Geochemical properties of aquifers and other geological formations in the UK

2012 Update

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Geochemical properties of aquifers and other geological formations in the UK

2012 Update

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Summary

The intrinsic geochemical characteristics of geological formations have a considerable influence in controlling solute and pollutant transport behaviour during groundwater flow through the shallow geosphere. The interactions between solute or pollutants and the surface geochemistry of the rock matrix will often determine both the extent and speed of solute transport in the saturated and unsaturated zones. Consequently, understanding these processes is of critical importance for a range of environmental management requirements, such as landfill leachate monitoring or contaminated land evaluation, including requirements related to statutory obligations for ensuring good groundwater status under the EU Water Framework Directive.

Risk assessment and management approaches frequently make use of numerical geochemical modelling to predict contaminant transport. These models necessarily require parameterization of the geochemical properties of the geological formations involved and the predictions which can be obtained are inevitably only as good as the quality of the data which are used. However, the natural variation in lithologies and extensive spatial heterogeneities of the UK rock formations result in considerable variability of the most important geochemical properties. Identifying or obtaining good relevant data for calculations can be difficult; new laboratory measurements can be expensive and time-consuming, published data are relatively sparse and existing data from previous site investigations are often held commercially and are difficult to get hold of.

This study, supported by the British Geological Survey and the Environment Agency, presents the first comprehensive national compilation of geochemical properties data of relevance to geochemical modelling. An assessment has been made of existing available primary data. Relatively few data are available, but those which are have been collated. To underpin this the project has undertaken an extensive programme of new experimental measurements on the geochemical properties of samples from geological formations across the country. Initially attention was focussed on England and Wales, but this was later expanded to include data and samples from Scotland. Over 600 new samples have been included, providing by far the largest high-quality internally-consistent dataset currently available for these parameters.

The geochemical properties addressed are those considered to be of greatest significance for the purposes of modelling and risk assessment, namely:

- cation exchange capacity (CEC);
- fractions of organic and inorganic carbon (f_{OC}, f_{IC});
- extractable (readily soluble) element contents of iron (Fe), manganese (Mn) and sulphur (S);
- whole-rock and clay-fraction mineralogy.

It is intended that the Geochemical Properties Manual represented by this report and database should provide a reliable reference resource for practitioners carrying out site investigations in the future. Whilst site-specific parameter measurements will always provide the greatest confidence, this manual will provide a benchmark of what is known and what can reasonably be expected for the geochemical properties of given types of geological formations. In this respect the manual is related to the manuals of physical properties of major and minor aquifers produced by BGS previously. However, for geochemical properties date have been included for any geological formations, not only aquifers, as aquitards and aquicludes also play an important role in constraining transport behaviour.

Chapters 1 and 2 of the report introduce the data compilation, structure and presentation. Chapters 3 and 4 provide a brief overview of the principles of geochemical modelling and of the use of geochemical data in geochemical modelling. Chapters 5-8 then provide the bulk of the report, cataloguing the available data by geology for a selection of the key geochemical parameters relevant to numerical modelling. The data are presented as numerical and graphical statistical summaries to try to assist the user in finding the most suitable parameter values to use in their own circumstances.

This report (OR/12/090) supersedes an earlier version (CR/06/216N) which is now withdrawn. It contains some corrections, updated lithostratigraphical classifications and additional data added to the database up to the end of December 2012.

1 Introduction

1.1 PROJECT DESCRIPTION AND SCOPE OF THE REPORT

1.1.1 Introduction

This report and the associated digital database are the principal products of a project to document intrinsic geochemical characteristics of the rocks of geological formations in the UK. It follows related, but not directly comparable, major projects and reports concerning the physical properties of major and minor aquifers in England and Wales (e.g.1997; Jones et al., 2000).

The study was predominantly funded jointly by the British Geological Survey (BGS) and the Environment Agency (EA) and was undertaken principally by BGS staff with some input from Environment Agency staff. In the later stages there was extension of the geographical scope of the project to enable inclusion of samples from beyond England and Wales.

For the Environment Agency the production of this report and database form part of the continuing commitment to the effective protection of groundwater resources in the UK. The Environment Agency has statutory obligations to implement the measures required by the EU Water Framework Directive for management of groundwater bodies and also has responsibilities to regulate the risk to groundwater from potential hazards, such as landfill or contaminated land management. These assessments involve the use of contaminant-transport and risk-assessment models such as LandSim or ConSim (Golder Associates, 2001-2009, 2003-2009). All the models require the input of geochemical parameter data, often in complex geological and hydrogeological situations. At present there are few, if any, reliable sources of such data other than site-specific investigation. There is a need for information which can be used as an impartial reference data set when reviewing submitted regulatory assessments or, for example, during emergency response situations (e.g. following a pollution incident or during disease epidemic control incidents, such as foot-and-mouth) where decisions need to be made extremely rapidly and there is no opportunity for any site investigation. It is hoped that this report will encourage a consistency of approach to the application of models and underpin the long-term objective of producing valid and defensible assessments and management strategies for protecting groundwater.

For BGS the project and report represent products from an important component of its basic scientific survey of the UK geological environment. The collection, collation, curation and dissemination of geochemical and hydrogeological information for public use form core functions within the Survey's role. This geochemical properties project, like the earlier physical properties projects, falls entirely within that remit.

The specific objective of this report is to provide a source of information on the magnitude and variability of basic geochemical parameters for the aquifers and other geological formations in the UK. This is the first time that such a systematic compilation, with such an extensive scope, has been produced for geochemical properties. Although it may legitimately be regarded as a companion and complement to the two predecessor volumes of physical property data, it is also anticipated that the Geochemical Properties Manual will be used as a stand-alone reference.

Since publication the two physical properties manuals have become established as arguably the primary reference works in their field. It is hoped that this volume too will serve as a valuable and accessible reference on the current state of knowledge and availability of data for the geochemical properties of geological formations of the UK.

1.1.2 Parameters and formations covered by the report

The geochemical properties addressed by this report are:

- cation exchange capacity (CEC)
- fractions of organic and inorganic carbon ($f_{\mathrm{OC}}, f_{\mathrm{IC}}$)
- extractable (readily soluble) element contents of iron (Fe), manganese (Mn) and sulphur (S)
- whole-rock and clay-fraction mineralogy

These parameters are defined and the choices explained in detail in Section 2.2. They were chosen because they represent the key intrinsic geochemical characteristics of a geological formation that are of significance in geochemical modelling. They include the parameters required by the current generation of stochastic risk-assessment models (e.g. ConSim, LandSim) widely used in the environmental industry. They also include parameters which go beyond the requirements of these models and can be used to support more sophisticated mechanistic geochemical models such as PHREEQC or ORCHESTRA (Meeussen, 2003; Parkhurst and Appelo, 1999).

In fact, the measurements of extractable elements and quantitative mineralogy provide simultaneous data for a large number of parameters, many of which are of secondary importance. They cannot all be documented fully in this printed report because of space constraints, but the full data sets are included in the underlying BGS database. For this volume, discussion of the extraction data is restricted to consideration of iron (Fe), manganese (Mn) and sulphur (S). The available mineralogy data are more limited and so most parameters have been tabulated.

An important difference from the previous reports on physical properties is that whilst they were concerned exclusively with aquifers the current study has considered all relevant geological formations. In the context of geochemical transport, aquitards and aquicludes may prove to be at least as influential in determining the behaviour of a given solute or contaminant as the aquifers themselves. It is as important to know about retardation and immobility as it is to recognise rapid or unhindered movement. All types of formation are therefore considered with equal emphasis.

1.2 PROJECT APPROACH

Given the project objective to provide a guide to the magnitude and variability of geochemical parameters in as comprehensive and reliable a manner as possible, it is necessarily important to consider the extent to which parameter values can be attributed to particular areas of the formations under study. In other words, how prescriptive can the manual be in providing values to be used at a specific site? There are three major factors to this question that need to be considered: the complexity of the geology, the quality and quantity of data available and issues of scale.

1.2.1 Geological complexity

The hydraulic and physical geological complexity of aquifers and other formations has been pointed out and discussed in some detail in the two manuals of physical aquifer properties (Allen et al., 1997; Jones et al., 2000). It was observed that aquifers in the UK do not generally conform to the text-book ideal aquifers on which most theory and models are based. Such complexity often led to imperfect estimates and understanding of the physical properties under discussion.

Complexity has a significant role to play in the understanding and application of geochemical properties too. The key observation for the physical parameters was that the hydraulic complexity of aquifers is to a large extent determined by the degree of fracturing. Yet at the same time knowledge of fracture frequency, location and geometry is poor. Where fractures are interconnected, the fracture aperture is the dominant, fundamental control on rock permeability and hence water flow. In general, the more fractured an aquifer, the less predictable its hydraulic behaviour and properties. As opposing examples, the Lower Greensand is considered to have minor fracturing and flow is predominantly intergranular (matrix). On the other hand, the rocks of the Carboniferous Limestone Supergroup have virtually no matrix permeability, so water flow is generally through conduits.

Geochemical properties are frequently used in reactive transport models, perhaps for regulatory or licensing investigations. If the aquifer has fast conduit flow then the likelihood and rates for some geochemical processes to occur will be radically different from an aquifer which has slow matrix flow allowing sufficient time for a quasi-equilibrium to establish. Understanding of the geochemical behaviour of water in a particular situation will therefore be influenced not just by the individual property measurements reported in this volume, but whether those measurements relate, for example, to fracture surface material or to intergranular matrix, and by the relative hydraulic complexity of the formation.

1.2.2 Data quantity and quality

Conceptually, if sufficient data of sufficient quality are available, then despite the complexity it should be possible to provide reliable descriptions of the geochemical properties at any location in the formations studied. Parameter values could be meaningfully estimated by interpolation from the plentiful data thoroughly distributed throughout the formation. In practice the data density required to achieve this ideal with any robustness would be enormous and is certainly far beyond the present data availability.

The sources, quantity and quality of the data collected during the project are discussed in more detail in Chapter 2. During the pilot stages of the project it very rapidly became apparent that existing data were sparse, inconsistently measured and unevenly distributed. Whilst there was some information on some of the major (i.e. geographically extensive, or geotechnically important) formations, there was simply no good information on a great many more. In addition, such data as did exist were often heavily biased to particular small areas, having been derived for specific site investigations or civil engineering projects. It was therefore decided at a very early stage that a major component of the effort in the project would be the systematic collection of a new set of high-quality data, measured using consistent and best practice techniques, for as extensive a range of parameters and geological formations as could be achieved.

1.2.3 Scale problem (heterogeneity)

The problem of heterogeneity as discussed in relation to the physical properties manuals does not apply in the same way to the discussion of geochemical properties. For the physical properties, many of the parameters are determined as bulk properties from measurements carried out on a significant volume of rock, possibly at field scale. In this situation the heterogeneity manifests as a scale related problem; measurements at one scale may not be appropriate for use at a different scale. For example, transmissivity calculated from hydraulic conductivity measurements on laboratory cores might be significantly different from those calculated from pumping tests. For the most part, physical parameter data intrinsically represent a bulk average, including the contributions made at different spatial scales by the rock matrix and fracture systems

By contrast, geochemical properties are almost invariably measured on a laboratory scale, often on only a few grammes or milligrammes of sample material. Bulk averaging is frequently impractical if not impossible. In these circumstances, the heterogeneity must be addressed by using a large number of measurements on highly localised small samples and assessing the variability, instead of being able to estimate the parameter directly at macro scale.

If anything, the problem of multi-scale heterogeneity is perhaps more significant in consideration of the geochemical properties of formations than for the physical properties considered by the previous manuals. The mineralogical scale nature of the geochemical properties means that significant changes in geochemistry of a material can be observed over very small distances. This variation may be due to the presence of secondary minerals or impurities in the rock matrix. Often, the geochemical characteristics of a minor component of a formation can exert a disproportionate influence over the apparent aggregate properties of the bulk rock. For example, it can easily be demonstrated that under the right geochemical conditions, a mineral occurring in unremarkable concentrations within a sediment may yield exceptionally high concentrations of a species mobilised in the groundwater interacting with that sediment. Alternatively, secondary mineral precipitation along fracture lines may dominate the geochemical and surface interactions with a contaminant in a groundwater flow, causing retardation that is not observed for the parent rock. Laboratory measurements carried out on material taken from such a fracture surface might then yield very different results to tests on material sampled from only a few cm away in the consolidated rock.

Heterogeneity on a geological scale will also contribute to variation in the observed geochemical parameters. The lithology of a given stratigraphy may vary vertically or spatially, over scales of metres or even kilometres such that the geochemical reactivity is altered within the same formation. For example, the occurrence of marl bands in parts of the Chalk, particularly the Grey Chalk Subgroup (Zig Zag Chalk and West Melbury Marly Chalk Formations), profoundly alters the flow regime compared to the surrounding chalk. Where possible the recorded geochemical properties should reflect these variations as accurately as possible, but of course the data density constrains the level of detail which can be captured.

Thus, the scale at which available data have been collected must be taken into account when using or interpreting the geochemical properties data. Ideally this should be coupled with a wider understanding of the physical geology concerned. Whilst spatially averaged parameter values may be appropriate for some applications they will be less valid for others, for example in reactive transport modelling, where actual flow-paths may need be considered.

1.2.4 Scope of report and database

In view of the complexities discussed in the preceding paragraphs no attempt has been made to produce a fully prescriptive document that provides a specific estimate of the parameter at every point. Rather, the focus has been on simply presenting the current state of knowledge, as far as it goes, and on understanding the limits on that state of knowledge. Extensive use has been made of statistical presentation techniques to try to convey to the reader the extent of the variability and uncertainty associated with the data. A full explanation of the statistical presentation is included in Section 2.4.

In geographical scope the report is as comprehensive as possible. Data from all parts of the country are included if available, although in practice there are appreciably fewer data available for Scotland and Wales than for the major geological formations of England where groundwater is abstracted on a large scale. There are currently almost no data for Northern Ireland.

Similarly, in geological terms no formations have been excluded although the majority of data relate to a subset of major geological units. The database has been intentionally designed with a fully scalable structure so it can accept data for any geology without modification.

Although the focus of the report is on the key parameters identified above, the database is again open-structured so as to be able to include data for any other parameter.

1.3 READERSHIP

This report is intended to be used primarily by hydrogeologists and workers in other related fields who will have the knowledge and skills necessary to understand the validity of the data when set in an appropriate hydrogeological context. The report does not attempt to explain the geological or hydrogeological contexts. It may be useful either as a source of specific data for those already familiar with a formation, or as a starting point for those looking to develop an understanding of the processes affecting a given formation.

Although brief discussions of key contaminant transport modelling concepts and procedures relating to the use of the parameters are provided, these cannot be considered to be thorough or comprehensive texts and the full breadth of understanding required for modelling is not addressed. For this the reader unfamiliar with geochemical modelling is referred to other standard texts and manuals, including those referenced in this report.

Users of the report will probably include those involved in groundwater protection work and site risk assessment, whether as regulators, researchers, or operators and consultants from the environmental and waste management sectors.

1.4 STRUCTURE AND USE OF THE REPORT

1.4.1 Introduction

The report is intended to be used both as a source of data for direct use and as a companion providing some context and background to the numerical data.

(i) Data are presented in detail for the six most important parameters in a way that enables numbers to be extracted directly for use in subsequent modelling.

(ii) The companion text explains how and why these data have been obtained, and attempts to indicate their significance within the field of geochemical modelling.

Insofar as the quantity and coverage of the available data allows, it is intended that the user should be able to obtain the information at the scale and level of detail most appropriate to their purpose.

1.4.2 Report structure

The report is divided into two main sections. The early chapters cover general discussion and explanation of geochemical parameters without discussing specific data. The second part of the report then provides detailed and systematic presentations of the data for the particular parameters currently considered to be of the greatest practical importance.

In the first section, Chapter 2 describes the procedures used for data collection, management and presentation throughout the Geochemical Properties Manual. It includes an explanation for the choice of key parameters. Chapter 3 outlines the main theoretical concepts which underpin geochemical modelling and which provide the framework for the use of geochemical parameters. Chapter 4 discusses the application of the geochemical parameter data for geochemical modelling in practice.

The second section, from Chapters 5 – 8, comprises the main body of the report and is designed to provide the user with easily accessible summaries of the data for the individual parameters in turn.

Each chapter then follows a similar structure beginning with discussion of the use and interpretation of the parameter in question. The possible approaches to experimental determination of the parameter are presented, with full details of the preferred analytical method that has been used for determinations carried out within this project. Where suitable data exist, the typical uncertainty margins associated with experimental measurements have been estimated. An overall tabulated summary of the available dataset follows, before the dataset is presented in detail as a series of statistical plots and summaries (see Section 2.4). For this purpose, the data have been subdivided at the Lithostratigraphical Group level.

1.4.3 Report use

The data for the geochemical properties are presented in this report in a form that does not presuppose any particular use or application. However, it is anticipated that the primary use of the data provided in the report and database will be for numerical modelling of geochemical processes and contaminant transport simulation or prediction. In the first instance one of the major applications will be for the parameterisation of the LandSim and ConSim models applied to specific site investigations. These are among the most widely used models in the UK for predicting contaminant transport behaviour for regulatory purposes. The models have been specifically developed in conjunction with the Environment Agency in order to provide standard tools whose code is verified and whose use is recognised and endorsed by the regulator. The choice of parameters considered by the project and now presented in this summary report is heavily influenced by the geochemical requirements for assessing natural attenuation processes in groundwater (Carey et al., 2000) or the data requirements of LandSim and ConSim.

Despite their widespread use and acceptance these stochastic models are recognised as having limitations so it is likely that the data will also find use in more complex, sophisticated, mechanistic approaches to geochemical transport modelling. PHREEQC and ORCHESTRA, discussed briefly in Chapter 4 are two of the most powerful and flexible such models currently available, and are also widely used in their field.

Although it is hoped that this compilation will provide an authoritative, easily accessible and reliable source of geochemical data, users should be aware that the data reported cannot be used indiscriminately or unthinkingly. The users retain the responsibility to derive and apply the most appropriate values of the parameters for their needs and to assess the validity of those values within the boundaries and context of what is known about the hydrogeology in a given study.

1.5 REPORT UPDATING AND CURRENCY

Inevitably, a printed report can present only a snapshot of the database at the time of writing. This report is issued during 2013 based on data accumulated or measured for the database compilation to date. The data tabulations and plots presented in this printed report therefore represent the state of the database in December 2012.

2 Information collection and use

2.1 TYPES OF INFORMATION COLLECTED

The data in the Geochemical Properties Manual database has been acquired from various sources. Some of it is derived from academic research (theses etc) at universities while other data has been collected by the Environment Agency as a result of its regulatory role and is ultimately derived from consultants' reports. Many of the data are derived from BGS archives or was newly acquired specifically for this project. The source of each datapoint is recorded in the database.

2.2 CHOICE OF PARAMETERS

2.2.1 Introduction

While much remains uncertain about how to apply contaminant transport models to the 'real world', the basic physical and chemical principles underlying contaminant transport are now well understood. The key to all such approaches lies in the ability to predict the partitioning of a chemical between solid (stationary) and solution (mobile) phases. The chemical processes that control this partitioning are also quite well understood although there are plenty of areas where uncertainty remains, e.g. coprecipitates and solid solutions.

Contaminant transport programs differ in the degree to which they *calculate* this partitioning as opposed to expecting its *specification by the user*. Programs such as MT3D and LANDSIM that expect K_d values or simple isotherms to be specified by the user belong to the latter group since they avoid the problem of how to estimate the K_d or the isotherm to use, especially given that the K_d may depend on the type of processes operating as well as the solution chemistry (see Section 3.2). In essence, forcing the user to enter a K_d is side-stepping one of the main difficulties in applying contaminant transport models – how to anticipate the solid/solution partitioning and its variation spatially.

The alternative is to try to estimate the partitioning from more fundamental properties of the solid and solution phases. This approach is widely adopted for organic compounds through the Quantitative Structure Activity Relationship QSAR–log K_{oc} approach and has also been used to estimate metal ion binding by oxides and natural organic matter. However, an inevitable prerequisite of this approach is to have a suitable and sufficient knowledge of the fundamental properties in question. That is the role of this study and report.

2.2.2 Dominant subset of environmental particles

Although it might seem at first sight that the number of minerals and substances in the natural environment is impossibly large to characterise properly, in practice this is not quite such a gargantuan task as it first appears. Strong geochemical reactivity arises either from:

- a *moderately high and reversible solubility*, for example carbonates such as calcite, dolomite and siderite; oxides of iron, aluminium, manganese and silica; sulphides of iron, but not rock salt which is so soluble that it rarely precipitates, or rutile and zircon which are too insoluble to dissolve at significant concentrations; or

- *very small particles with high surface areas*, e.g. oxides of iron, aluminium and manganese; natural 'humic' type colloids; phyllosilicate clays like montmorillonite, vermiculite, biotite or illite and chlorite. The specific surface area of the smallest particles (colloids) is orders of magnitude greater than that of sand-sized minerals and dominates many aspects of the surface chemistry and reactivity of soils and aquifer materials. Often the bulk of soils and aquifers is simply that, rather unreactive bulk material.

