling of the datasets.

3.8. Geochemical Character of the DBC

Table 7 provides a statistical summary of DBC data, showing median values (50th percentile) for the various elements along with 90th, 95th and 98th percentile values and the Upper Whisker value. Determination of characteristic concentration ranges is not feasible for some elements in the database, specifically Hg, Sb and Se, for which the data have too many non-detects (Hg, Sb) or the reported concentrations are unreliable (Se) owing to being typically at, or close to, the LLD.

Table 7 also shows the GALs for both SRF Domain 2 (Carboniferous limestone and related rocks) and SRF Domain 5 (Lower Palaeozoic sandstone, shale and igneous rock). The DBC is within Domain 2 but, as discussed above, also bears comparison geochemically to Domain 5, and specifically to Irish Sea Till that includes Lower Palaeozoic material. While Table 7 suggests that the bulk of the data recorded for the DBC are below the GALs of one or both of these domains, it is important to emphasize that definitive background values for the DBC can only be determined on the basis of a detailed geochemical study, incorporating comprehensive QC measures for sampling and analysis. Thus, the various possible representations of the upper limit of geochemical variation in the DBC, presented in Table 7, should not be interpreted as definitive background, baseline or threshold values for the elements concerned. Instead, the ranges of concentrations should simply give an impression of the character of the geochemistry of the DBC and serve as a point of reference for the user.

	As (mg/kg)	**Ba (mg/kg)**	**Cd (mg/kg)**	**Cr (mg/kg)**	**Cu (mg/kg)**	**Mo (mg/kg)**	**Ni (mg/kg)**	**Pb (m/kg)**	**V (mg/kg)**	**Zn (mg/kg)**
DBC										
n (Total)	214	177	214	214	214	206	214	214	40	214
Median	17.0	76.0	1.70	28.1	25.0	3.60	40.1	22.5	24.0	84.0
90 %ile	27.5	162	2.95	53.6	42.5	5.70	64.5	48.0	37.9	162
95 %ile	30.0	213	4.20	60.0	54.2	6.50	74.9	89.2	45.6	200
98 %ile	46.9	290	5.30	71.8	64.8	8.50	95.5	219	46.0	366
Upper whisker	39.6	199	3.70	79.4	50.0	7.10	66.5	54.1	44.6	178
GAL SRF D2	24.9	N/A	3.28	83.9	63.5	N/A	61.9	86.1	N/A	197
GAL SRF D5	41.5	N/A	1.42	122	77.6	N/A	65.7	109	N/A	224

Table 7 Possible measures (concentrations) of the upper limit of geochemical variation for certain elements in DBC, along with GALs for SRF Domains 2 and 5.

4. Conclusions and Recommendations

A database of third-party geochemical data has been compiled for the DBC, in the absence of data based on a systematic DBC sample collection programme. The DBC data has been examined with respect to data quality, data distribution, spatial patterns, depth trends and has been compared with baseline data available from the Tellus survey. The DBC data are not accompanied by detailed quality control data that would enable a thorough evaluation of their quality. Moreover, several elements, notably Hg, Mo, Se and Sb, are reported with a high proportion of non-detects, further limiting the scope for data interpretation. Nevertheless, the database does allow for generation of basic statistics for most elements, identification of broad trends in the data, and semi-quantitative/qualitative comparison of the DBC with other datasets.

4.1. Conclusions

With reference to the original objectives, the following conclusions can be drawn.

4.1.1. Is there potential for determining baseline concentrations of naturally-occurring elements in the DBC?

As illustrated in the boxplots for DBC data (Figures C.1 – C.13) most elements in the database display a relatively narrow range of concentrations. This suggests that it should be possible to define a range of concentrations for these elements that reflects the typical geochemistry of the DBC, using whichever statistical approach is preferred. This assumes that the compiled data are an accurate reflection of the composition of the DBC for the elements concerned. However, determination of such characteristic concentration ranges is not feasible for some elements in the database, specifically Hg, Sb and Se, for which the data have too many non-detects (Hg, Sb) or the reported concentrations are unreliable (Se) owing to being typically at, or close to, the LLD.

Various measures of geochemical “background” or “threshold” values found in the literature, including the 90^{th}, 95^{th} and 98^{th} percentiles and the Upper Whisker value, applied to the DBC data and compared to the GALs for SRF Domains 2 (Carboniferous limestone and related rocks) and 5 (Lower Palaeozoic sandstone, shale and igneous rocks), suggest that the majority of the data recorded for the DBC fall below the GALs of one or both of these domains. However, as no detailed geochemical study of the DBC with a comprehensive quality control programme has been undertaken to date, it is not possible to define specific background values for naturally-occurring elements in the DBC. Additionally, a comparison of WAC leach test data with solid soil data for DBC samples (for which both values were reported) found that not all samples with high solid soil concentrations had correspondingly high leach test concentrations, or vice-versa. Therefore, it cannot be assumed that a concentration of an element in a solid soil sample which exceeds the GAL for a given domain, or some other defined threshold value, will fail to meet the WAC for inert, stable non-reactive or hazardous waste landfill based on leach test data.

4.1.2. Is the DBC geochemically distinct from neighbouring soil and subsoil deposits?

Reported concentrations of Cd, Mo and Ni in the DBC appear to be somewhat higher than those in Tellus 'S' samples, as shown in the boxplot comparisons (Figures C.3, C.7 and C.8). However, statistics for Cd, Mo and Ni in Tellus periurban samples are affected by a significant number of these soil samples that overlie bedrock of Lower Palaeozoic metasediments and Leinster Granite in south Dublin. Such samples have relatively low Cd, Mo and Ni concentrations (median values of 0.72, 1.48 and 25.6 mg/kg, respectively) compared to the remaining Dublin periurban samples, which mostly overlie Carboniferous limestone bedrock (median values of 2.13 mg/kg Cd, 3.25 mg/kg Mo and 47.7 mg/kg Ni). Median DBC concentrations for these three elements are 1.70 mg/kg, 3.60 mg/kg and 40.1 mg/kg, respectively (Table 4). Reported Cd concentrations in the DBC slightly exceed those observed in made ground while Mo concentrations in these two classes are comparable.

Anecdotal evidence has been reported that suggests Sb and Se concentrations are relatively high in the DBC, leading to DBC samples exceeding waste acceptance criteria (WAC) limits. WAC limits are based upon analyses of leachates and as such cannot be readily compared to analyses of solid material. The quality of Sb and Se data in the DBC database is not sufficient to determine if these elements are present in concentrations in excess of concentrations typical of soils in the region, as recorded, for example, in the National Soils Database or Tellus data.

The geochemistry of the DBC, as reflected in the database compiled for this work, most closely resembles that of made ground and Tellus soils classified as Irish Sea till (particularly IrSTLs) and till with dominant limestone clast composition. The similarity of DBC to material logged as made ground does raise a number of questions. The chemistry of made ground, which typically overlies the subsoil, might be expected to reflect some degree of anthropogenic contamination. Such made ground intervals, as recorded in the borehole logs in this study, span a range of textures but typically have a matrix of clay (± sand and gravel) with various "contaminants" such as brick and plastic fragments, which may have limited impact of its inorganic chemistry. Made ground may also be expected to be affected by atmospheric deposition and other sources of diffuse anthropogenic contamination. Assuming samples are sieved to < 2 mm prior to grinding and analysis then the coarser contaminants may be removed, leaving a sample largely of clay matrix. The similarity of DBC and made ground chemistry, as shown in the boxplots (Figure C.1 – C.13), suggests that the matrix to made ground in the study area is of similar composition to DBC itself. If the chemical composition of made ground samples reported for this study reflects anthropogenic contamination then so too should that of the DBC. Alternatively, made ground samples may not be affected to a significant degree by anthropogenic contamination.

As noted, apart from made ground, the compositions of the DBC samples reported for this study most closely resemble those of Tellus soils classified as Irish Sea till (particularly IrSTLs) and till with dominant limestone clast composition. These samples include periurban soil that shows evidence of diffuse anthropogenic contamination for some elements in the Greater Dublin area, e.g. Pb and Sn (Geological Survey Ireland 2021), but in general the Tellus soil samples carry a strong geogenic signature. The similarity of the DBC geochemistry suggests that its composition is also largely geogenic in origin. An example is the relatively high Cd concentration in the DBC that is likely evidence of the influence of Carboniferous Calp limestone and shale on its geochemistry. The similarity of the DBC composition to that of soils classed as tills dominated by Lower Palaeozoic clasts is consistent with the contribution of Lower Palaeozoic sediments to Irish Sea Till, which has been observed as a component of the DBC (Skipper *et al.* 2005).

The Dublin region is largely within SRF Domain 2 and reported DBC data largely fall below GALs for this SRF Domain for As, Cd, Cr, Cu, Hg, Ni, Pb and Zn. GALs were not estimated for Mo, Sb and Se for which anecdotal evidence has been cited to suggest DBC may have relatively high concentrations. However, in general, the DBC does not appear to have a composition that is intrinsically rich in the elements of interest. Therefore, where samples of DBC exceed GALs for SRF Domain 2 the possibility of anthropogenic contamination should be considered as a possible cause.

4.2. Recommendations

4.2.1. Higher quality data needed

The DBC geochemical database compiled for this project has helped identify potential geochemical affinities for the DBC. However, the absence of QC data, the limited range of elements for which data are available and high lower limits of detection for some elements mean that application of the database is necessarily limited and uncertain. It is recommended that a baseline geochemical survey of the DBC be carried out using modern analytical techniques to allow direct comparison with regional and urban Tellus geochemical data.

4.2.2. More detailed geochemical characterization of the Irish Sea Tills

In the geochemical comparisons conducted for this work, concentrations of elements are typically highest in the DBC, made ground and in Tellus samples classed as Irish Sea till and till with dominant limestone clasts. These classes have broadly similar median values and interquartile ranges. However, only limited geochemical data are available for Irish Sea tills, or soils classified as such, as they have only limited geographical extent in the Greater Dublin area. It is recommended that sampling and analysis of Irish Sea tills be carried out to characterize its geochemistry. Sampling should target deeper samples to minimize the risk of anthropogenic influence.

4.2.3. Comparison with Tellus Urban Dublin

The Tellus programme has recently completed sampling of the Dublin urban area, i.e. within the M50, at a sample density of four samples per km^2. It is recommended that the DBC data should be compared to the data for these urban samples, once analysis has been completed, in order to further understand the geochemical context of the DBC.

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