The components in the natural environment which most commonly exhibit strong chemical reactivity combine these characteristics and in addition, often are abundant and common.

A strongly varying solubility under various pH, redox and other environmental conditions makes certain minerals especially important, and the classes identified above all fall in this category. Carbonate solubility is strongly dependent on the atmospheric partial pressure of carbon dioxide ($pCO_2(g)$). The solubility of iron oxides has both a strong pH and redox dependence. All sulphides are very sensitive to redox conditions and iron sulphides are abundant in the natural environment.

Iron oxides and humic substances are also ubiquitous in the natural environment. Aluminium oxides are likewise very abundant, and although aluminium oxides are not so visually obvious as iron oxides, they are more soluble (and toxic) than iron oxides under both moderately acid and alkaline conditions. All oxides have somewhat similar surface properties irrespective of their basic 'building block'. The reactivity of clays is largely determined by their cation exchange capacity (CEC) and all phyllosilicate clays behave somewhat similarly irrespective of their precise structure. Therefore, the overall CEC is the single most important factor that characterises clays.

2.2.3 Choice of parameters

From this assessment of the key processes dominating geochemical reactivity it is possible to derive the subset of parameters selected for routine determination, namely:

- CEC
- organic carbon content
- carbonate content

- free iron and aluminium oxide content
- pyrite content
- bioavailable (readily soluble) iron and manganese; and
- specific surface area.

These parameters have a particularly strong influence on the environmental fate of a wide range of chemicals.

The variety of geochemical tests that could be undertaken on a given sample is vast and it would be prohibitively expensive to undertake a complete set of analyses on each sample. The parameters suggested for collation and measurement are fundamental parameters that characterise basic features of all environmental materials, and specifically soils and aquifer materials. The large number of scientific papers concerned with these parameters, especially in relation to modelling, attests to their significance.

It should be recognized that the selected parameters do not of themselves define the complete behaviour of the particles since they are largely related to extensive properties such as *abundance* rather than model-dependent characteristics such as log K values. The data collected will have to be combined with some model-specific parameters, as outlined in Table 4.1. The best models and their parameters will evolve with time and it will be necessary to update that aspect of the modelling approach, but the intrinsic properties, such as the abundance of iron oxides, are of such obvious importance that they should have long-term applicability and benefits.

2.2.4 Analytical considerations

A further consideration during choice of parameters is the practicability of experimental measurements. Ideally all measurements would be easy, reliable and inexpensive. In practice, the viability of measurement for complex geochemical behaviours and properties constrains the nature of the parameters which can meaningfully be considered. This is inherently reflected in the nature of the parameters which are used in geochemical modelling and hence in the choices identified here.

Cation exchange capacity of a sample is estimated directly, by measuring the uptake or release of metal ions which are loaded onto the material during experiment.

Various classical and modern instrumental methods exist for measuring carbon in samples. By using suitable sample preparation techniques, it is possible to use these to determine organic and inorganic carbon separately. Carbonate content can be considered to be represented directly by the inorganic carbon content of the rocks.

Analytical determination of metals and other elements, such as sulphur, is also possible using modern, sensitive, high-throughput and often cost-effective instruments. The challenge in this case is in being able to isolate the correct fraction of the element to be analysed. Some instruments, or aggressive preparation techniques will yield data for the total content of the sample material, but this will not distinguish between the fraction of the element, iron for example, which is strongly bound into the matrix of the rock and that which is available in mobile form or on the surfaces for reaction. A huge range of extraction and separation techniques have therefore been developed to try to target particular phases or fractions, but often these are more laborious and expensive to undertake than the subsequent analysis. Choosing which approaches to use to get consistent data which can be related successfully to geochemical properties and behaviour requires careful thought.

These measurement techniques are in general well-established, and well documented. Although not always trivial, they can be carried out by competent laboratories using equipment which is commercially available. Some methods have been described in published standards or texts for a number of years. Detailed discussions of the analytical methods available and those used in this study are given in the following chapters.

2.3 GEOLOGICAL CLASSIFICATION OF SAMPLES

Considerable effort was taken to locate the source of the samples accurately, not only in terms of 3-dimensioanl geographical coordinates (Easting, Northing, Depth) but also in terms of the geological sequence from which the samples were derived. This is important considering the high variability of geochemical properties with type of geological material and the fact that the majority of the applications for the data will be approached from a geological, rather than geographical perspective.

2.3.1 Lithostratigraphy

The geological classification of samples followed the standard BGS stratigraphic definitions detailed in the BGS Lexicon of Named Rock Units (accessible via the BGS website: www.bgs.ac.uk/Lexicon) based on the various BGS data dictionaries. This classification follows a hierarchical scheme, in sequence of decreasing rank (from the broadest to narrowest categories) as follows: Supergroup, Group, Formation, Member and Bed. Sometimes an additional classification of Subgroup is used but it is relatively uncommon and so has been disregarded for the purposes of this work. Over 60 Groups are currently represented in the geochemical properties database.

The Lexicon uses the combination of a unique short code (usually 2–4 letters, occasionally 5), which serves as the primary key in the database, and a longer description for each individual stratigraphy. Both have been used in the data presented here. The boxplots are labelled along the axis using the short code, but the legend for each plot provides the translation to the full name in each case. In a few cases, some codes have been defined in the dictionaries but not yet the longer descriptions.

One of the difficulties with using the Lexicon is that although the nature of the hierarchical classification is well-defined and established by the International Stratigraphic Guide (Murphy and Salvador, 1999), it is not necessarily applicable from the top down. The primary level of lithostratigraphical classification is the Formation, but these are not always considered to form part of an identifiable lithostratigraphic Group. There are thus a significant number of Formations for which higher hierarchies are not fully defined. The Supergroup level in particular is only used for some stratigraphies, which means that only some 30% of samples measured here can be assigned to a Supergroup. In other cases, samples could properly be attributed at Group level but not be allocated to a Formation because there was insufficient information available to identify the site stratigraphy at this level of detail or because the primary geological mapping of the area remains undifferentiated. These samples have been allocated their formal Group codes but the Formations are recorded as U (for Undifferentiated).

As the Formation is the primary classification then it is logical and appropriate to try to summarize and interpret the geochemical data at this lithostratigraphical level. However, many hundreds of identified and defined Formations exist and the current database already contains data for over 150 of them. Presentation of the data according to Formation only still has the potential to be unwieldy. It is helpful to use a higher classification to provide additional structure and therefore in the preparation of this manual Groups have also been used as a fundamental classification. Several of the data presentations use Groups to illustrate the variations or similarities of associated daughter Formations. It is therefore desirable that samples (and hence data) are attributed at both Group and Formation level.

In order to cope with the gaps in full formal hierarchical allocation a small number of new codes have been created specifically for the geochemical properties project and database. All the new codes are identified by having the first letter X in the code. There are no official Lexicon entries associated with these codes as they exist only within this project and database. Descriptions are generally of the form "XP – Other Permian" or equivalent with one such code for each of the major geological Periods and some for major Supergroups, such as "XNRS – Other New Red Sandstone". These additional codes have been used to ensure full attribution of samples at Group level, which is important for facilitating the statistical analysis. Where a Formation can be identified for a sample, but no Group is defined for that Formation, then a pseudo-Group has been allocated on the basis of the geochronological age of the formation. It ensures that the data are fully populated at the Group level and hence that all data are captured correctly when the database is queried.

2.3.2 Chronostratigraphy

One respect in which the Lexicon is very extensively and rigorously populated is for the age of each of the stratigraphies listed, using the codes for chronostratigraphical Stages. The actual numerical ages corresponding to the codes are well described. For many rocks a single Stage is sufficient to completely define the age, but the Lexicon allows for both upper and lower ages to be listed where necessary for a rock whose age bridges multiple Stages.

The extensive age attribution within the Lexicon has made it possible to attribute chronostratigraphical ages to the samples and lithostratigraphy codes used in the Geochemical Properties Manual. In this case the allocation to the finer level of Stage is not so significant, but the higher level of Period provides a useful classification. The Periods (Triassic, Jurassic etc) are often used during everyday discussion of geological and hydrogeological issues so they are, for the most part, terms which are already familiar to those working in the field.

A dilemma arises when a particular stratigraphy is considered to bridge two geological Periods between the upper and lower ages. Some of the stratigraphies affected can be very important ones, which bridge the Periods precisely because they are substantial rocks which formed over a very long timescale. The difficulty is in deciding which Period to allocate to the stratigraphy for the purpose of the geochemical properties database so that the data can be found and queried effectively. A significant example is for the Permo-Triassic sandstones which form a major aquifer sequence, especially in central and northern England. The rocks are commonly known as Permo-Triassic, but within the hierarchical searches used by the geochemical properties database this dual attribution is difficult to use. A single attribution is better. So, should the data be allocated to the Permian or to the Triassic? For the purposes of this study and report two rules of thumb have been applied, although not rigorously:

- for the most part the dominant or common-usage Period for a formation is generally preferred (the Lexicon frequently defines dominant age in addition to minimum and maximum ages); and/or
- alternatively, the upper (younger) dates are preferred.

Thus, for example the Lias Group (LI) is formally considered to span from the Rhaetian Stage in the late Triassic, to the Aalenian Stage of the Middle Jurassic. However, the majority of the formation, and the popular usage, is that the Lias is a Jurassic rock. It is therefore classified accordingly, as the younger Jurassic Period, for the geochemical properties database. A similar approach has been applied to the Purbeck Limestone Group (PB). According to the Lexicon, the Purbeck Limestone Group formally runs from the late Jurassic to the early Cretaceous. The basal part being Jurassic but the greater part being Cretaceous. Therefore, although it may sometimes be considered to be a Jurassic rock the geochemical properties allocation is as Cretaceous, to the predominant younger Period of the range.

Users of the database and this report manual must therefore recognise that the chronostratigraphical classifications are not regarded as or intended to be rigorous. The aim has been to be able to structure the data within a broad chronostratigraphical framework and hence to facilitate convenient searching and visualisation of the data. Whilst every effort has been made to make the allocations as correct and reliable as possible, there are some occasions where the allocation used could be regarded as incorrect, or at least only partially correct. If a particular Group or Formation is not listed under the Period expected, the user should consider searching the adjacent Period.

2.3.3 Lithology

The geological sub-division by stratigraphy does not provide the only potential classification scheme for geochemical properties. It is easy to see that some form of classification by lithology might also provide useful and meaningful insight into the behaviour. For example, there may be greater similarities between lithologically similar samples from different formations and stratigraphies, than between samples of the same formation but where the lithology varies, for example by grading between a sandstone and a mudstone. Unfortunately, although the BGS scheme for lithological classification is detailed, extensive and well-documented, it is much harder to establish a hierarchical structure of classifications. The consequence is that, although individual samples can be rigorously classified and the database attributed with the appropriate RCS code for each sample, there is no reliable method of linking or

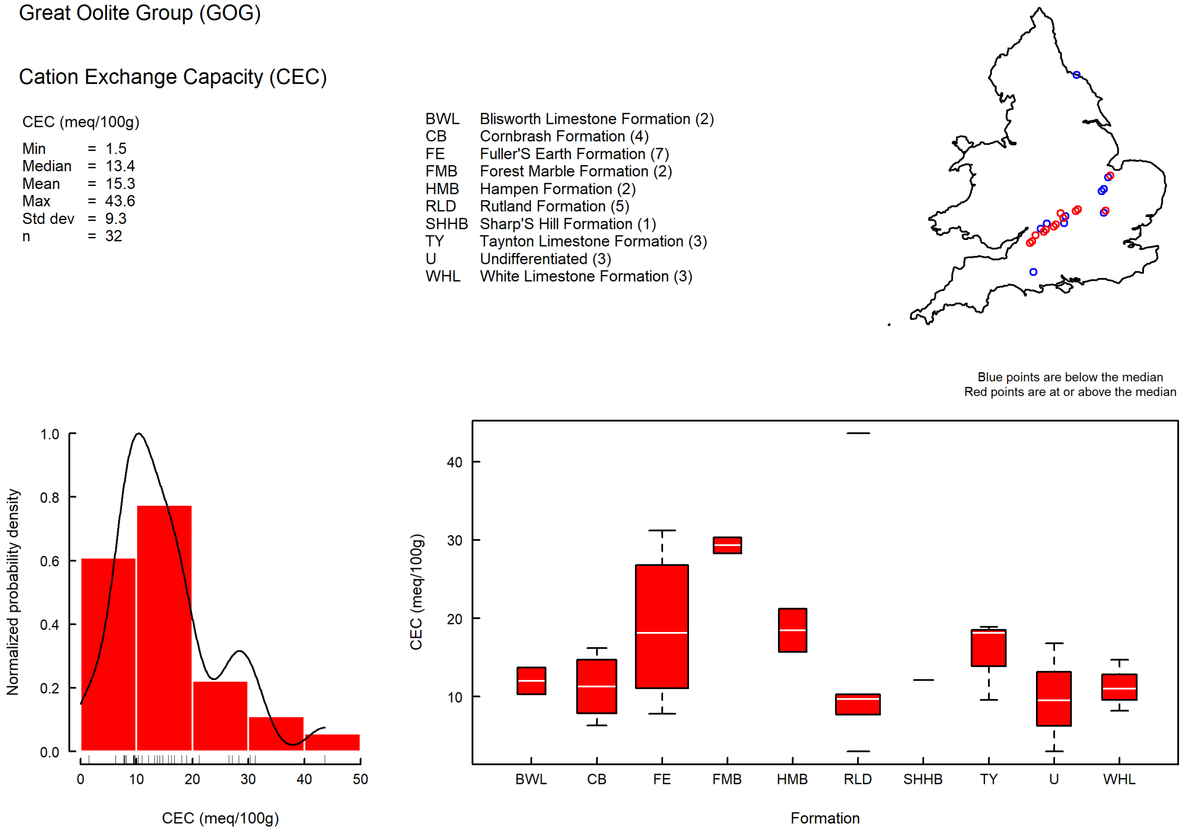


Figure 2.1 An example of the standard layout and plot types used to present the main data summaries in this report. The layout comprises from left-to-right, on the top row (a) tabulated summary statistics, (b) key to the sub-classifications contained within the target classification, (c) location map; and on the bottom row (d) normalized histogram and probability density plot and (e) box and whisker plot. The interpretation and characteristic of each component are discussed in the main text.

grouping the very large number of lithological codes which is produced. It is hoped that it may be possible to develop and apply a suitable scheme in the future.

2.4 PRESENTATION OF THE DATA

Summary statistical tables and plots for six of the better-populated parameters are presented in Chapters 5-7.

For the purposes of this report the data are organised at a lithostratigraphical Group level, subdivided by Formation. Each presentation includes some further breakdown of the dataset. The overall statistics for the whole sample set of the Group selected, are analysed with tabulated summary statistics and a histogram plot. In addition, a box-and-whisker plot is used to illustrate the division of the data into the Formations. An example of the layout used to display the data is shown in Figure 2.1.

All the calculations and plots have been generated using the R environment for statistical computing and graphics. This has the advantage, not only of being able to handle large datasets efficiently, but also of being highly versatile.

2.4.1 Summary statistics

The minimum, median, mean, maximum and standard deviation were calculated using standard methods except that where censored data were present half the detection limit was substituted for the censored value. This is only approximate and where the data are of particular importance, more sophisticated methods (both parametric and non-parametric) should be used to determine the summary statistics.

The number of samples in the sample population (n) is also given. This should provide an indication of the potential reliability/representivity of the statistical summaries. The standard deviation/mean provides a rough guide to the variability. Values greater than one are considered very variable. Values less than 0.25 indicate quite a narrow distribution of values.

2.4.2 Location map

An outline map shows the geographical location of the sample points in the dataset selected. There are three variations of the map available showing respectively England and Wales, Scotland, or the whole of Great Britain. The selection of outline is based simply on the 500000 National Grid northing; if data points exist only to the south of this line then the England and Wales map is shown, if only to the north then the Scotland map is used; if data exist to both sides of the line then the GB map is displayed.

Each sample is shown as a small circle centred at the correct grid reference. Points coloured blue are below the median value; points coloured red are at or above this value. This simple division enables strong spatial patterns to be seen. Where two or more points overly each other, as will happen when samples are taken from the same borehole but at different depths, a small random displacement is added to the x- and y-coordinates to make all the points visible. This process is known as 'jittering'. Where there is a small population with a number of data having the same value, the plot may appear to suggest that all the data are above the median – clearly impossible – but this usually reflects the large number of data occurring at the median value.

2.4.3 Histogram and probability density plot

A histogram plot is only drawn if there are three or more data points in total. Otherwise the message 'Not enough data for plotting' appears.

The histogram provides a better indication of the distribution of samples with particular values of a parameter. The y-scale is the probability density which in simple terms shows the likelihood of a particular value occurring. The data are shown broken down into various histogram 'boxes'. The number of boxes is automatically chosen and the boxes are equi-spaced. The height (or area) of the box or rectangle is proportional to the number of points falling into the region.

The plotted line is the kernel density distribution based on a Gaussian distribution. It is calculated by dispersing the empirical distribution over a regular grid of at least 512 points and then uses a Fast Fourier Transform to convolve this approximation with a discretized value of the kernel and then uses linear approximation to evaluate the density at the specified points. This is estimated using the `density()` function in R. When calculated the area under the density curve always sums to one so that the values the density function takes vary considerably depending on the measured parameter values. For example, observations for extractable Fe of >10,000 mg kg^{-1} may produce density functions with values of $<10^{-4}$, while measurements of f_{IC} (in the range 0–1, potentially <<1) may give density function values of >>1. When plotted this gives extreme variation in the y-scales of the plots which can be confusing and is to some extent arbitrary (if measurements were simply converted from mg kg^{-1} to g kg^{-1}, the value of the density function would also change by a factor of 10^3). It is the shape of the curve that is important. Thus, for clarity the plotted density functions and histograms have been normalized to a value of 1 at the maximum of the density function. The plots will then remain independent of the number or scale of data used and can be updated easily when fresh data are available.

The density function is applied to untransformed data – it might be better in some circumstances to base it on log-transformed data. However, this option has not been implemented in the current presentation.

Beware that with small sample sizes, the plotted distribution may make little sense.

2.4.4 Box and whisker plot

'Box-and-whisker' plots are only drawn if there are three or more data points in total

The box-and-whisker plot divides the data into the next lower level of the stratigraphical hierarchy. Therefore, for this report where the primary data reporting level is by Group, the box plots subdivide the data for a given Group by the Formations within that Group. The data availability simply does not support meaningful analysis at the lower Bed or Member levels. Indeed, analysis of Groups by Formation is normally only worthwhile where there are data for many samples within the Group.

The x-axis of the plot shows the Groups/Formations arranged in alphabetic order, one tick mark per Group/Formation. The x-axis labelling gives the Group/Formation code. Where the codes would overlap on printing, one or more is omitted. The full list of codes and descriptions is given in the legend above the plot. Where the geology is unattributed, the code "NA" is used.

Box-and-whisker or box plots provide a good way of seeing if there are distinct sub-populations within a dataset.

The main 'box' of the box plot extends across the interquartile range (IQR, the range covered by the 25th – 75th percentiles or 'hinges') with the median (50th percentile) shown by a thick white band within the box. The box extends at both ends with whiskers which end at 'notches' which are located at ± `1.58 IQR/sqrt(n)`, where `n` is the number of samples. These values represent typical lower and upper limits and are always located where there is an actual sample value. Box plots are designed such that if the ranges of two boxes (the red areas) do not overlap, then they are probably derived from different populations.

Individual outliers are shown as separate horizontal lines both above the upper notch and below the lower notch.

The widths of the boxes within the plots are proportional to the square-root of the number of data points – thus wide boxes correspond to the groupings with the most data.

If there are four or fewer groups to be displayed in the box plot, then the entire plot is given a narrower width than plots with more samples.

2.5 LIMITATIONS OF GEOCHEMICAL PROPERTIES DATA

For the reasons discussed earlier, concerning geological complexity and heterogeneity there are some limitations inherent in the application of any geochemical property data. In practice the available data density provides a further significant constraint. These factors were pivotal in the early decision within the geological properties project to provide data as statistical summaries rather than fixed 'recommended' values. The statistical presentations have the advantage that if interpreted correctly they, by their nature, include information on the confidence and variability of the parameter values.

In most cases, a close look at the statistical summaries and plots will give a quick and easy guide to the variability of the dataset, and as such to the reliance that can be placed on particular values being representative of greater populations.

- the maximum and minimum values indicate the overall range of values observed.
- the difference between the mean and median can give a clue to the possibility of a skewed (e.g. lognormal) distribution.
- the relative standard deviation (i.e. standard deviation divided by the mean) provides an indication of the overall variability of the data but does not capture the

nature of the distribution, for example, whether skewed or bimodal; and

- the number of data (n) indicates the size of the body of data available, and hence gives an indication of the significance and confidence which can be attributed to the figures shown.

The histogram and density distribution provide a guide to the most probable values and whether there are two (or more) populations but are limited in their usefulness with small datasets. The box plots indicate whether further geological subdivision shows distinct differences within the overall population. All of these tests are clearly unreliable when the sample population becomes very small, which is why the histogram and box plot are not plotted for fewer than three samples.

The LandSim and ConSim risk assessment models recognise the uncertainty associated with parameter data and both allow for parameter values to be entered with a probability distribution function (PDF) so that Monte-Carlo calculations can provide an estimate of the range of possible behaviours and outcomes. However, in the absence of substantive evidence, and based on a handful of actual measurements, these distributions are often entered as simple linear pyramidal distributions, with perhaps arbitrary widths. The statistical presentations here should help to provide more realistic and defensible estimates of the PDFs for these applications. Ultimately perhaps it may be possible to take the experimentally derived distributions and apply them directly to the models.

2.5.1 Limitations of acid extraction data

The use of experimental extraction measurements requires particular care in application. The different approaches and benefits of individual extraction approaches are discussed extensively in Section 7.1. As they are experimentally contrived measurements, rather than direct and absolute measurements of content there are inevitably limitations in how the data can be used. However, there is no doubt that the technique does provide a valuable tool for describing and comparing the geological formations, provided the data are used with the appropriate understanding of the limitations.

The 0.5 M acid-extraction used here is neither sufficiently strong to extract all elements from rocks (i.e. it will not dissolve most minerals) nor is it so weak that it reflects only soluble and readily-exchangeable elements. It should dissolve all the material that can be reasonably be expected to be labile under rather extreme environmental conditions such as acidic conditions and even to some extent reducing conditions. In particular, it provides an estimate of the readily soluble (and probably high-surface area) oxide materials notably of iron, manganese and aluminium, so-called ‘free’ material.

The concentration of extractable trace elements, many of which will often be associated with the above oxides, provides an indication of differences between different rock types. There is as yet no set of standards with which to relate the concentration of 0.5 M extractable trace elements to other properties but the opportunity for this will increase as the dataset increases.

Finally, it should be recognised that the concentration of extractable trace elements derived from these extraction experiments cannot be directly related to the likely concentrations found in water in contact with the mineral. A high concentration might indicate a particularly high ‘source’ term; equally, it might indicate a high ‘sink’ term. The acid extractant itself may actually enhance the uptake of some elements. For example, iron and aluminium oxides strongly bind phosphate, particularly at low pH. Therefore, addition of acid will dissolve and release phosphate associated from oxides that actually dissolve but will enhance the uptake of phosphate on the less soluble oxides that do not dissolve. The overall effect, as measured in the extract, will reflect the balance between these two processes.

3 Principles of geochemical modelling

3.1 INTRODUCTION

There is no point in collecting aquifer chemical properties data if they are not going to be used. One of the main benefits of a chemical property database for the UK formations is that it can be used in contaminant transport models in the place of site-specific measurements (which even for well-studied sites are unlikely to be very comprehensive). If this is to be the case, as we believe it should be during initial assessments, then it is important from the outset to have a vision of the link between measurements and modelling. Ideally the parameters should be as intrinsic/generic as possible and not related to a single model, since the models used will change with time and application.

While 'simple' models such as LandSim are by their nature very basic in terms of their capabilities (in a chemical sense), the 'real world' is very complex and so a number of simplifications and assumptions have to be made in order to apply such simple models to the real world.

Adsorption and ion exchange reactions are two of the principal mechanisms by which the movement of chemicals is retarded, or slowed down, in the environment. Precipitation, degradation, dispersion and volatilisation are others. Collectively these processes are sometimes called 'natural attenuation'. Models which describe the natural attenuation of chemicals in the environment are called reactive transport or contaminant transport models. Implicit in these models is some definition of the amount of adsorption, ion exchange, precipitation or degradation taking place.

The simplest and perhaps most widely used way of describing adsorption is through the 'K_d concept'. This is one of the options in the LandSim contaminant transport model widely used and promoted for the rapid assessment of the possible impact of landfills on groundwater (Golder Associates, 2001-2009). The use of cation exchange capacity (CEC) is another option for describing the retardation in LandSim. However, even relatively straightforward concepts such as that of K_d and cation exchange used by LandSim and other contaminant transport codes are the source of some confusion and misunderstanding. It is probably easier to understand these concepts if their underlying basis is appreciated. Mineral precipitation is only included in contaminant transport models that include quite detailed geochemical concepts such as that of solubility products (and hence implicitly also activity coefficients, since solubility depends on the 'ionic strength' or salt content of natural waters). Degradation models can either be customised models concentrating on organic degradation (e.g. Bioplume III, (Rafai et al., 1998)) or general purpose geochemical models such as PHREEQC-2 (Parkhurst and Appelo, 1999) or the Geochemist's Workbench (Bethke, 2006) which can be programmed to deal with a wide variety of degradation and other reactions.

Here we explain some of the underlying concepts of adsorption and ion exchange including the relationship between the K_d and CEC approaches, their limitations and some of the implicit assumptions made when using them. This is important in view of the excellent and widely-used reactive transport software now available and their ease of use. It is all too easy for the implicit assumptions or 'silent' variables in these models to be forgotten or ignored and the model to become a 'black box', with the assessor relying on the results obtained without understanding how they have been obtained.

3.2 THE PARTITION COEFFICIENT OR K_d

The solid/solution *partition coefficient* or K_d is a measure of the partitioning of a substance between solid and solution phases

$$K_d = q/c \qquad (1)$$

where q is the concentration in the solid phase and c is the concentration in solution. Units vary but q is usually in units of mg/kg solid or mol/kg solid and c is in units of mg/L or mol/L. K_d therefore has units of L/kg (numerically equivalent to mL/g). The fundamental concept of K_d is a sound one: there is a finite K_d for each reactive solute. It is how it is applied that causes most concern because it is frequently assumed to be a constant value when in fact it is not. K_d can vary with changes in the concentration of the solute, with competition from other adsorbed solutes and with the nature of the rock/matrix. It can also vary through more subtle effects such as changes in ionic strength.

The concentration q does not refer to the total concentration of substance in the solid phase but just that which is in rapid equilibrium with the solution. This is usually located on the particle surfaces and is often called the adsorbed or exchangeable phase. Substances embedded deep within an insoluble solid phase are essentially isolated from the solution and therefore 'do not count'. Implicit in the definition of K_d is some sort of reaction of the substance between the solid and solution phases. The simplest suitable reaction can be written as

$$\mathrm{S} + \mathrm{M} = \mathrm{SM} \qquad (2)$$

with

$$K = (\mathrm{SM})/(\mathrm{S})(\mathrm{M}) \qquad (3)$$

where S represents a surface site, M is the adsorbed chemical and K is the corresponding equilibrium constant. Parentheses refer to activities. Already implicit in this formulation is that one surface 'site' reacts with one molecule of M (however we define these things). Using this formulation, and assuming activity coefficients of one (see Section 3.3 below), q=[S] and c=[M] where [ ] refer to concentrations on a 'per litre of solution' basis.

K_d is important in environmental science because it is a direct measure of the scavenging ability of a solid phase for a substance; conversely, K_d is also a measure of the tendency for a solid phase to release or desorb a substance from an already contaminated solid surface. These concepts are important in terms of contaminant attenuation and cleanup, respectively. The concepts underly the behaviour of many chemicals in the natural environment but are also the basis for many important industrial processes including some of those involved in water treatment, e.g. phosphate and arsenic removal. Few chemicals do not interact with soils and aquifers to some extent, although the exceptions, such as Cl, NO_3 and some solvents, are very important exceptions (it is their lack of interactions which makes them especially problematic in groundwater). K_d therefore partially controls (or reflects) the concentration of dissolved substances in groundwater.

K_d is also directly related to the rate at which a substance can move through a porous medium such as a soil or aquifer. If the substance is adsorbed to a solid particle and if this is immobile, the adsorbed substance (q) will not (normally) move, only the dissolved part (c) will. Hence high K_d values mean slow movement.

The total amount of substance is given by summing the sorbed and dissolved parts

$$c_T = q\,(\rho/\varepsilon) + c \tag{4}$$

where c_T is the total concentration (mol/L solution) and ρ is the bulk density of the aquifer material and ε is the water-filled porosity. The factor ρ/ε converts the amount of material in the solid phase to units of mol/L solution.

3.3 ACTIVITY AND CONCENTRATION SCALES

While mass balances (‘the book-keeping’) necessarily refer to concentrations of chemicals in solution, the chemical behaviour of these chemicals as reflected in the ‘laws of mass action’ relate to their activities or ‘effective concentration’. These two are related through an activity coefficient which is used to account for the deviation from thermodynamic ideal behaviour which is observed in mixtures. Thus:

$$a_i = f_i\, c_i \tag{5}$$

where a_i is the activity of species i with concentration c_i and f_i is its activity coefficient. Fortunately, there are good models for calculating these activity coefficients for dissolved, charged substances, e.g. the Debye-Hückel and Davies models.

3.4 ADSORPTION ISOTHERMS

An *adsorption isotherm* is the relationship between the amount of a substance adsorbed and its concentration in solution (or in the gas phase) measured at a constant temperature, i.e. normally plotted as q (y-axis) against c (x-axis). *Multicomponent* adsorption refers to the simultaneous adsorption of several chemicals. This is sometimes called *competitive adsorption*. In the case of multicomponent adsorption, the amount of a substance adsorbed not only depends on its own concentration but also on the concentrations of the other adsorbing substances. This situation is common in environmental systems.

3.4.1 The Langmuir isotherm

Most adsorption isotherms are based on a *site* model. Consider a lattice of adsorption sites (Figure 3.1) and monocomponent adsorption. Molecules (or charged molecules = ions) are in constant motion in solution and randomly hit the surface; the more molecules in solution the greater the probability that one will hit an empty surface site. There is a certain probability that when a molecule hits an empty surface site it will stick. This probability depends on the ‘stickiness’ of the molecule for the surface, the concentration of molecules in solution and the fraction of empty sites

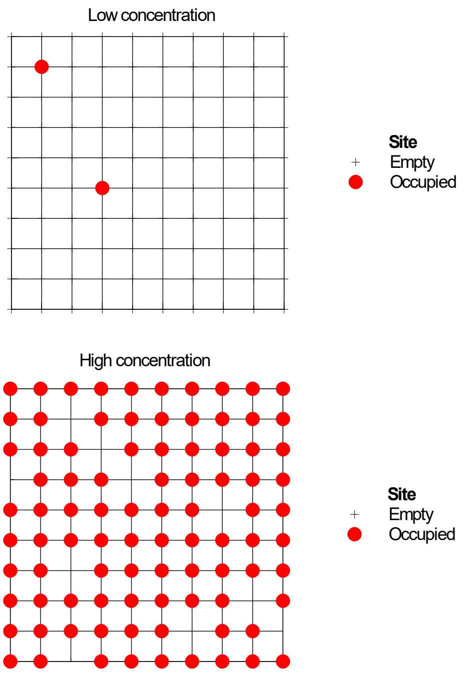


Figure 3.1 A hypothetical view of a lattice of adsorption sites on a surface.
The Langmuir adsorption isotherm can be simply derived by considering the probability that a solute molecule randomly landing on the surface will land on an empty site: almost certain at low concentrations and low surface coverages (top) and very unlikely at high concentrations and high surface coverages (bottom).

The rate at which molecules ‘stick’ to an empty site = $k_{on}\, c\, (1–\theta)$ where k_{on} is a rate constant reflecting the ‘stickiness’ of the surface for the solute in question and θ is the fraction of *filled* sites. Note that when most sites are filled, i.e. θ approaches 1, there is little likelihood of the molecule sticking no matter what its ‘stickiness’.

There is also a probability that adsorbed molecules will desorb from the surface. This is simply proportional to the fraction of filled sites

The rate at which molecule desorbs from a filled site = $k_{off}\, \theta$ where k_{off} reflects the rate at which sorbed molecules are released once they have become attached. At equilibrium, the number of molecules sticking will equal the number of molecules leaving. Therefore

$$k_{on}\, c\, (1–\theta) = k_{off}\, \theta \tag{6}$$

or

$$\theta/(1–\theta) = K_L c \tag{7}$$

This is known as the Langmuir isotherm and K_L is the Langmuir adsorption constant, sometimes called the affinity constant. θ is dimensionless but it is often useful to express it with dimensions

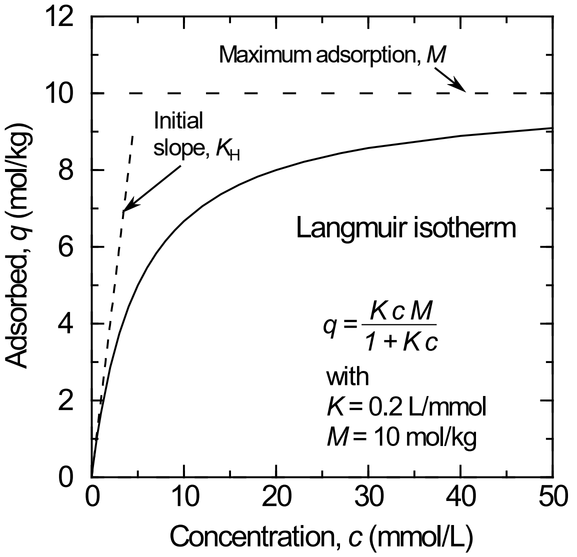


Figure 3.2 A typical plot of a Langmuir adsorption isotherm. It shows the amount adsorbed plotted against its solution concentration. The line shows the form of the Langmuir isotherm with the given parameters. The Langmuir K parameter shown here is written as K_L in the main text.

$$q = K_L\, c\, M / (1+K_L\, c) \qquad (8)$$

where c is the amount of adsorption in say mg/kg solid or mol/kg solid and M is the total number of adsorption sites or adsorption maximum in the same units.

This isotherm can also be simply derived from Eq. (3) by noting that the total number of sites is given by SM + S.

The Langmuir isotherm has a characteristic shape – it is linear at low concentrations, then becomes noticeably curved and then asymptotically approaches the adsorption maximum, M, at high concentrations (Figure 3.2). The isotherm is a nonlinear isotherm since a plot of q vs c is not linear over its entire range.

Many other equations are used for adsorption isotherms but the Langmuir isotherm is fundamental to them all. It has two parameters, K_L and M. Note that combining equations (1) and (8)

$$Kd = K_L\, M / (1+K_L\, c) \qquad (9)$$

In this case, K_d is not a constant but decreases with increasing concentration – it asymptotically approaches zero at high concentrations. If a surface is nearly saturated then little further adsorption can or will take place and the surface behaves like a non-adsorbing surface. This equation differs from that given in the EA guidance publication on Natural Attenuation (Carey et al., 2000 p.85).

In a multicomponent system, the Langmuir isotherm may be extended in a straightforward way which for component i is

$$q_i = K_{L,i}\, c_i\, M / (1 + \Sigma K_{L,j}\, c_j) \qquad (10)$$

where each component has a distinct K_L and the summation is over all j adsorbed species. Multicomponent adsorption is also often called *competitive adsorption* since the various components all compete with one another for adsorption sites.

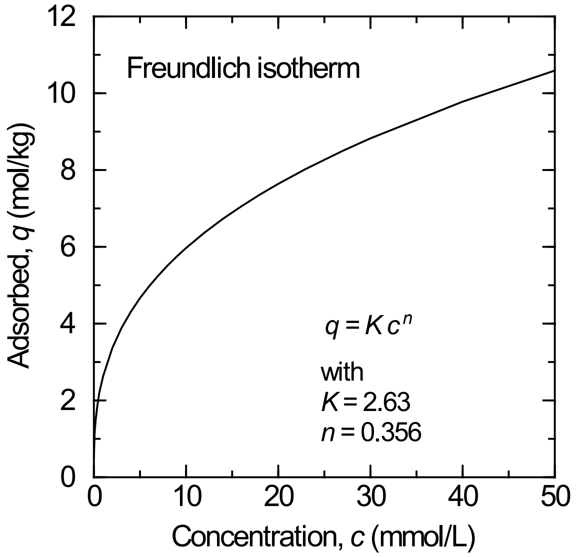


Figure 3.3 A typical plot of a Freundlich adsorption isotherm. It shows the amount adsorbed plotted against its solution concentration. The line shows the form of the Freundlich isotherm with the given parameters. The Freundlich K parameter shown here is written as K_F in the main text.

3.4.2 The linear isotherm

The linear isotherm is simply

$$q = K_H\, c \qquad (3.11)$$

where K_H is the linear (Henry's) adsorption constant. Clearly this is a special case of the Langmuir isotherm for low concentrations where

$$K_H = K_L\, M \qquad (3.12)$$

i.e. the slope of the isotherm is a measure of both the Langmuir adsorption constant *and* the number of sites. Using Figure 3.3, the linear isotherm represents the case where practically every molecule hitting the surface hits an empty site.

It is only possible to separate these two from the curvature in the isotherm. If there is no significant curvature, it is not possible to separate these parameters. The linear isotherm is a special case – it is unreasonable to expect the linear isotherm to work at high concentrations because that would mean that there are an infinite number of adsorption sites and that is impossible. It is also reasonable to expect the linear isotherm to be true at low concentrations and this is found to be true in practice in a very wide range of conditions even when there are many substances adsorbed and when there is some heterogeneity. The only case where it manifestly does not apply is for the binding of cations to pure natural organic matter ('humics').

Note that for a linear isotherm

$$K_d = K_H \qquad (13)$$

and so, in this case, K_d is a constant independent of concentration.

3.4.3 The multisite Langmuir isotherm

The Langmuir isotherm assumes that all surface sites have the same affinity for the chemical of interest. This is rarely the case in practice – most soils and aquifer solids contain a variety of minerals, each with their own characteristic adsorption affinities. Even individual minerals are made up of various crystal planes each potentially with its own affinity and some substances, like humic materials, are so heterogeneous that there may be literally thousands of different types of sites.

We can calculate the overall amount of adsorption by summing the contributions of each the different types of sites. Using the Langmuir model, this means we need to know the affinity (K_j) of each type of site present and the number of them (M_j).

$$q_i = \sum[K_{Li}\, c\, M_j / (1 + K_{Lj}\, c)] \qquad (14)$$

where j extends over all site types present. Eqn (14) is known as the multisite Langmuir isotherm for a single component. You need to know the number (M_j) and binding affinity (K_{Lj}) of each type of sites. Normally the maximum number of sites for which these parameters can be resolved from an experimental isotherm is 3 or less.

3.4.4 The Freundlich isotherm

In practice because of the experimental errors inherent in all experimental data, it becomes difficult to estimate reliably more than about three sets of K_{Lj}'s and M_j's parameters by fitting to experimental isotherm data. While there are ways that attempt to do this in a sensible way, a slightly different approach is to assume a continuous distribution of site affinities of some particular shape. One such distribution is called the Sips distribution which looks somewhat like a normal distribution. Integrating this over the full range of affinities gives the so-called Langmuir-Freundlich isotherm:

$$q = (K_L\, c)^n\, M / [1 + (K_L\, c)^n] \qquad (15)$$

where n is known as the heterogeneity factor and normally $0 < n \leq 1$. The smaller the value of n, the broader the Sips distribution, i.e. the more heterogeneous it is. This isotherm is like the Langmuir isotherm in that it approaches a maximum adsorption, M, which is useful since this is a reasonable thing to expect. The Langmuir-Freundlich isotherm has three parameters: K, M and n. Note that when n=1, the isotherm reverts to the Langmuir isotherm.

The limiting case of the Langmuir-Freundlich isotherm at low c can be derived from Eqn (15). It is

$$q = (K\, c)^n\, M = K_F c^n \qquad (16)$$

Eqn (16) is known as the Freundlich isotherm and is probably the most widely used and most successful isotherm for simple applications to real world situations. It implicitly takes into account the heterogeneity or variability found in real-world situations. A plot of log s vs log c (called a 'Freundlich' plot) is linear with a slope n and an intercept at log c=0 equal to log K_F (Figure2.3). The smaller the slope of the Freundlich plot, the more the apparent heterogeneity of the material. The Freundlich isotherm has been widely used for trace metal adsorption to soils and sediments. Typically, n is in the range 0.5–0.8. It has also been widely used for describing the sorption of organics including pesticides to soils. For $n \neq 1$, the Freundlich isotherm is nonlinear. Note that when n=1, it reverts to the Linear isotherm.

Just to confuse the situation, the Freundlich isotherm is sometimes written as

$$q = K_F c 1/N \qquad (17)$$

where N=1/n with correspondingly transformed limits. This is an archaic form and best not used.

Inspection of Eqn (16) shows that $K_F = K_L{}^n M$, i.e. K_F is a complex factor that implicitly includes both an affinity factor and a site density factor. It also has awkward non-integral dimensions.

The K_d for the Freundlich isotherm is given by

$$K_d = K_F c n{-}1 \qquad (18)$$

which illustrates that like the Langmuir isotherm, the K_d decreases with increasing concentration. Again, this equation differs from that given in the EA guidance publication on Natural Attenuation (Carey et al., 2000 p.85).

Although the Freundlich isotherm does not have as good a 'theoretical pedigree' as the Langmuir isotherm, it has actually been shown to work better than the Langmuir isotherm in many 'real world' situations. It is probably the best isotherm for most organics transport modelling, e.g. pesticides. Remember when n=1, it reverts to a linear isotherm and so also represents the constant K_d situation. It also often works well for trace metal binding by soils and aquifer materials albeit at constant pH.

3.4.5 Multicomponent Freundlich isotherm

It was widely appreciated that trace metal sorption is often strongly pH dependent and so attempts have been made to extend the traditional Freundlich isotherm to include this. This involves extending the Freundlich isotherm to two or even three components. These extensions are known as the two-species Freundlich isotherms and three-species Freundlich isotherms, respectively.

Two species Freundlich:

$$q_i = K_{F2}\, c_i n_i\, c_j\, n_j \qquad (19)$$

Three species Freundlich*:*

$$q_j = K_{F3}\, c_i n_i\, c_j\, n_j\, c_k\, n_k \qquad (20)$$

When, as is usually the case, the coefficients n_j and n_k are negative, the components j and k are known as competitors and increasing their concentrations will decrease the amount of component i adsorbed.

It is easy to see how this equation could be extended to 4 or more species but there is a problem. As new components are added, K_{Fi} changes its value and so any tabulation of K_F values will depend on how many components are included. This makes it awkward to extend to systems other than those under study. In the above example, $K_{F2} = K_{F3}\, c_k{}^{nk}$. Therefore, K_F has no pretensions of being an intrinsic property of the material, i.e. a property of the interaction of a single molecule with the surface.

3.4.6 Adsorption stoichiometry

It has been implicit in the isotherms discussed above that one molecule occupies one surface site but sometimes a molecule has to bridge between two or more surface sites. This ratio is known as the *adsorption stoichiometry*. For a 2:1 stoichiometry, we have to calculate the probability that two molecules will hit adjacent sites at the same time. In this case, it is possible to show that the Langmuir model becomes

$$\theta/(1-\theta) = (K_{LC})^{1/2}. \tag{21}$$

Note that the exponent is directly related to coordination stoichiometry. Eqn (21) has exactly the same form as the Langmuir-Freundlich isotherm, Eqn (15). It is known in the field of biochemistry as the Hill equation and is often used for ligand binding to biomolecules.

Therefore, equations of this form, Eqns (15) and (21), can either be interpreted as: (i) a quasi-Gaussian distribution of sites obeying the Langmuir isotherms (with its implicit 1:1 site coordination), *or* (ii) as a single Langmuir model with a n:1 coordination stoichiometry. This ambiguity gives the equation great flexibility and probably accounts for the great success of the Freundlich isotherm in many situations.

3.4.7 Multi-component binding to a heterogeneous surface

An isotherm that does attempt to preserve the K terms as intrinsic adsorption or binding constants is the NICA isotherm (Kinniburgh et al., 1999). This extends the above equations to multi-component binding to a heterogeneous surface using the continuous distribution model of binding site K values. It encompasses the properties of both the Langmuir-Freundlich isotherm (quasi-Gaussian distribution of site affinities) with those of the Hill equation (non-integral reaction stoichiometry), and essentially entails the resolution of both these approaches. It is now being used quite successfully for modelling metal ion binding to humics (natural organic matter). The only other model of similar scope is WHAM/Model VI or VII which uses discrete affinity distributions to describe the available binding sites (Tipping, 1998; Tipping et al., 2011).

The following NICA isotherm equation can be derived which for the binding of component i gives

$$\theta_i = \frac{(\widetilde{K}_i c_i)^{n_i}}{\sum_i (\widetilde{K}_i c_i)^{n_i}} \times \frac{(\sum_i (\widetilde{K}_i c_i)^{n_i})^p}{1 + (\sum_i (\widetilde{K}_i c_i)^{n_i})^p} \tag{22}$$

$\widetilde{K}_i$ is the median affinity parameter and n_i is the 'non-ideality' parameter for component i and p is the heterogeneity parameter which is a characteristic of the surface.

The above equation is divided into two parts: the second part (after the multiplication symbol) represents the competition of all species for the binding sites. The first part provides the ratio (always less than one) of any particular ion being bound compared with the rest. In all cases, the $(Kc)^n$ term for each ion provides a measure of its ability to 'fight for surface sites'. The larger the K, c or n terms for a particular ion, the greater its competitiveness. All ions compete on this basis resulting in an equation like Eqn (22).

Note that all of isotherms described above can be viewed as special cases of the NICA isotherm. Comparing with the NICA model enables some of the assumptions in the simpler models to be understood more clearly.

In practice, the NICA model for specific ion binding is combined with a Donnan model for non-specific binding to natural organics. Non-specific binding refers to the binding of ions to the residual negatively-charged sites after the specifically bound ions have bound to the surface.

A discrete site model that behaves somewhat like the NICA isotherm can be derived where the number of types of site is relatively small (Tipping, 1998).

3.5 ION EXCHANGE

In the models discussed, the chemicals may be charged or not. Many chemicals, especially organic chemicals such as some pesticides, are not charged. Also, no mention was made of any surface charge on the mineral. There are many circumstances where both the adsorbing chemical and the mineral surface are electrically charged and this leads to special types of interaction. These depend to a large extent on the nature of the charge – is it formed deep inside the mineral or at the surface. Below we discuss this in some detail and follow its consequences in terms of the types of equation that can be used to describe the binding.

3.5.1 Permanent charge cation exchangers

Historically, the adsorbed molecules were envisaged to bind to so-called empty sites. In practice, they probably displaced some solvent (water) molecules. A more interesting case is ion exchange. A few minerals, most notably certain clay minerals, are not neutrally charged. This contradicts Pauling's rule which states that there should be a local neutralisation of charge within minerals. Clay minerals negate this rule through the isomorphous (=similar-sized) substitution of Al^{3+} for Si^{4+} and Mg^{2+} for Al^{3+} within their structures. Because the substitution is in both cases of cations with a lower positive charge, the clays ends up with a net negative electrical charge. The amount of this negative charge depends on the amount of isomorphous substitution but for clays is up to about 1 eq/kg although typically less than half this. This quantity is called the *cation exchange capacity* or CEC. This type of charge is called *permanent charge* because it does not depend on the solution chemistry but is fixed by pre-existing and unchangeable structural features.

This negative charge is balanced by the adsorption of cations (positively-charged ions) which are attracted to the negative charge which emanates from the clay surface. Indeed, the charge always has to be completely balanced by adsorbed cations – there are no 'empty' sites and the mineral and accompanying solution must always have a net zero charge. When there is more than one type of cation present in solution (as in the real world), all cations present will play some part in neutralizing the net negative charge of clays. The various ions present all compete with each other for exchange 'sites' with the loading of each dependent on its concentration in solution, its charge and its intrinsic affinity for the clay surface (Figure 3.4).

HOMOVALENT EXCHANGE

Homovalent exchange refers to the exchange of equally charged ions. In a simple binary system consisting of just Na^+ and NH_4^+, the ion exchange equation is given as

$$Na^+ + NH_4X = NaX + NH_4^+ \tag{23}$$

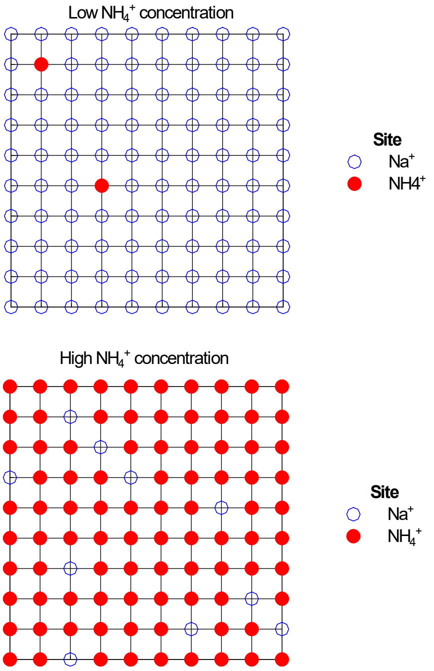


Figure 3.4 A hypothetical view of a lattice of ion exchange sites on a surface.
The ion exchange isotherm can be simply derived by considering the probability that a target ion such as NH_4^+ randomly landing on the surface will land on a site occupied by a different type of ion (Na^+): almost certain at low target concentrations and low surface coverages of the target ion (top) and very unlikely at high concentrations and high surface coverages (bottom). Note that there are no 'empty' sites: this figure refers to a permanent charge cation exchanger.

where X represents the negatively charged clay exchanger (X^-). An equilibrium constant for this reaction can be written as

$$K_{GT} = \{NaX\}(NH_4^+)/\{NH_4X\}(Na^+) \qquad (24)$$

where {} represent surface activities and () represent solution activities.

Various models exist, the three most important are the Gaines-Thomas, Vanselow and Gapon models. Probably the most widely used is the Gaines-Thomas model (e.g. as in PHREEQC-2) which assumes that the surface activity of a particular component is given by its *equivalent fraction* in the exchanger phase (the Vanselow model uses the mole fraction which is the same in the case of homovalent exchange but not in the case of heterovalent exchange), e.g. $\{NaX\} = n_{Na}/(n_{Na} + n_{NH4})$ and n_i is the number of moles of i bound.

$$\theta_{NH4}/(1-\theta_{NH4}) = \theta_{NH4}/\theta_{Na} = KGT\ (a_{NH4}/a_{Na}) \qquad (25)$$

Note that the θ's here are exchangeable fractions. In this case of binary, homovalent exchange, the relative occupancy of the two ions is simply given by the ratios of the two solution activities. As far as an NH_4^+ ion is concerned, if it hits a site occupied by a Na^+ ion, it displaces it. In that sense, the Na^+ sites behave like empty sites.

The amount of NH_4^+ bound, n_{NH4}, is now given by

$$n_{NH4} = K_{GT}\,AR\,CEC\,/(1 + K_{GT}\,AR) \qquad (26)$$

where *CEC* is the cation exchange capacity and *AR* is the activity *ratio*, a_{NH4}/a_{Na}. For homovalent exchange, the AR is very close to the concentration ratio because the activity coefficients of similarly charged ions are very similar (D-H theory). Note the similarity between this equation and the Langmuir isotherm, Eqn (8). The only difference is that the activity of one species (Langmuir isotherm) has been replaced by the activity ratio of two species (homovalent, binary ion exchange isotherm)

The K_d for NH_4^+ is then given by

$$K_d = n_{NH4}/c_{NH4} = K_{GT}\,CEC\,\alpha_1 \qquad (27)$$

where

$$\alpha_1 = (f_{NH4}/f_{Na})\,(1/c_{Na})\,/(1 + K_{GT}\,AR). \qquad (28)$$

Note that the K_d is not constant but depends inversely on the concentration of Na^+, the competitor, as well as the concentration of NH_4 through the AR term. At *very low* NH_4 *concentrations*, $1 + K_{GT}$ AR approaches 1 and so $K_d \sim K_{GT}\,CEC/c_{Na}$, i.e. K_d/c_{Na} is constant and for a constant Na concentration is directly proportional to the CEC and K_{GT}. At higher NH_4 concentrations, which are common in pollution plumes, K_d varies with the concentration of NH_4 and Na in a more complicated way.

Cation exchange isotherms are often plotted in completely normalised form, i.e. the equivalent fraction of an ion in an exchanger versus its equivalent fraction in solution.

HETEROVALENT EXCHANGE

Heterovalent exchange refers to the exchange of unequally charged ions. This situation is more complex than for homovalent exchange. For example, for calcium-ammonium exchange

$$CaX_2 + 2NH_4^+ = Ca^{2+} + 2NH_4X \qquad (29)$$

where, as before, X represents the negatively charged clay exchanger (X^-). An equilibrium constant for this reaction can be written as

$$K_{GT} = \{NH4X\}^2(Ca^{2+})\,/\,\{CaX_2\}(NH_4^+)^2 \qquad (30)$$

where according to the Gaines-Thomas convention, e.g. $\{NH4X\} = n_{NH4}/(2n_{Ca} + n_{NH4})$. In this case, the activity ratio, AR, is given by

$$AR = a_{NH4}^2/a_{Ca} = (f_{NH4}^2/f_{Ca})\,(c_{NH4}^2/c_{Ca}) \qquad (31)$$

The K_d for NH_4 binding is now given by

$$K_d = K_{GT}\,CEC\,\alpha_2 \qquad (32)$$

where

$$\alpha_2 = [AR\,/2c_{NH4}]\,[\surd(1 + 4\,K_{GT}\,AR) - 1] \qquad (33)$$

As for monovalent exchange, at low NH_4 concentrations and a constant Ca concentration, K_d again directly depends simply on K_{GT} and CEC whereas at higher NH_4 concentrations, it also depends on a complicated function of the NH_4 and Ca concentrations.

The CEC is an important characteristic of a clay, soil or aquifer. For pure clay minerals, the CEC varies from just a few meq/kg for kaolinite up to 1000 meq/kg for smectites such as montmorillonite. Loamy soils typically have CECs of 100-500 meq/kg.

3.5.2 Variable charge exchangers – surface complexation models

Many natural solids, notably oxide minerals and organic matter, do not have a permanent electrical charge due to isomorphous substitution but can acquire a surface electrical charge through the preferential binding of certain ions, called *potential determining ions* (pdi's), at the solid surface. The resultant surface charge varies continuously with the concentration of these pdi's in solution. The most important pdi's are H^+ and OH^- which give the surface a net positive or negative charge, respectively, which varies with solution pH (pH-dependent charge). The CEC of these materials is not a constant but increases with increasing pH and can even be negative. This has important implications for both the laboratory determination of CEC (what pH is it measured at?) and for its application in models (what is the field pH and does it vary with space or time?).

Surface complexation models are used for modelling ion (cation or anion) binding to charged surfaces particularly oxides and the edges of clay minerals. They combine an 'ordinary' ligand binding concept (formulated like complexation in solution) with an additional term to account for the extra attraction accounted for by bringing a charged ion to a charged surface (like charges repel; opposite charges attract). This electrostatic term acts as a multiplication factor for the solution concentration (strictly activity) and can be thought of as defining a surface concentration (activity). Alternatively, the factor can be thought of as an activity coefficient, as in solution, albeit its size can be much greater than that in solution (it can be 30 or more).

The simplest surface complexation model is the Diffuse Layer Model (DLM) as used by Dzombak and Morel (1990) in their analysis of ion binding to amorphous iron oxide (ferrihydrite). This has a single potential. This model is incorporated in PHREEQC and many other modelling packages.

More complex surface complexation models can be built up by adding more surface planes, each with its distinct electrical potential and corresponding multiplication factor or activity coefficient. The triple layer model (TLM) is one such, popular in the 1980's but now falling into disuse partly due to the number of difficult-to-observe parameters involved. The Basic Stern and CD-MUSIC models fall somewhere between these two types of model and appear to provide a useful compromise between unmanageable complexity and over-optimistic simplicity.

The theory for ion binding to these materials is somewhat different from that of permanent charge cation exchangers and is often called *surface complexation* theory. It is rather similar to the Langmuir isotherm in that it allows for 'free' or unfilled sites but because the surface charge and surface potential vary with the number and type of ions adsorbed, the binding constant, K_i, also systematically varies

$$K_i = K_{i,int} \exp(-zi\ e\ \psi / kT) \tag{34}$$

where ψ is the surface electrical potential, $K_{i,int}$ is the intrinsic binding constant for ion *i*, i.e. K_i at zero surface potential or charge. This complicates the calculations because K_i now varies with solution chemistry and so adsorption or binding has to be solved iteratively. A further complication is that ψ varies with distance from the surface and different ions bind at different distances from the surface which gives rise to models with one, two, three or more different sorption planes, each with their characteristic ψ. Well-known surface complexation models are the diffuse double layer model, the Basic Stern model, the Triple Plane model, the Triple layer model and the Constant Capacitance model.

A characteristic of many variable charge materials, including iron, aluminium and manganese oxides common in the environment, is that $K_{i,int}$ can be very large on account of some specific chemical interaction with the surface. This is called *specific adsorption*. Some surfaces can even bind some cations when they have a net positive charge, contrary to what might be expected. Therefore, it is wrong to say that because a surface has a positive charge (pH less than the so-called 'point of charge') that it will not adsorb cations such as Cd^{2+}. It might do so. Oxides can also bind anions such as phosphate very strongly especially at low pH.

Variable charge materials normally have a net surface charge as a result of specific adsorption. Since the overall charge of a particle must be zero, this charge is exactly balanced by the binding of an equal number of *counter-ions* of opposite charge, e.g. Cl^- or HCO_3^- on a positive surface. This is called non-specific adsorption since it merely responds to the net electrical charge (positives attract negatives and *vice versa*) and does not involve any chemical interactions. It can in principle be negative for like-charged ions but this is normally very small. The overall amount of a chemical bound therefore consists of the sum of specifically and non-specifically bound chemical.

An important practical difference between cation exchange and surface complexation is that while ion exchange does show a characteristic selectivity sequence for different ions, often following their sequence in the periodic table, e.g. $Cs^+ > K^+ > Na^+ > Li^+$. the differences are not so great, perhaps an order of magnitude or so. Surface complexation, on the other hand, can give selectivity differences of six orders of magnitude or more and so can be very important for some elements.

3.6 SORPTION AND TRANSPORT

If a substance is adsorbed, it cannot move with the mobile water. Therefore it is not surprising that there is a direct relationship between sorption and transport (for a detailed discussion, see Appelo and Postma, 1993). For a chemical obeying a linear isotherm (constant K_d), its velocity of movement, v_i, is directly related to the rate of movement of water, v_{H2O}, and the slope of the isotherm which in this case is given by the K_d

$$v_i = v_{H2O} / R_f \tag{35}$$

and R_f is the retardation factor given by

$$R_f = 1 + (\rho/\varepsilon)\ K_d \tag{36}$$

where ρ/ε is the solid/solution ratio often about 5–10 kg/L for soils and aquifers, i.e. for K_d = 1 L/kg, R_f is 6–11 or the chemical in question moves 6 to 11 times slower than water. If a non-dimensional K_d, K_d', is defined by expressing q in terms of mol/L porewater rather than in mol/kg solid then

$$R_f = 1 + K_d' \tag{37}$$

This shows clearly that K_d' is directly related to the additional retardation experienced by the chemical over that experienced by a non-adsorbed solute ($R_f = 1$).

Complications arise when the isotherm is nonlinear. Then the K_d varies with concentration and so does R_f with the retardation being greatest where the isotherm slope is greatest, i.e. the speed of movement of a chemical depends on its concentration. Since the concentration is constantly changing as a result of dilution, adsorption/desorption, degradation etc so is its speed. We should therefore write $K_d(c)$ and $R_f(c)$ to indicate that these parameters vary with the concentration of the chemical itself or with the concentration of others in solution especially competitors.

The shape of the isotherm becomes very important for transport calculations, particularly whether the shape is concave or convex concentration (to the x-axis). With a Langmuir isotherm, (dq/dc) is greatest at low concentrations and so the retardation is greatest there. When a slug of contaminant moves as a plume into an uncontaminated aquifer, the front of the plume will have the lowest concentrations and will move slowly with the high concentrations in the centre of the plume moving fastest. There is therefore a tendency for the high concentrations to overtake the low concentrations. This leads to a very steep or self-sharpening front sometimes called a sharp front or shock wave.

With binary ion exchange, the shape of the normalised isotherm reflects the relative strength of binding of the two ions and can be either concave or convex to the solution concentrations axis depending on whether the incoming ion is preferred to the bound ion (*favourable* exchange) or *vice versa* (*unfavourable* exchange). There is some symmetry here: if Na-Ca exchange is unfavourable, then Na-Ca exchange must be favourable so adsorption fronts are quite different from desorption fronts. The shape of the isotherm usually varies with the concentration of salts present – it becomes more non-linear at low concentrations.

3.6.1 Transport with favourable exchange

Favourable exchange leads to the development of self-sharpening front. The number of pore volumes, V, of component i that must pass through an aquifer before i emerges at with its initial concentration can be related to the number of pore volumes of water, V_0, that has passed through

$$V/V_0 - 1 = (CEC/A_0)\,(\Delta\beta_i/\Delta\alpha_i) \tag{38}$$

where A_0 is the total normality (anion concentration) of the inflowing solution, β is the equivalent fraction of i on the exchange sites and α is the equivalent fraction of i in solution. [$\Delta\beta_i/\Delta\alpha_i$] is the slope of the normalised isotherm either side of the sharp front, i.e. $(\beta_2 - \beta_1)/(\alpha_2 - \alpha_1)$. $V/V_0 - 1$ is a measure of the number of pore volumes after the arrival of a conservative solute, such as Cl, that component i arrives at a given place. It has been called the *flushing factor*, *Ψ condition* and *throughput parameter*.

CEC/A_0 is a measure of the overall importance of adsorbed and solution ions in general rather than for a specific substance. It is closely related to the total time to exhaust the CEC, T_{exhaust}, as used in LANDSIM:

$$T_{\text{exhaust}} = CEC_{\text{avail}}/LR \tag{39}$$

where CEC_{avail} is the 'available' CEC of the aquifer in the system (meq) and LR is the loading rate in meq/s. In LANDSIM, it is assumed that LR is dominated by a single cation, e.g. NH_4^+, i.e. it does not consider multi-component ion exchange. The 'available' CEC relates to the geometry of the clay liner and the wetting properties, and is the total CEC of the liner, not the CEC of a sample.

The higher the CEC, the longer it will take for i to emerge. Also, the lower the total normality (salt content) of the inflowing/recharging groundwater, the slower that solute i will emerge.

3.6.2 Transport with unfavourable exchange

With unfavourable exchange, a weakly bound ion (e.g. NH_4^+) attempts to move through a column already containing a strongly bound ion (e.g. Ca^{2+}). Movement of the NH_4^+ at low concentrations is relatively fast and at high concentrations is relatively low leading to a long forward tail or diffuse front in the effluent. The shape of this curve is independent of concentration. It is possible to derive the exchange isotherm by integration of this curve.

The flushing factor for the elution of an ion undergoing unfavourable exchangeable exchange, i.e. is given by

$$V/V_0 - 1 = (CEC/A_0)\,(d\beta_i/d\alpha_i) \tag{40}$$

where $d\beta_i/d\alpha_i$ is the slope of the normalised exchange isotherm at the concentration given by α_i.

3.6.3 Transport with multicomponent ion exchange

The theory of multicomponent ion exchange chromatography is now well understood and is discussed by Appelo and Postma (1993). Analytical solutions for homovalent ion exchange are available but more generally the results must be calculated numerically. Movement of a multicomponent solution, like a polluted groundwater, through a soil or aquifer is characterised by a series of diffuse fronts (unfavourable exchange), sharp fronts (favourable exchange) for each component with plateaus of constant composition in between.

Most major anions in groundwaters are not strongly adsorbed by soils or aquifers and so pass through the aquifer unretarded. These are eluted from a column after one pore volume. Because of the electroneutrality constraint, they must always drag along an equal number of cations. As the input solution changes normality (i.e. the concentration of anions), so the number of cations changes too. Cation exchange equations can be used to derive the proportions of the various cations that are eluted at the normality front.

3.7 CONCLUSIONS

The K_d or partition coefficient is simply calculated from the ratio of adsorbed to solution concentrations. It is an important parameter that determines the 'solubility' of a chemical and its ease of movement in a soil or aquifer.

Under special conditions (a linear isotherm, no competition, low concentrations), K_d is independent of the concentration of other chemicals in solution but more normally K_d varies with the concentration of both the chemical of concern and that of others. This is true of nonlinear isotherms and is particularly common at high concentrations. If competition is involved, then both the concentration of the sorbing chemical and of all the competitors are important.

Charged chemicals (ions) frequently bind to charged surfaces. This surface charge can be derived in two ways – permanent charge due to isomorphous substitution as on many clays and a variable surface charge due to specific adsorption as on many oxides. The former gives rise to cation exchange and the latter to surface complexation. In both these cases, K_d will vary with the concentration of some other ion either as a competitor or as a potential determining ion.

An implication of this is that K_d must not be assumed to be a constant. It almost certainly is not an intrinsic property of the mineral itself but will also depend on the solution chemistry. Therefore, whenever laboratory K_d measurements are used in a model, it must be clearly demonstrated that an appropriate K_d is being used. In practice, when a chemical is bound by a cation exchange process, the K_d will *always* vary with the concentration of competitor cation(s) and maybe with the concentration of the ion itself and so K_d is not a very good way of capturing this. Better would be the ion exchange constant(s) for the reactions involved, the CEC and measurement of all the main competitors especially Ca, Mg and Na.

The concept of K_d itself is not a bad one – it is the assumption that it is *constant* that can be misleading and lead to erroneous conclusions. It has been demonstrated in the discussion above how the K_d can be expected to vary in a systematic way depending on the processes involved. It is often therefore better to deal with this variation explicitly by using more sophisticated solid/solution partition models rather than rely on a ‘constant’ K_d approach. Where a constant K_d is assumed, it is incumbent on the user to establish that the K_d does not vary systematically with the relevant environmental variables.

4 Using geochemical parameter data for groundwater modelling

4.1 MODELS

There is now an abundance of good software available for calculating sorption and transport in environmental systems. PHREEQC-2 is one of the best and is freely available over the web. It can calculate both chemical speciation including ion exchange and simple surface complexation as well as 1D transport. It can deal with complex chemical situations but only simple transport ones. Other models specialise in the transport part. PHREEQC-2 is being linked with more detailed 3D hydrogeological transport models to provide a comprehensive reactive transport model (e.g. PHAST).

The advantage of these chemical models is that they do the chemistry 'correctly', e.g. keep charge and mass balances, calculate competitive interactions, solubilities, activities etc. This provides a degree of robustness. A disadvantage is that they are complex. However, much of this complexity can be hidden from the user with a well-designed user interface and the use of default values, so it is not the limitation that might appear. In the medium to long term, the benefits of these more rigorous models are likely to outweigh their disadvantages.

4.2 DATA REQUIREMENTS

Having established that a rather small subset of natural minerals and particles have a disproportionate influence, it is instructive to see how geochemical programs deal with them. This is largely governed by the chemical processes operating. We discuss these below with particular reference to how the geochemical speciation and mass transport program, PHREEQC-2, deals with them.

Two major approaches are possible: the individual component approach and the whole soil/aquifer material approach. The individual component approach is closely related to the dominant particle concept. This assumes that the behaviour of the whole system can be calculated from the sum of the behaviour of the individual components (this is the implicit approach in most chemical speciation programs such as PHREEQC-2). For this to be valid, the interactions between the behaviour of the individual components must be negligible. This is often, but not always, true. For example, interactions may be important in the organic matter-clay-oxide system. Where the individual components cannot be quantified, then the soil or aquifer has to be treated as a whole. Because of the (unknown) heterogeneity of such systems, valid predictions based on this approach are necessarily likely to be of a much narrower scope. Here we concentrate on the individual component approach.

4.2.1 PHREEQC-2 implementation

The various processes that control solute concentrations in natural waters can be grouped under the following headings (PHREEQC-2 keywords in parentheses): precipitation and dissolution of a pure mineral (`EQUILIBRIUM_PHASES`) or coprecipitation/co-dissolution (`SOLID_SOLUTIONS`), adsorption (`SURFACE`), ion exchange (`EXCHANGE`), degradation (`KINETICS`). Each is controlled by a different set of equations and requires different input parameters (Table 4.1).

Most of the processes outlined in Table 4.1 require both generic and site-specific information. Even some of the 'generic' data may need to be tuned to the specific site of interest. However, this may be possible to do with more accuracy and confidence than, for example, extrapolating with a statistical model that has no in-built constraints related to the 'real world' (and could make totally unrealistic predictions if the extrapolation is great). Furthermore, the modelling approach will improve as more data are collected with time. Indeed, it can usefully be used to help guide the collection of 'critical' data by highlighting unknowns that are likely to play a key role.

One parameter from the list considered in this project, but which is usually not considered by the chemical speciation and modelling packages such as PHREEQC, is bioavailable Fe and Mn. Natural attenuation is a low-technology approach to groundwater remediation that makes use of natural degradation processes which can often be biologically mediated, and the major chemical models do not include biological processes. In the absence of oxygen one of the most common degradation processes within contaminant plumes involves biologically mediated oxidation of organic compounds by mineral oxidants, Fe^{III} and Mn^{III} or Mn^{IV}. These oxidants, particularly Fe^{III} are widely available in mineral form in aquifers and are often present in much larger quantities than soluble oxidants (O_2, NO_3^-, SO_4^{2-}). However, not all of the Fe/Mn minerals present are available to microbes for use in biodegradation reactions and only a fraction of the total Fe/Mn minerals present may be reducible under field conditions. Therefore, to evaluate the potential contribution of mineral oxides to natural attenuation at a given site, methods of determination that resolve the bioavailable fraction are required. By quantifying bioavailable Fe/Mn, these methods may provide a basis on which to predict the buffering of aquifer contaminant plumes and to understand redox processes at contaminated sites (Heron et al., 1994a).

Table 4.1. The processes considered by the general-purpose speciation and mass transport program, PHREEQC-2, and their data requirements.

Process	**PHREEQC-2 keyword(s)**	**Data Requirement(s) Generic needs**	**Data Requirement(s) Site-specific needs**
Solution speciation including redox	`SOLUTION`	Thermodynamic data (log K etc.) for each species (various databases supplied).	Total element and ligand concentrations in water (from comprehensive chemical analysis).
Mixing of waters from different sources	`MIX`	None	Mixing fractions (from water fluxes).
Irreversible reaction	`REACTION`	List of substances reacting & equations (likely to be known from local geology).	Amount of substance reacting (difficult to know *a priori* but estimate from mineralogy).
Solubility of pure minerals (precipitation and dissolution)	`EQUILIBRIUM_PHASES`	Thermodynamic data (solubility products) (various thermodynamic databases supplied for pure minerals).	Amount and identity of each reactive mineral phase needs to be known (from XRD and bulk chemical analysis).
Solubility of impure minerals (precipitation and dissolution)	`SOLID_SOLUTIONS`	As above plus choice of model for ‘non-ideal’ behaviour. Assumptions also need to be made about the type of equilibrium existing during growth and dissolution.	Data for chemical composition of mineral & solution phases would help calibration (difficult but can be estimated from electron microprobe analysis or selective dissolution).
Gas solubility	`EQUILIBRIUM_PHASES and GAS_PHASE`	Thermodynamic data (Henry’s law constants or log K_H) (supplied for common gases).	Partial pressure of the various components or the composition of the gas phase (field/lab measurements of gas composition).
Adsorption	`SURFACE and SURFACE_SPECIES`	Need to be able to specify precisely the adsorption reaction (appropriate ‘model’ is not always obvious) (site density may be known from crystallography or literature) .	Amount of oxides present from selective dissolution, XRD analysis etc.
Ion exchange	`EXCHANGE and EXCHANGE_SPECIES`	Specify ion exchange reaction. (CEC and log K known for a range of reference materials).	Cation exchange capacity and log K (from specific lab expts or estimated from clay content and type if known, or some other highly-correlated parameter).
Kinetics	`KINETICS and RATES`	Specify reaction(s) and supply parameters. Non-standard but some available in literature or supplied with PHREEQC-2.	Difficult to generalise and may be related to particle size (basic principles are often quite well understood and can be ‘tuned’ for specific examples).
Biodegradation	see `KINETICS`	Basic principles quite well understood but need to establish particular reaction stoichiometry which can be difficult in strongly heterogeneous systems.	Microbial activity (difficult to estimate a priori – use inverse modelling).
Oxidation/reduction	`EQUILIBRIUM_PHASES and SOLUTION`	Fix *pe* or the concentration/partial pressure of a redox-sensitive species.	Often determined by diffusion of oxygen (difficult to fix), availability of electron donors/acceptors (organic matter, nitrate, Fe^{III} etc.). Invariably controlled by biological activity (difficult but can look to constrain by measurement of by-products).
Transport	`TRANSPORT and ADVECTION`	1-D transport depends on water flux and porosity. Diffusion coefficients known from literature.	Assumes flow is known (use a hydrogeological model or recharge rate and assume piston flow; porosity from literature, direct measurement or inference; can use knowledge of ‘fraction of immobile water if known. Dispersion coefficient usually not known but not critical.
Evaporation	`REACTION`	No chemical reaction need be specified.	Specify amount of water ‘disappearing’ (estimate from evaporation model).

4.3 APPROACHES TO ESTIMATING PARAMETERS FROM INCOMPLETE DATA

4.3.1 Introduction

Descriptions of soils or aquifers are typically supplied to a contaminant-transport modelling program either in the form of a grid of values of the various properties (porosity, transmissivity, K_d etc) or as the spatially-averaged value for the properties for a particular unit. A question that always arises is how to derive this type of information. Given the overall paucity of relevant direct measurements evidenced in the preceding sections of this report, some assumptions and extrapolations need to be made. Below we discuss different approaches to this problem and the nature of the assumptions involved.

To be worthwhile, the approach adopted needs to capture something about the specific environment of interest but it should also make use of 'the science base' – an understanding of the processes involved – as far as possible. This will make interpolation to new areas more reliable. For example, if we had data for the transport of Zn through an aquifer but not for Pb, we might be able to make use of the Zn data to estimate the transport of Pb. But first we would have to estimate the likely mechanisms controlling the retardation of the two chemicals. If they were the same – most likely cation exchange on clays or sorption to oxides – then we could extrapolate accordingly by adjusting the appropriate binding constant or 'log *K*' for the reaction based on published studies of the sorption of the two chemicals. This adjustment is likely to be greater if sorption on oxides is involved than if cation exchange is involved since sorption on oxides is more pH-dependent.

There are also likely to be 'adjustments' to be made because the best available literature data may have been obtained under conditions somewhat different from those of interest, e.g. rather than true adsorption data, perhaps only data some kind of selective extraction results (e.g. HCl extractions) might be available.

In essence, we combine the available field information (here some observations on Zn transport and aquifer properties for Zn binding) with our general knowledge about how chemicals behave in the environment. Generic databases are an important part of this approach. Such databases include thermodynamic databases (solution speciation, redox reactions, mineral solubility, sorption, octanol-water partition coefficients, etc.).

This approach has the advantage in that we might be interested in the question of what happens if the pH of a soil drops by one pH unit say and we have no information about the behaviour of Pb or Zn under these more acidic conditions. Then we can use our knowledge of the pH-dependence of the underlying processes – if cation exchange on clays is the dominant sorption process then this will show relatively little pH dependence but if sorption to oxides is dominant then this will show much greater pH dependence. We can adjust our 'log *K*' appropriately.

If there was a small amount of site-specific information about the pH dependence of Pb sorption available, then this could either be used to refine the process-based model or could be used to derive some statistical relation between log *K* and pH, for example by linear regression. Which method is likely to be most reliable is hard to say but as more information becomes available and as the understanding of the underlying processes improves, the process-based approach is likely to prove more efficient since it is able to use a broader range of 'data' (knowledge) to constrain the parameter values.

Taking this example forward, if there were no information available about Zn mobility then our task would be even more difficult. In this case, we might know from our 'aquifer properties database' that there in the area of interest there was so much clay and so much iron oxide in the aquifer. We could then resort to generic models of Pb sorption by clays and oxides. If we know nothing about the properties of the aquifer in the area at all, then we would have to assume some average value for the aquifer over the whole country, and so on.

Such 'blind' modelling inevitably involves many assumptions and extrapolations and the uncertainties in the transport estimates are likely to be large. It relies on being able to identify the key processes involved, having a sound understanding of them at a quantitative level, and having software and modellers available to make the necessary predictions. Nevertheless, as our basic knowledge of the underlying processes improves and their capture by modelling software increases, then so will the reliability of predictions. Such an approach can play a particularly useful role in making 'what if?' predictions at a generic level. This may be all that is required.

The problem of predicting parameters for chemical transport in the absence of site-specific data can be divided into categories, in the first instance, according to the level of information which is available:

- *spatial infilling*: capturing site-specific, geographically-based information about the property of interest existing from nearby areas and interpolating that to the area under consideration. In the absence of significant information about the parameter of interest, either at the study area or nearby, then purely spatial infilling is impossible; and
- *chemical infilling* is required. Spatial infilling is always necessary to some extent but clearly chemical infilling is the more challenging of these two tasks since it involves an element of spatial infilling as well.

Chemical infilling can be further subdivided according to the conceptual approach used to tackle the problem:

- Proxy measurements: direct measurement of an easy-to-measure parameter which can be interpreted to predict the harder-to-measure parameters of interest (clearly sample material must be available for this approach);
- Correlation-based predictions: application of statistical or regression techniques to other known measurements of parameters not directly related to the geochemical properties;
- Process-model based predictions: estimating parameters (physical, chemical or microbiological) using assumptions about the underlying processes involved and (where available) knowledge or estimates of other relevant properties.

There can be overlaps between any or all of these approaches. For example, new measurement of proxy parameters could provide further data used for regression analysis, or knowledge of a process model could be used to constrain the scope of a multiple regression analysis. However, the merits of each approach are different. They are discussed in more detail below.

4.3.2 Spatial infilling

It is impossible to measure the properties of a soil or aquifer at all locations of interest – which may include 'everywhere' if a spatially-averaged property value is required – and so some form of interpolation or extrapolation from known locations to unknown locations is required. There are many ways of doing this, most of which use a weighted-average of the value of the property at nearby locations ('nearest neighbour weighting'). It is not unreasonable to expect that 'nearby' samples should contribute more to the estimated property value than distant values, although if the nearest sample is already very distant then this might not necessarily be the case. Clearly the definition of 'nearby' and the choice of how the weighting varies with distance is important and will depend on the nature of the spatial variability of the property and the approach adopted.

The spatial variability of soil or aquifer property is best quantified by a systematic study of how the property varies from one point in space to another. This may involve grid sampling, stratified random sampling or some more sophisticated sampling scheme. Clearly the greater the sample density, the greater the information available and the greater the ability to interpolate to unknown points with confidence. Various methods have been used for spatial interpolation (Venables and Ripley, 2002). These include:

(i) *Trend surfaces* fitted by polynomial regression. The 'degree' of the polynomial can be increased to provide greater resolution but such global surfaces tend to give large errors at the margins of area;

(ii) *Local trend surfaces* can be used to avoid the problems of global surfaces. This involves either fitting a polynomial to each predicted point based only on the nearby data points (loess fitting) or by Dirichlet tessellation and the associated Delauney tessellation (tessellation is the process of dividing an area into 'tiles', each of which is associated with a data point and includes all points nearer to that data point than any other);

(iii) *Kriging* is based on the use of the variation of the covariance between pairs of points as a function of their separation for estimating the weights to be applied to nearby points when calculating the value of a predicted point from neighbouring data points. There are many forms of kriging, the simplest of which assumes a constant trend surface over the area of interest.

The extent of smoothing varies between the methods and can also be varied with a given method by adjusting the implicit model or assumptions. An important characteristic of kriging is the extent of the 'nugget' effect – this is the estimated covariance at zero separation which, if the underlying processes are smooth, should be zero apart from measurement errors. Non-zero nugget effects lead to a discontinuity at the data points and in this case kriging does not interpolate but smooths.

As the distance between adjacent samples increases it is likely that the differences in the value of a particular property at the two points will increase. Eventually when the distance is so large that the there is no similarity between the two locations, then the difference will become more-or-less independent of separation and will reflect the overall variability of the property of interest.

A plot of the variation against separation or distance apart is known as the *experimental variogram* and the study of this kind of spatial variation in the earth sciences is known as *geostatistics*.

Often the variogram reveals various scales of variation from micro-scale heterogeneity (over mm) through local variation (over metres), which may arise from, for example, small-scale fluvial processes, to much larger-scale or regional variation (over tens to hundreds of kilometres) reflecting major geological differences arising from tectonics say. All aquifer properties can be expected to show such spatial variability although the nature of the spatial dependence may either be similar for the various properties or different depending on whether there is a common underlying process or not. Once the variogram has been established, it can be used in kriging to help to interpolate the value of a property at an unmeasured location by weighting the influence of adjacent observations – the closer the location, the greater the influence and vice versa, but the exact nature of the weights is given by variogram.

Establishing the nature of the variogram is achieved by measuring a property at many locations and then analysing all pair-wise differences in terms of their separation and orientation (direction). Typically, it takes at least 100 observations to establish a reasonably reliable variogram. Therefore, variogram analysis and kriging are often not worthwhile for many of the small, sparsely-populated geological datasets currently available and a more pragmatic approach along classical lines is probably best, e.g. the average value of the property for the aquifer of interest.

Recent studies have used the Bayesian maximum entropy approach to combine 'soft' but extensive data contained within maps with accurate but sparse analytical data to produce. Such an approach may be applicable to the interpolation of aquifer chemical properties.

4.3.3 Proxy parameters

As we have discussed, one of the major difficulties in obtaining primary experimental measurements of geochemical parameters is the cost and complexity of some of those measurements, even when suitable sample material is available. If an alternative measurement can be used which will allow derivation or prediction of the parameters of interest then this has the potential to extend geochemical understanding and data more easily and economically.

The cost-benefit balance of using proxy experimental measurements has to be considered carefully. If the proxy data are of low reliability and confidence then it may still be a wiser use of resources to measure the true geochemical parameters directly on a smaller number of samples, even when the proxy measurements are very cheap. If the cost of the proxy measurements is only marginally cheaper than direct measurements then again it may be better to direct effort to making true measurements. However, where the proxy measurements generate data of reasonably high value but at low cost then this may be more cost effective than making the traditional measurements on all samples.

Recent literature has suggested that many of the key geochemical parameters such as organic carbon content, cation exchange capacity, clay content, specific surface area or carbonate content can be accurately predicted using the Near Infra-Red (NIR) reflectance spectrum of soils and sediments (e.g. Bendor and Banin, 1995; Chang et al., 2001; Confalonieri et al., 2001). The advantage of this method is that the NIR spectrum of the soil is very quick and simple to obtain, at a fraction of the cost of the standard laboratory methods needed to measure the geochemical parameters of interest. In addition, there are possibilities that the measurement can be made in-situ (Sudduth and Hummel, 1993) or by remote sensing (Bendor and Banin, 1994). In order to predict the geochemical parameters of interest, a multiple regression model has to be established which relates the NIR spectra to the parameter in question. The model must then be calibrated using a proportion of the samples that are measured by traditional means. Some further work is needed to establish the validity of the interpretation of geochemical parameters from the NIR measurements before the technique could be applied routinely to preparation of the geochemical properties manual.

It is also possible to make use of proxy parameters without the need for new experimental work. There are many circumstances where aquifer materials are sampled and characterised for properties that are not directly linked with their geochemistry. An example is that of engineering geology parameters such as the Atterberg limits. There is evidence to show that these parameters can be related to geochemical parameters such as CEC and organic carbon content (e.g. Dejong et al., 1990; Dejong et al., 1992; Petersen et al., 1996) and can thus be used in a similar manner to the NIR spectra as proxy variables for prediction of geochemical properties.

There are a number of ways in which the geochemical parameters of interest can be estimated from their proxy counterparts.

There is a purely statistical approach that has been shown to be quite successful for a variety of applications (e.g. Walczak and Massart, 2001a, b). These techniques, however, do not provide any insight into which of the proxy variables is contributing to the predicted properties. This is a ‘black-box’ methodology in which the propagation of errors into the predicted variable could be difficult to follow.

A better option is to use multivariate regression techniques such as Multiple Linear Regression, Principal Component Regression and Partial Least Squares. Although the final model is entirely empirical, the diagnostic statistics of each of these methods clearly shows how each of the proxy variables contributes to the final prediction of the parameter of interest and the error on the prediction can be clearly defined. This allows the model to be validated by checking the importance of predictor variables with theoretical first principles. There are many examples of this type of approach in soil and sediment applications (e.g. Bengtsson and Ekere, 2001; Brubaker et al., 1992; Goldberg et al., 2000).

Various procedures are available for using basic chemical information to make inferences about the value of some unmeasured property. The most general of these is the Quantitative Structure-Activity Relationship (QSAR) approach which establishes the relationship between the structure or composition of a compound and the activity that the compound displays under various experimental conditions, e.g. solubility, vapour pressure (Eriksson and Hermens, 1995). This approach is widely used in organic chemistry to estimate unmeasured physical and chemical properties of organic compounds (e.g. toxicity, soil sorption properties) from a knowledge of their chemical structure (e.g. hydrophobicity, molecular weight, electronegativity, density) and the behaviour of similar compounds. The use of the octanol-water coefficient to estimate the solubility of a wide range of organic chemicals is well known (Appelo and Postma, 1993). There are too many organic compounds to measure everything for all of them and so the QSAR approach is important.

A variant of the SAR approach (indeed a forerunner of it) is the Linear Free Energy Relationship which uses a plot of the standard free energy of a reaction, ΔG, for a series of related compounds against some chemical property related to the structure of those compounds, e.g. molecular size or ionic radius. Since ΔG is directly related to the equilibrium constant, $\log K$, of a reaction, this provides a way of interpolating the $\log K$ for unknown solutes from known values for other, related solutes.

For example, Dzombak and Morel (1990) used it to estimate the sorption constants for anions on hydrous ferric oxide (HFO) when no reliable data were available. It makes use of the known similarity in the stability of surface complexes between different anions on HFO to constrain the values for the unmeasured ones. The same approach has been used by Tipping (1998) and Milne et al. (2003) for estimating metal binding parameters to natural organic matter. A similar approach could in principle be taken for soils and aquifer materials. However, the LFER approach is not an absolute predictor but rather a good way of interpolating unknown parameters from the known parameter values of a number of related compounds.

The most scientifically sound method for predicting geochemical parameters from proxy variables is through theoretical modelling where the exact physico-chemical processes relating the proxy variables to the geochemical parameter of interest are mathematically modelled (e.g. Benedetti et al., 1996; Ganguly et al., 2001). This has the advantage of having a sound scientific basis for the prediction but, in practice, many of the relationships are very complex and poorly understood giving limiting the use of the model. In some instances, these problems can be alleviated by combining theoretical and empirical approaches.

With all of the different methods discussed here it is necessary to calibrate (in the case of regression models) or validate (in the case of theoretical models) the predicted geochemical parameter of interest against laboratory-based measurements. The chosen method of prediction ultimately will depend on the parameter to be predicted and the nature of the proxy variables that are available.

4.3.4 Process modelling

Here, the aim is to use our existing knowledge of chemistry to help to infill unknown parameters. This approach differs from the purely statistical and spatially-orientated approaches outlined above which do not explicitly take into account any chemical principles like mass action, mass balance and the similarity in chemical behaviour between different chemical compounds. Of course, the chemical approach may also involve some statistics, e.g. optimization.

Frequently, an established modelling package such as PHREEQC is used. For example, by assuming the composition of an aquifer material, and using speciation model to calculate the adsorption of a component according to an assemblage of individual adsorption models, it is possible to calculate an effective K_d value for the bulk material. The sophistication and precision of the calculations are improved with increasing knowledge, and hence decreasing assumption, about the proportions of the composition used as input parameters for the speciation model. The processes which can be considered, and the way in which they are used in PHREEQC were described in fuller detail in Section 3.

4.3.5 Summary

Some of the methods discussed here are still considered to be research topics and would require development, which is outside of the scope of this current project. However, prediction methods based on regression are tried and tested and could be used for some simple predictions where data are unavailable. In particular, given the large amount of data available on Atterberg limits of different aquifer materials, a small-scale trial of prediction of CEC and organic carbon could be carried out to establish the value in filling in sparsely populated areas of the GPM.

5 Cation Exchange Capacity

5.1 USE AND INTERPRETATION OF CEC

5.1.1 The origin of natural cation exchange

The cation exchange capacity (CEC) is a measure of the number of cations that a solid can bind in a readily-reversible way. It arises from the fact that many solids have a net electrical charge at their surfaces. This is balanced by binding ions of an opposite charge to exactly neutralize the surface charge. The CEC is a measure of the number of ions bound in this way, and therefore also reflects the surface charge of the solid.

There are two ways in which a surface charge may be built-up.

1. So-called isomorphous substitution of one cation for another of similar size but different charge can leave a solid having a net electrical charge – the most important example is the partial substitution of Al^{3+} by Mg^{2+} in phyllosilicate clays. This leaves clays with a net negative charge at the surface even though the source of the charge is some way away in the interior of the mineral. The net negative charge means that to neutralize the charge cations must be adsorbed; the total number that do so is a measure of the CEC. This form of negative surface charge is called a *permanent charge* since being caused by structural reasons, is fixed and is not affected by changes is solution chemistry. In principle, the CEC of these materials does not depend on particle size.

2. At the surface of particles, the uniformity of structure seen in the interior is broken and ions are free to move between solid and solution phases. Some prefer the solid phase more than others and this imbalance in preferences means that the local electrical neutrality seen in the bulk solid phase is no longer maintained at the surface. Rather it is maintained by other solution ions compensating for the resulting net surface charge roughly in proportion to their abundance (concentration) and affinity to the surface (log K). Protons (H^+) are some of the most strongly bound of all ions (they bind strongly to oxygen, sulphur and nitrogen atoms) which means that the surface charge is often determined by the pH of the solution with which the solid is intact – the lower the pH, the higher the concentration of H^+, the more H^+ will be bound to the surface and the greater the surface positive charge. Anions will therefore be bound at low pH. At high pH, the concentration of protons in solution will be relatively low and few will be bound allowing the structural anions like O^{2-} to dominate at the surface, attracting 'inner sphere' cations especially H^+. At some pH, the point of zero charge or pzc, the net surface charge will be zero and the surface will not attract a surplus of either cations or anions. For these reasons, these types of surface are called *variable charged* surfaces.

Solid organic matter (humic material) has a large charge, usually negative, because of these types of reactions. Clay minerals, such as montmorillonite that have a permanent charge due to isomorphous substitution, also have a *variable charge* due to the gain and loss of protons at their frayed edges. Most oxides also have a pH dependent surface charge. The smaller the particles, the greater the charge on a weight basis. Therefore, colloidal or clay-sized (<2 μm) particles are particularly highly charged.

It turns out that many natural solids (soils and sediments) are very finely-grained and so quite highly charged. The high solid/solution ratio of most soils and aquifers means that these reactions are very important in controlling natural water chemistry. Cation exchange is a natural reaction that helps soils retain nutrients that might otherwise be rapidly lost. Cation exchange was first discovered by chemists trying to understand the retention of ammonium by soils. Cation exchange buffers rapid changes in the ratio of one cation to another in the surrounding water – rather like preventing a see-saw going up and down too rapidly. In this sense, it attenuates changes in solution chemistry. But once the exchanger has equilibrated with the new solution chemistry, there will be no further binding of solution cations, and hence no retardation to the flow of cations.

Most standard methods of CEC measurement are aimed at measuring the permanent charge. More difficult methods must be used to characterize the variable charge.

5.1.2 Modelling cation exchange reactions in soils, sediments, aquifers and aquicludes

The theory of cation exchange is quite advanced and is built into many modern geochemical speciation and transport programs such as PHREEQC, The Geochemist's Workbench and MINEQL+. The main problem is that different minerals have both different capacities for adsorbing cations and different preferences for the various ions. And natural waters contain a wide variety of ions, in principle most of the periodic table to a greater or lesser extent, and all of these ions are competing amongst themselves for surface sites on the various minerals present. The problem then is to database the minerals present, their cation exchange capacities and their affinities for all of the major ions and any minor ions of interest.

Alternatively, rather than treating natural materials as mixtures of minerals, organic matter etc, the CEC of the whole solid phase can be treated as a single entity. Like its individual components, this too will have a cation exchange capacity and affinities for all the ions present. However, in this case, the behaviour may be more complex than for the individual minerals since the various components will all be operating separately and in different modes. There is also likely to be a mixture of permanent charge materials (notably certain clays like smectite) and variably-charged surfaces like clay edges, oxides and solid organic matter.

The best models depend on the type of reactions involved. These may be summarized as follows:

- Permanent charge clay minerals: Gaines-Thomas cation exchange;
- Variably-charged oxides: there are numerous models of varying complexity ranging from the diffuse double layer model (Dzombak and Morel, 1990), the constant capacitance model (Stumm et al., 1980) , the triple layer (Davis and Leckie, 1978) and triple plane models and the CD-MUSIC models (Hiemstra and VanRiemsdijk, 1996). The more complex models tend to work better in the more complex systems (more realistic water chemistry) but are more difficult to set up, and thermodynamic databases are not so comprehensive for them.
- Variably-charged humic materials: complex due to the natural heterogeneity of such materials but Model V/VI (Tipping, 1998) and the NICA-Donnan model (Milne et al., 2001; 2003) are the two front-runners, now both with reasonable starting thermodynamic databases. The binding capacity of natural organic (humic) materials can be very high, exceeding that of clay on a weight basis, i.e. greater than 100 meq/100g. However, this capacity is strongly pH dependent and is considerably lower than this under acid conditions (<pH 4).

Unfortunately, the commonly-used geochemical and environmental risk assessment software that is widely available includes only a subset of these models. Sometimes the best that can be done is to use the Langmuir or Freundlich isotherms – essentially empirical equations that can only deal with simple situations and which are specifically not designed for charged surfaces, and may fail because of this. Charged surfaces differ significantly from uncharged surfaces because the build-up of charge repels ions of a similar charge and attracts those of an opposite charge in a complicated way.

Nevertheless, simple models can often be tailored to work reasonably well over a narrow range of conditions and it is certainly better to adopt this approach rather than to ignore what is there simply because no state-of-art model is available.

In their simplest forms, cation exchange reactions are characterized by two types of parameters:

The cation exchange capacity (CEC) which indicates the number of charged sites per unit quantity of material. Traditionally given in units of meq/100 g but now often given in units of eq/kg. The CEC is essentially a scaling factor that indicates the size of any cation exchange effects;

The relative affinity of a given cation for a given surface often given in terms of the log *K* of a chemical reaction of one ion exchanging for another but more simply for databasing as a relative affinity compared to some reference ion. The PHREEQC (Parkhurst and Appelo, 1999) database uses Na+ for this purpose (Table 5.2). Relatively simple for homovalent exchange (when the two ions have the same charge) but more complex for heterovalent exchange (ions have differing charges) where different conventions exist for defining the standard state, e.g. the Gaines-Thomas approach based on equivalent fractions is the most popular and soundly justified. Each mineral-ion pair potentially has a different log *K* but the similarity between different minerals and the lack of specific data means that often generalized log *K*'s are used in modelling. These are usually good enough to indicate the magnitude of cation exchange effects.

Table 5.1 Typical cation exchange capacities (CEC) for a variety of clays and humic acid (from Grim, 1968; McBride, 1994)

Mineral	**CEC (meq/100 g)**
Kaolinite	1–15
Halloysite $2H_2O$	5–10
Halloysite $4H_2O$	40–50
Smectite	70–120
Illite	10–40
Vermiculite	100–150
Chlorite	10–40
Sepiolite-attapulgite-palygorskite	3–15
Humic acid	-600 + 500 pH

Table 5.2 Default Gaines-Thomas cation selectivity values for ion exchange reactions in the PHREEQC database (X denotes the ion exchanger)

Reaction	**log K_{GT}**
Na+ + X- = NaX	0
K+ + X- = KX	0.7
Li+ + X- = LiX	-0.08
H+ + X- = HX	1.0
NH4+ + X- = NH4X	0.6
Ca+2 + 2X- = CaX2	0.8
Mg+2 + 2X- = MgX2	0.6
Sr+2 + 2X- = SrX2	0.91
Ba+2 + 2X- = BaX2	0.91
Mn+2 + 2X- = MnX2	0.52
Fe+2 + 2X- = FeX2	0.44
Cu+2 + 2X- = CuX2	0.6
Zn+2 + 2X- = ZnX2	0.8
Cd+2 + 2X- = CdX2	0.8
Pb+2 + 2X- = PbX2	1.05
Al+3 + 3X- = AlX3	0.67

Heterovalent ion exchange results in complex and sometimes non-intuitive behaviour. The relative affinity of different ions for an exchanger not only depends on their log *K* but also on their concentration in solution. For example, higher-charged ions are usually strongly preferred over lower-charged ions but this preference diminishes at high concentration. Because the source of the attractive charge is in the mineral structure quite far from the bound ion, the affinity of the ions is largely controlled by their charge and size, and the ease with which they can lose their surrounding water molecules. The subtleties of fitting into tight spaces are not involved.

The above comments apply to *normal* cation exchange reactions. There are also some cation exchange reactions that apply to specific ions on specific minerals, and that enhance the binding of that ion well above that expected from its position in the normal selectivity sequence outlined above. For example, K^+, Cs^+ and NH_4^+ binding by micaceous minerals is much greater than expected at low concentrations because these ions are able to lose their surrounding water molecules quite easily and to enter tightly between the interlayers of micas at their weathered edges. This *specific adsorption* needs a special formulation – often the assumption of a small number, say 1%, of high affinity sites (Hormann and Gruber, 2002). The Langmuir isotherm is often used for this.

Specific adsorption also applies to the binding of many trace metals and most multivalent ions to oxides and humic materials, and for these the normal theory of cation exchange does not apply. These require some form of surface complex model. The edges of clay act rather like oxides with a pH-dependent charge and models now exist which consider these and their interactions together (Krapiel et al., 1999).

The upshot of this is that normal cation exchange reactions often apply to the major cations such as Na^+, Ca^{2+}, Mg^{2+}, K^+ and in some cases NH_4^+, but not for the solubility of most trace cations. These tend to be largely controlled by specific interactions with a particular mineral phase although ordinary cation exchange reactions will still operate to some extent.

5.1.3 Databases of cation exchange parameters for environmental modelling

As discussed above, such databases require:

- an appropriate ion exchange model
- CEC either of each exchanging solid or the solid as a whole;
- log *K* for each solid-cation pair;
- maybe other parameters/models to correct for specific behaviour.

Because of the essentially infinite number of solids (and therefore CECs), the large number of mineral-cation combinations of interest and the various models in use, preparing databases for general use is both difficult and often unrewarding.

Some ‘sorption databases’ such as those compiled by the nuclear industry for performance assessment implicitly consider ion exchange reaction for specific rocks of interest (e.g. the NEA database) but also mix in other reactions and are therefore not of so much generic interest.

A thorough discussion of cation exchange as applied to soils and a large compilation of Gaines-Thomas selectivity coefficients is given in Bolt (1979) but this does not include a survey of CEC’s. In the UK, the now discontinued series of soil series memoirs from the Soil Survey of England and Wales included CEC as one of the measurements carried out on a number of selected profiles used to characterize each soil mapping unit (a soil series). We are not aware of any systematic review of the CEC of soil/clay materials even though many thousands of such determinations must exist worldwide. This is undoubtedly partly due to the difficult of relating such measurements to other parameters such as clay content or clay mineralogy since these measurements are often not undertaken at the same time.

5.1.4 CEC data from other sources

Most literature data for CEC values are for soils, usually temperate soils where silicate clays having a permanent charge dominate. Sands and sandstones which do not contain much clay have a very low CEC (at most a few meq/100 g) – most of their charge arises from the pH-dependent variable charge from the iron and aluminium oxide coatings, and from the silica surface itself.

The CEC of a large number of samples from the unsaturated zone of a Danish sand aquifer were mostly in the range 0.1–1.0 meq/100 g and typically 0.3 meq/100 g (Hansen and Postma, 1995). Illite and kaolinite were present in all samples with gibbsite and chlorite identified in some. These clays do not have high CECs. CEC’s of 0.1–0.5 meq/100 g were also found for a Quaternary/Tertiary Danish sandy aquifer (Heron et al., 1998).

The CEC of the alluvial Cape Cod aquifer ranged from 0.5±0.3 meq/100 g for very coarse to coarse sand to 2.1 ±0.8 meq/100 g for fine to very fine sand with silt and clay (DeSimone et al., 1997).

5.2 MEASUREMENT OF CEC

5.2.1 Analytical approaches

The Cation Exchange Capacity (CEC), usually expressed in milliequivalents (meq) per 100g of dry sample, is a measure of the quantity of readily exchangeable cations neutralising negative charges in the test material (Rhoades, 1982). Review by Gillespie et al (2000) has shown that there are a variety of methods available for CEC determination. The majority of methods begin with the displacement of existing cations with a saturating salt to provide an index cation on the exchange complex. Thereafter, the methods used to determine the quantity of cations displaced can be divided into two categories; single displacement methods and double displacement methods. In single displacement methods the concentration of exchanged cations or the decrease in concentration of the index cation in solution provides a measure of CEC. Double displacement methods use a second displacing solution to remove the index cation from the sample and the decrease in concentration of the displacing solution or the increase in concentration of the index cation provide a measure of CEC. In the double displacement method, the choice of salts can be designed so that the index anion reacts with the displacement cation to form an insoluble salt, which is precipitated from solution (often referred to as compulsive displacement). The advantage of this approach is that there is no need for the repeated washing steps that would otherwise be needed.

Bias in results of CEC measurements is very much associated with the type of material being measured. Gillespie et al. (2000) point to three main problem areas:

- dissolution of soluble salts, calcium carbonate and gypsum leading to overestimation of CEC
- specific adsorption of K^+ and NH_4^+ in interlayer positions in vermiculites and micas leading to either an over- or under-estimation of exchangeable K^+ when NH_4^+ is used as the index cation.

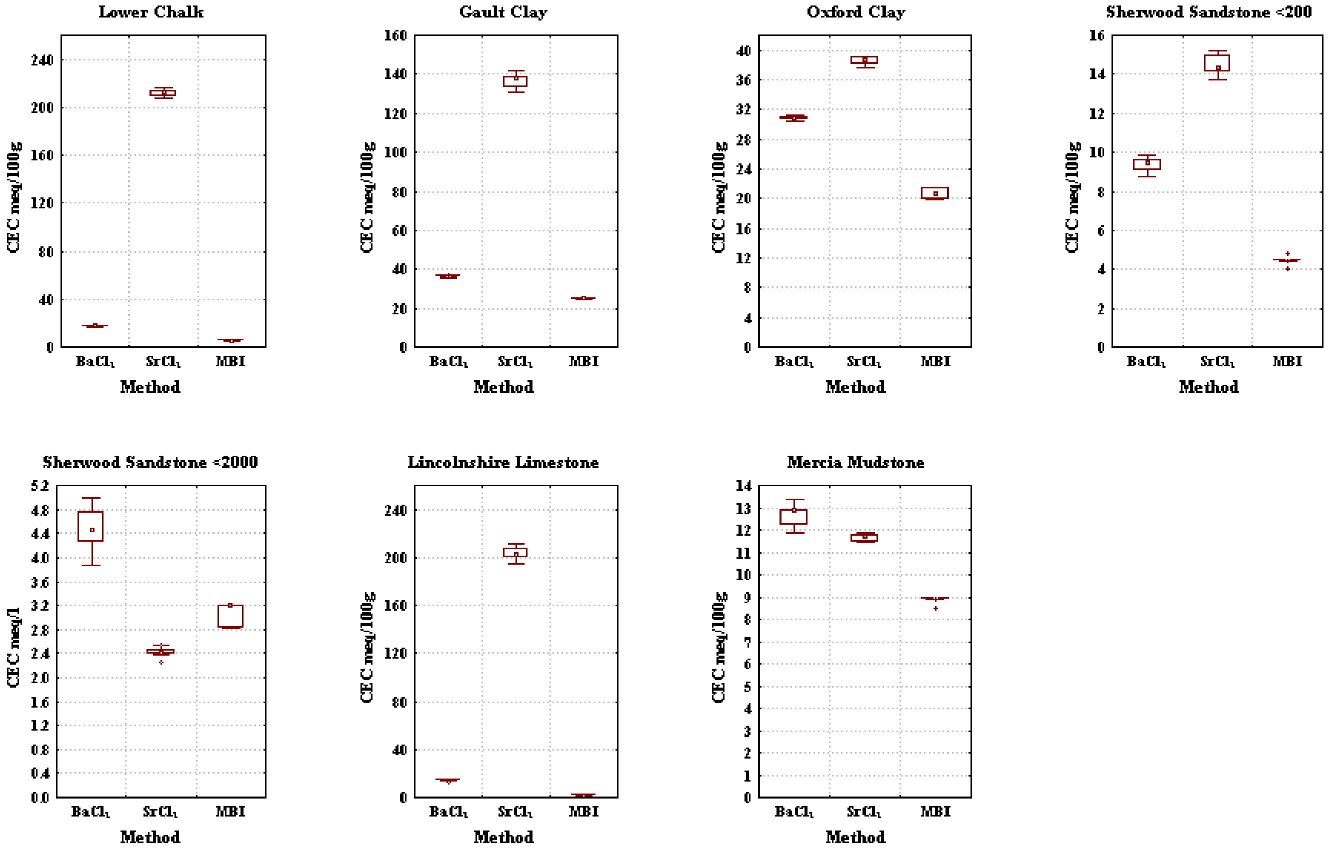


Figure 5.1 Comparison of CEC measurement method on aquifer materials (from Gillespie et al., 2000)

- specific adsorption of trivalent cations such as Al^{3+} or Fe^{3+} on surfaces leading to an underestimation of CEC.

The ammonium ion has been used as the index cation in many methods because its selectivity and extremely weak hydration enables it to move rapidly to a well-defined number of exchange sites, sealing off access to other sites. It also has a number benefits related to its practical use (Gillespie et al., 2000). However, as indicated above, for some materials its use leads to significantly biased results. Despite this, the USEPA have recommended the use of a single displacement method with an ammonium index cation for soil CEC determination during long-term monitoring in environmental programmes (Schumacher et al., 1995).

The method that has been adopted as both the British Standard and ISO method (British Standards Institute, 1997; International Standards Organisation, 1994) is based on that developed by Bascomb (1964) specifically to overcome the overestimate in CEC introduced by the presence of calcite or gypsum in the samples. The method uses Ba^{2+} as the index ion, introduced in the form of $BaCl_2$. The Ba is subsequently compulsively displaced with Mg^{2+} by adding $MgSO_4$ to form the insoluble salt $BaSO_4$. The index-cation salt is made up in an ethanolic solution with triethanolamine that minimises the soluble-salt interference and the Ba^{2+} ion does not cause collapse of expanded phyllosilicates as the NH_4^+ ion would. It has been shown, however, that this method still suffers from a positive bias in the presence of samples containing high concentration of gypsum. Stuart and Vickers (1989) suggested a modified method to help overcome these problems.

Gillespie et al. (2000) compared three methods of CEC determination applied specifically to a selection of UK aquifer materials: the Bascomb $BaCl_2$ compulsive exchange method, a single displacement method using $SrCl_2$ as the index salt and a Methylene Blue index method that uses an organic dye to displace cations from the sample. Summary results are illustrated in Figure 5.1 using box-and-whisker plots to show the data obtained from five replicate measurements of each material type. The three methods show profound differences for all the materials. The $SrCl_2$ method gave notably higher results than the other two for samples containing high quantities of calcite (Lower Chalk and Lincolnshire limestone samples). The results for the two size fractions of the Sherwood Sandstone also illustrate that, as has been noted by other workers (Barton and Karathanasis, 1997; Deutschmann et al., 1997), for consolidated materials the sample preparation has a significant effect on the final results produced.

On balance, Gillespie et al. (2000) preferred a modified version of the Bascomb $BaCl_2$ compulsive exchange method on the grounds that it was already widely used and proved suitable for a wide range of geological materials They subsequently applied the method to samples of 30 geological formations drawn from across the country. Although 30 samples is by no means a large study, these data do represent a very significant, internally consistent, portion of the overall available body of data for CEC. There is merit in ensuring that future measurements are consistent with them and hence the use of the $BaCl_2$ method is also recommended here as the preferred experimental method for determination of CEC.

The fact that current literature contains many modifications and new methods for CEC measurement (e.g. Barton and Karathanasis, 1997; Bergaya and Vayer, 1997; Cerri et al., 2002; Ciesielski and Sterckeman, 1997; Liu et al., 2001;

Skinner et al., 2001; Zhao et al., 1997) supports the view that current standard methodologies are not applicable to all material types. Most of the literature is related to CEC measurement of soils but the CEC of rocks is also being investigated (Deutschmann et al., 1997; Duquette and Hendershot, 1993; Gualtieri et al., 1999; Osman and Suter, 2000).

5.2.2 Preferred method of analysis

CEC was determined using a modified version of the British Standard $BaCl_2$-ethanolamine compulsive displacement method. The BS7755 method (British Standards Institute, 1997) is based on that of Bascomb (1964).

Milled sample is shaken with buffered (pH 8.1) $BaCl_2$-ethanolamine solution to saturate the exchange sites with Ba, then separated from the supernatant and washed. The Ba is then exchanged with Mg using $MgSO_4$ solution, forming insoluble $BaSO_4$ as a precipitate. The loss of Mg from the displacing solution is estimated by titration with EDTA and is considered to be equivalent to the CEC.

As a more recent development, trials using Inductively-Coupled-Plasma Optical-Emission-Spectroscopy (ICP-OES) to determine the residual Mg concentrations spectroscopically, rather than by classical titration, have been promising. If successful, this development could facilitate quicker and cheaper determinations.

5.2.3 Uncertainty

There are few easily available reference materials for CEC measurement. No such materials are listed in the catalogues for the internationally recognised National Institute of Standards and Technology (NIST, USA) or the Institute for Reference Materials and Measurements (IRMM, Belgium). However, the Chinese National Research Centre for Certified Reference Materials (NRCCRM, China) does list four soils with certified cation exchange capacity data which are available in the UK through the Laboratory of the Government Chemist (LGC). Proficiency-testing schemes operated by the Wageningen Evaluating Programmes for Analytical Laboratories (WEPAL) and the North American Proficiency Testing Program (NAPT) both allow laboratories to evaluate their performance on CEC determination of soils. Given the difficulty and expense of obtaining suitable reference materials, none were used for this study. However, the earlier work of Gillespie et al. (2001), carried out in the same laboratory provide extensive evidence for the reliability of the analysis.

5.3 SUMMARY AND OVERVIEW OF DATA

Available data for measurement of CEC in rocks are presented in the following table for lithostratigraphical attributions at the Group level. For finer resolution showing data at Formation level please consult the figures in Section 5.4.

Table 5.3 Overall summary statistical values for CEC data, tabulated by lithostratigraphical Group.

LEX code	Group name	Min	P25	Median	Mean	P75	Max	n
	Quaternary							
GDU	Glacial Deposits	16.5	20.2	23.9	21.7	24.4	24.8	3
DUNW	Dunwich Group	4.6	4.6	4.6	4.6	4.6	4.6	1
CRAG	Crag Group	3.5	7.8	12.1	10.5	14	16	3
	Palaeogene							
BA	Barton Group	1.5	1.5	1.5	1.5	1.5	1.5	1
BRB	Bracklesham Group	4.9	6.98	9.05	9.05	11.1	13.2	2
THAM	Thames Group	3.4	14	18.9	18.8	25.4	31.2	12
LMBE	Lambeth Group	3.6	8.05	16.3	18.7	25.9	42.4	15
XG	Other Palaeogene	1.5	3.8	14.8	15.1	18.2	39.8	10
	Cretaceous							
CK	Chalk Group	5.7	8.9	11.2	11.9	13.4	29.4	63
SELB	Selborne Group	3.7	17	22.2	23.1	30.1	38.4	9
LGS	Lower Greensand Group	1.5	3.4	13.1	10.8	15.8	18.3	16
W	Wealden Group	1.5	6.2	13.2	13.1	17.1	35.7	18
PB	Purbeck Group	23.3	24.4	25.6	25.6	26.7	27.8	2
XK	Other Cretaceous	1.5	5.4	13.1	13.8	16	39.9	13
	Jurassic							
PL	Portland Group	1.5	4.5	8.85	8.28	12.6	13.9	4
AMG	Ancholme Group	4.3	18.2	21.8	20.2	25.5	26.5	14
CR	Corallian Group	8.6	12.7	14	16.9	19.3	35.3	9
GOG	Great Oolite Group	1.5	9.48	13.4	15.3	18.3	43.6	32
INO	Inferior Oolite Group	3.4	5.72	10.1	9.79	14	15.4	12
RAG	Ravenscar Group	1.5	5.25	9	9	12.8	16.5	2
LI	Lias Group	9.7	17.4	23.6	22.4	27.6	32.5	24
XJ	Other Jurassic	6.2	6.2	6.2	6.2	6.2	6.2	1
	Triassic							
PNG	Penarth Group	33.1	34.4	35.8	35.8	37.2	38.5	2
MMG	Mercia Mudstone Group	1.5	8.18	14.4	15.2	19.6	35	22
SSG	Sherwood Sandstone Group	1.5	1.5	5.25	7.09	11.2	20.6	34
	Permian							
ZG	Zechstein Group	1.5	4.2	5.9	10.7	18.7	25	9
APY	Appleby Group	1.5	1.5	3	2.67	3.58	4.8	34
EXE	Exeter Group	4.9	5.4	5.9	5.9	6.4	6.9	2
WAWK	Warwickshire Group	4.5	6.22	9	11.5	14.3	23.5	4
XP	Other Permian	1.5	1.5	3.5	4.93	8.55	10.1	12

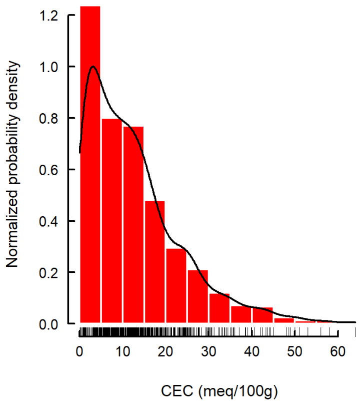
LEX code	Group name	Min	P25	Median	Mean	P75	Max	n
	Carboniferous							
PCM	Pennine Coal Measures Group	1	3.82	7.15	6.95	9.25	19.6	26
CMSC	Scottish Coal Measures Group	1.5	3.58	5.65	5.65	7.72	9.8	2
HOWY	Holsworthy Group	4.5	4.72	4.95	4.95	5.18	5.4	2
CKN	Clackmannan Group	0.1	1.5	10.3	9.21	13.8	24.5	11
MG	Millstone Grit Group	1.5	3.2	6	9.67	15	27.1	17
YORE	Yoredale Group	4.3	5.72	7.15	7.15	8.57	10	2
CRAV	Craven Group	4.8	6.7	8.2	11.3	13.9	27.5	9
GSCL	Great Scar Limestone Group	3.4	3.6	3.8	3.8	4	4.2	2
SYG	Strathclyde Group	1.5	4.75	6.35	15.2	26.4	44.3	14
PKLM	Peak Limestone Group	1.5	1.88	3.5	4.65	7	9.9	6
BOHI	Bowland High Group	1.5	1.5	5.85	8.34	14.6	19.9	8
INV	Inverclyde Group	11.5	15.4	19.4	17.6	20.6	21.8	3
TRG	Transition Group (Devonian-Carboniferous)	13.2	13.2	13.2	13.2	13.2	13.2	1
XCL	Other Carb. Limestone Supergroup	1.5	1.5	3.2	6.37	7.82	20	6
XC	Other Carboniferous	7.9	9.07	10.2	10.2	11.4	12.6	2
XCU	Other Culm Supergroup	1.5	1.5	1.5	1.5	1.5	1.5	1
	Devonian							
FSA	Forres Sandstone Group	7	7	7	7	7	7	1
EXM	Exmoor Group	3.2	3.2	3.2	3.2	3.2	3.2	1
SAG	Stratheden Group	0.6	2.02	3.45	3.45	4.88	6.3	2
FIL	Fair Isle Group	7.3	14.5	21.6	21.6	28.8	36	2
INS	Inverness Sandstone Group	3.6	3.88	4.15	4.15	4.42	4.7	2
MDT	Meadfoot Group	1.5	1.5	1.5	1.5	1.5	1.5	2
LORS	Lower Old Red Sandstone	1.5	4.9	8.35	8.79	12.9	17.3	10
DOW	Downton Group	23.7	23.7	23.7	23.7	23.7	23.7	1
ATGK	Arbuthnott-Garvock Group	4.9	6.78	8.85	8.6	10.7	11.8	4
XD	Other Devonian	3	3.78	6.45	7.3	10.8	12.8	6
	Pre-Devonian							
LLUS	Lower Ludlow Shales Group	14.7	15	15.4	15.4	15.7	16	2
AGF	Aberystwyth Grits Group	3.2	3.6	4	4.43	5.05	6.1	3
XS	Other Silurian	1.5	2.4	4.65	7.26	11.6	17.7	16
BUVO	Builth Volcanic Group	11.2	14.8	18.4	18.4	22.1	25.7	2
MWG	Mawddach Group	1.5	1.5	1.5	1.5	1.5	1.5	2
XO	Other Ordovician	1.5	1.5	5.7	10.4	17.9	25.4	5
XA	Other Pre-Cambrian	1.5	1.5	1.5	1.5	1.5	1.5	1
NMG	Mona Gneiss Suite	6	6	6	6	6	6	1
YST	Stretton Group	6.9	6.9	6.9	6.9	6.9	6.9	1
ARGY	Argyll Group	8.6	8.6	8.6	8.6	8.6	8.6	1
LEIL	Loch Eil Group	1.5	2.72	3.95	3.95	5.18	6.4	2

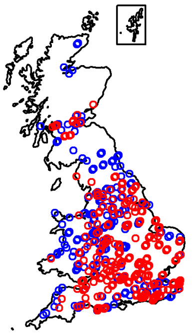
5.4 GEOLOGICAL ATLAS OF DATA FOR CEC

All Groups (All)

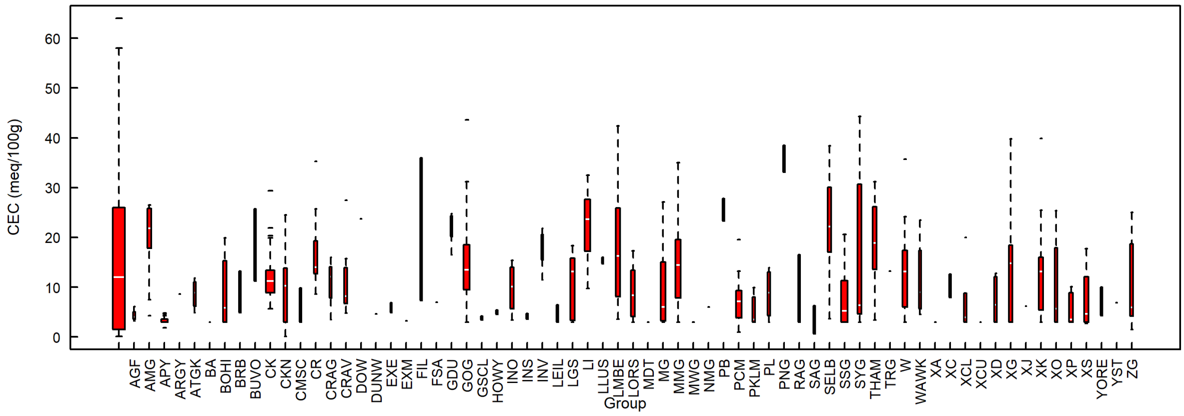
Cation Exchange Capacity (CEC)

CEC (meq/100g)





Blue points are below the median
Red points are at or above the median



5.4.1 Quaternary and Neogene

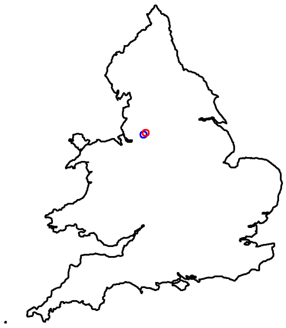
Glacial Deposits (GDU)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 16.5
Median = 23.9
Mean = 21.7
Max = 24.8
Std dev = 4.55
n = 3

U Undifferentiated (3)



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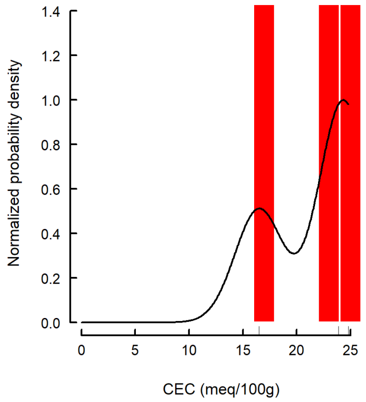
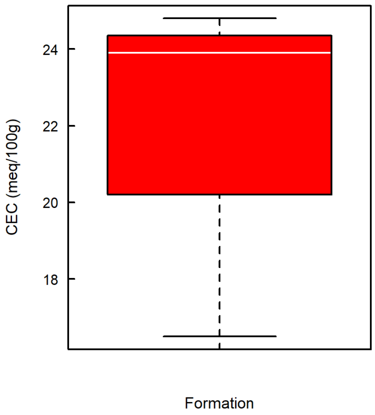




Dunwich Group (DUNW)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 4.6
Median = 4.6
Mean = 4.6
Max = 4.6
Std dev = NA
n = 1

KGCA Kesgrave Catchment Subgroup (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Crag Group (CRAG)

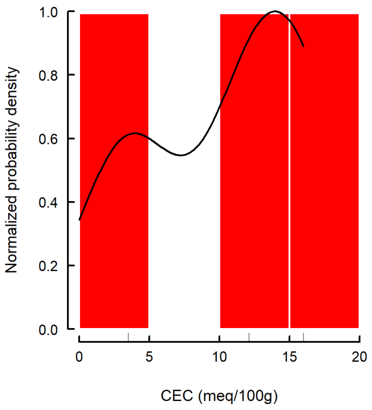
Cation Exchange Capacity (CEC)

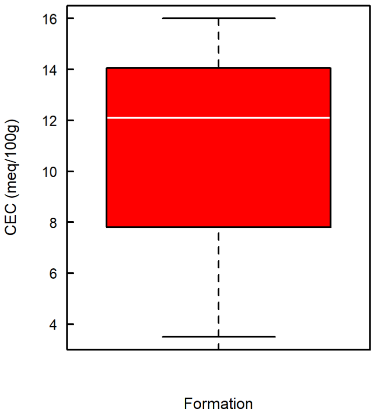
CEC (meq/100g)

Min = 3.5
Median = 12.1
Mean = 10.5
Max = 16
Std dev = 6.4
n = 3

NCG Norwich Crag Formation (3)

Blue points are below the median
Red points are at or above the median





Palaeogene

Barton Group (BA)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 1.5
Median = 1.5
Mean = 1.5
Max = 1.5
Std dev = NA
n = 1

BECH Becton Sand and Chama Sand Fms (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

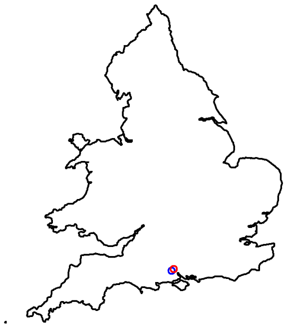
Bracklesham Group (BRB)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 4.9
Median = 9.05
Mean = 9.05
Max = 13.2
Std dev = 5.87
n = 2

WTT Wittering Formation (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

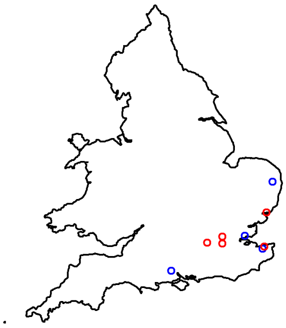
Thames Group (THAM)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 3.4
Median = 18.9
Mean = 18.8
Max = 31.2
Std dev = 9.3
n = 12

HWH	Harwich Formation (2)
LC	London Clay Formation (10)



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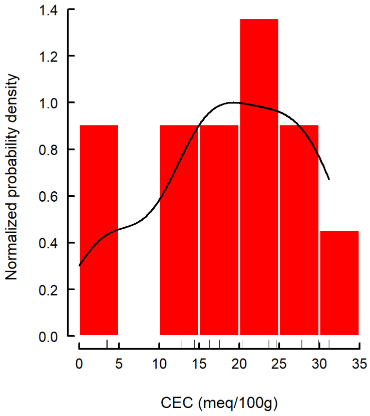
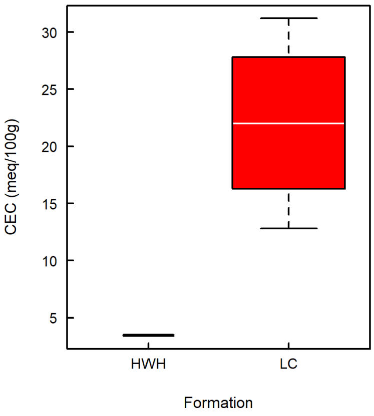
Red points are at or above the median





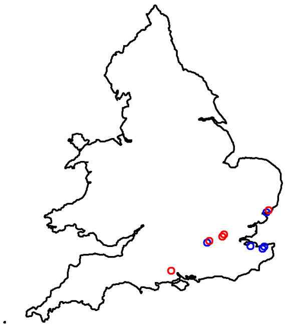
Lambeth Group (LMBE)

Cation Exchange Capacity (CEC)

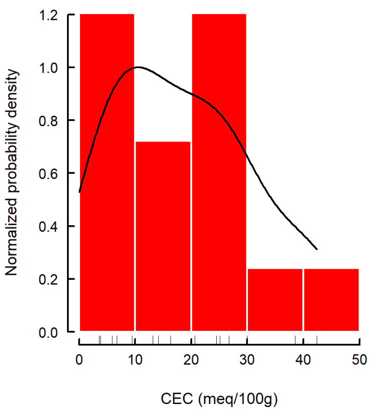
CEC (meq/100g)

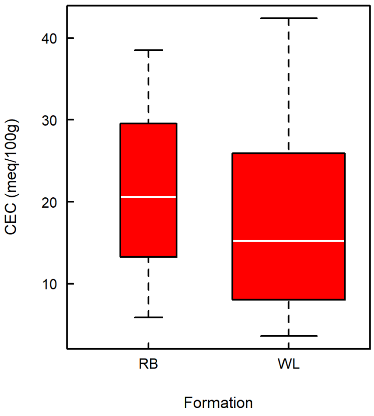
Min = 3.6
Median = 16.3
Mean = 18.7
Max = 42.4
Std dev = 12.3
n = 15

RB	Reading Formation (3)
WL	Woolwich Formation (12)



Blue points are below the median
Red points are at or above the median





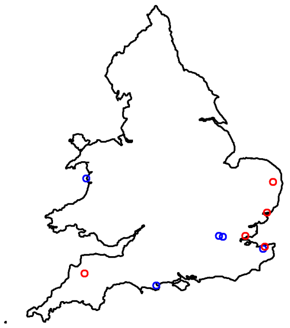
Other Palaeogene (XG)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 1.5
Median = 14.8
Mean = 15.1
Max = 39.8
Std dev = 12.6
n = 10

BGS	Bagshot Formation (3)
BOF	Bovey Formation (1)
TAB	Thanet Formation (5)
U	Undifferentiated (1)



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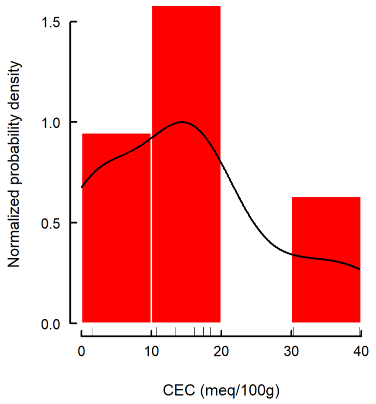
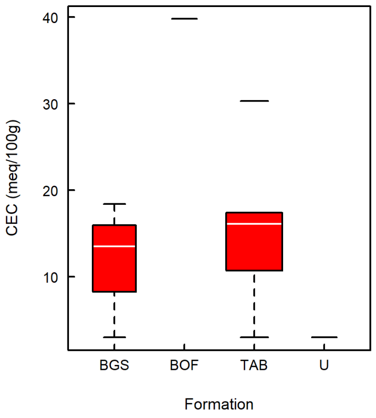




5.4.2 Cretaceous

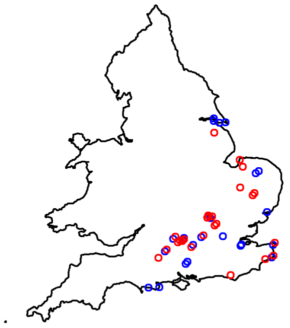
Chalk Group (CK)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 5.7
Median = 11.2
Mean = 11.9
Max = 29.4
Std dev = 4.22
n = 63

BCK	Burnham Chalk Formation (2)
CUCK	Culver Chalk Formation (1)
FCK	Flamborough Chalk Formation (2)
FYCK	Ferriby Chalk Formation (3)
HCK	Holywell Nodular Chalk Formation (6)
LECH	Lewes Nodular Chalk Formation (5)
NCK	Newhaven Chalk Formation (6)
NPCH	New Pit Chalk Formation (7)
SECK	Seaford Chalk Formation (17)
U	Undifferentiated (1)
WMCH	West Melbury Marly Chalk Formation (5)
ZZCH	Zig Zag Chalk Formation (8)



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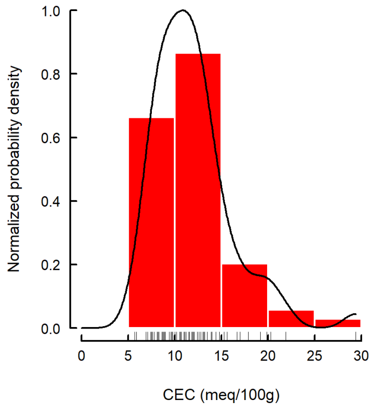
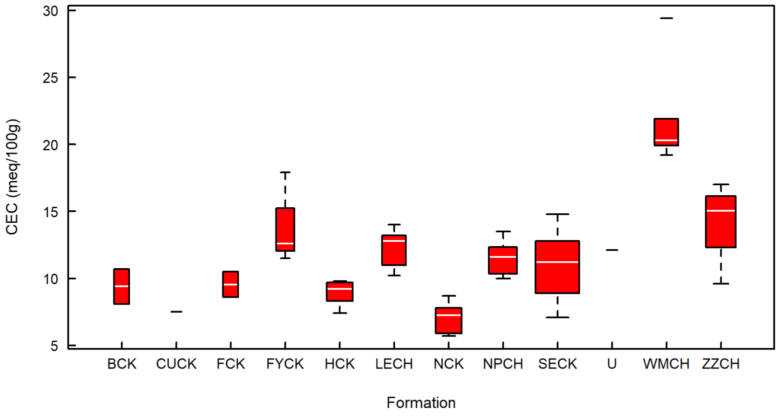
Red points are at or above the median





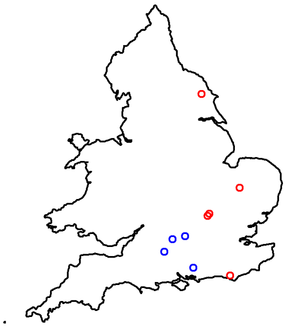
Selborne Group (SELB)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 3.7
Median = 22.2
Mean = 23.1
Max = 38.4
Std dev = 10.4
n = 9

GLT	Gault Formation (4)
UGS	Upper Greensand Formation (5)



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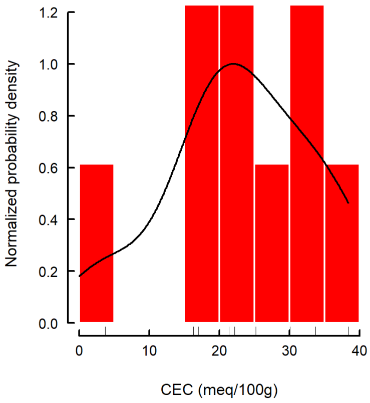
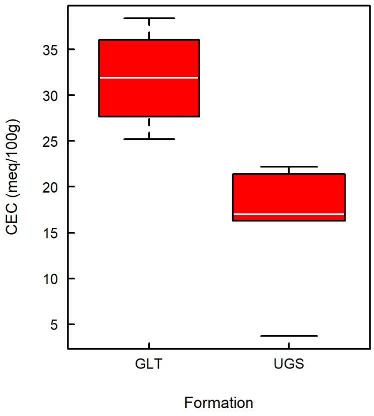




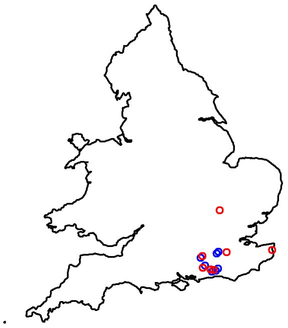
Lower Greensand Group (LGS)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 1.5
Median = 13.1
Mean = 10.8
Max = 18.3
Std dev = 6.32
n = 16

FO	Folkestone Formation (6)
HY	Hythe Formation (5)
SAB	Sandgate Formation (4)
U	Undifferentiated (1)



Blue points are below the median
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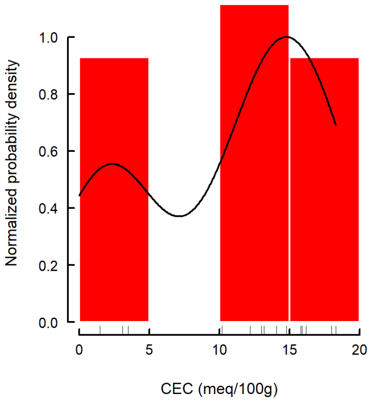
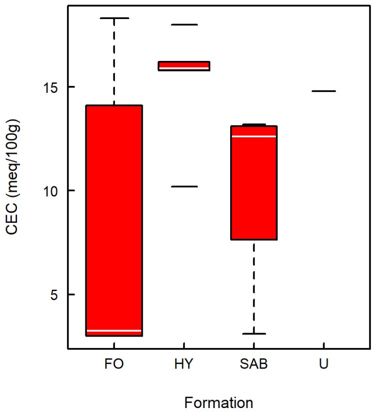




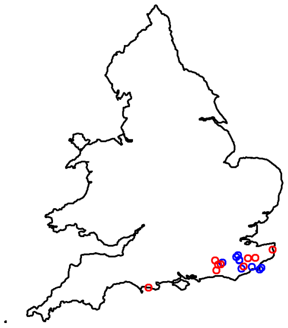
Wealden Group (W)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 1.5
Median = 13.2
Mean = 13.1
Max = 35.7
Std dev = 9.28
n = 18

ASD	Ashdown Formation (4)
HAS	Hastings Beds (Subgroup) (2)
TWS	Tunbridge Wells Sand Formation (4)
U	Undifferentiated (1)
WC	Weald Clay Formation (7)



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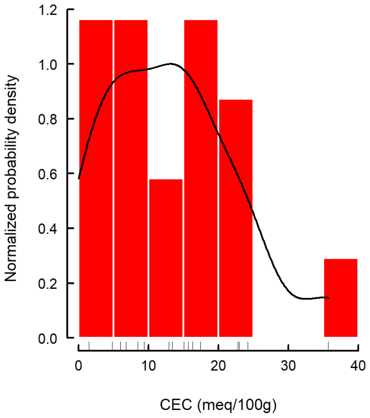
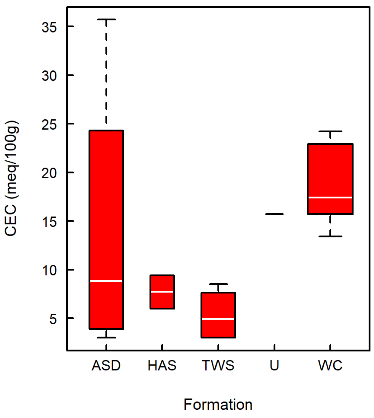
Red points are at or above the median





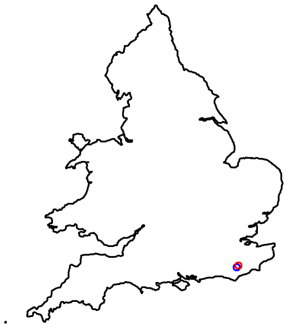
Purbeck Group (PB)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 23.3
Median = 25.6
Mean = 25.6
Max = 27.8
Std dev = 3.18
n = 2

DURN	Durlston Formation (1)
LULW	Lulworth Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

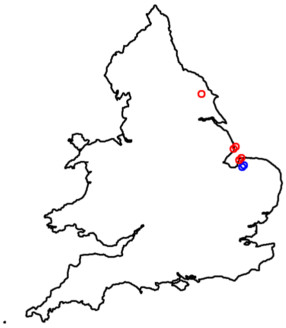
Other Cretaceous (XK)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 1.5
Median = 13.1
Mean = 13.8
Max = 39.9
Std dev = 10.7
n = 13

CA	Carstone Formation (2)
DEB	Dersingham Formation (2)
HUCK	Hunstanton Formation (3)
ROH	Roach Formation (2)
SAS	Sandringham Sand Formation (3)
SPC	Speeton Clay Formation (1)



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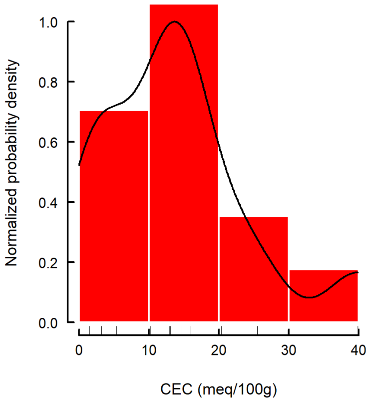
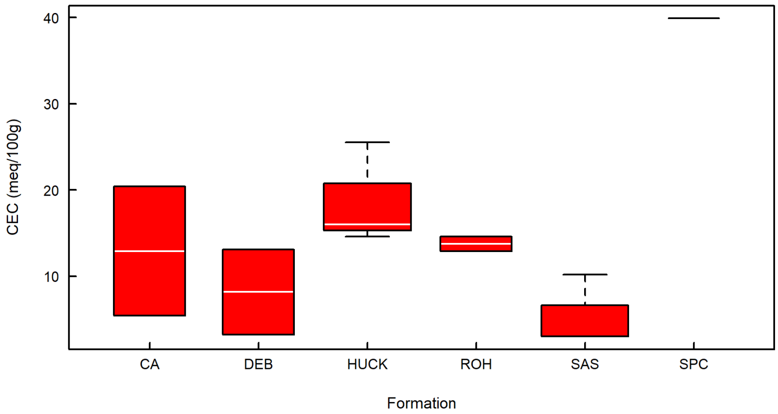




5.4.3 Jurassic

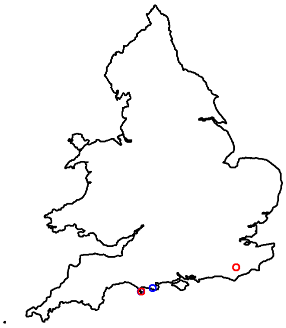
Portland Group (PL)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 1.5
Median = 8.85
Mean = 8.28
Max = 13.9
Std dev = 5.79
n = 4

POST	Portland Stone Formation (3)
U	Undifferentiated (1)



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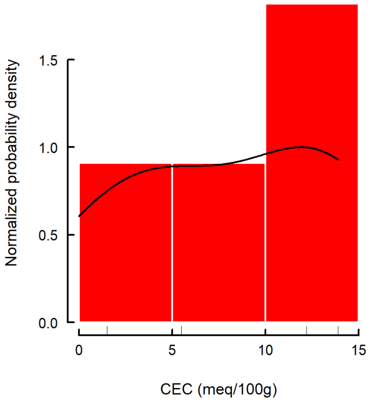
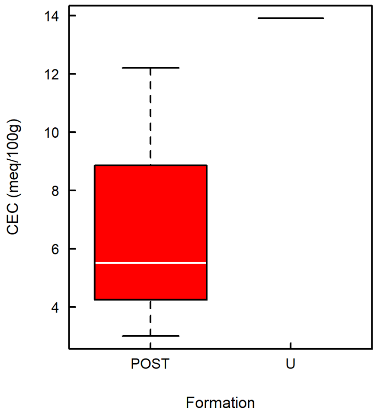




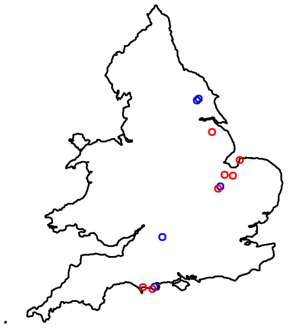
Ancholme Group (AMG)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 4.3
Median = 21.8
Mean = 20.2
Max = 26.5
Std dev = 6.92
n = 14

AMC	Ampthill Clay Formation (2)
KC	Kimmeridge Clay Formation (6)
KLB	Kellaways Formation (2)
OXC	Oxford Clay Formation (4)



Blue points are below the median
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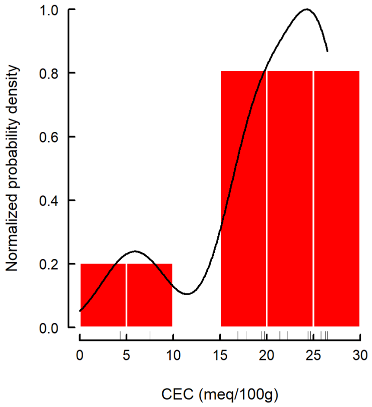
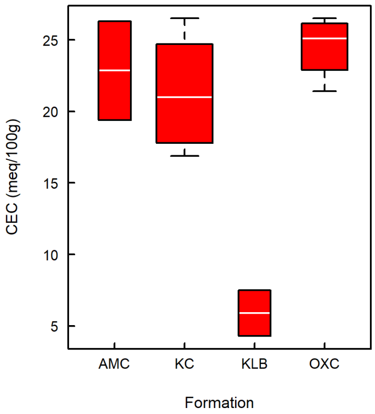




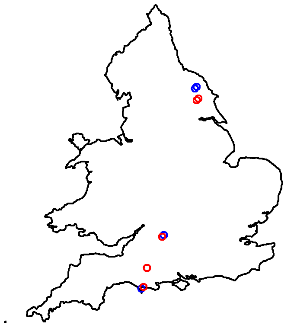
Corallian Group (CR)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 8.6
Median = 14
Mean = 16.9
Max = 35.3
Std dev = 8.62
n = 9

CLAV	Clavellata Formation (1)
OSS	Osmington Oolite Formation (1)
RECF	Redcliff Formation (1)
STOU	Stour Formation (1)
U	Undifferentiated (5)



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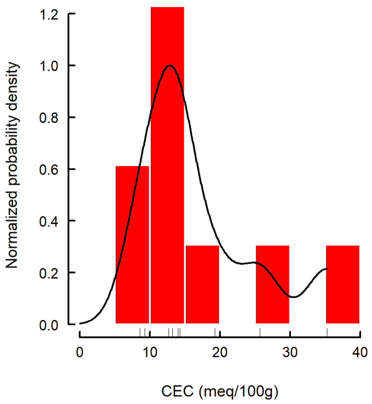
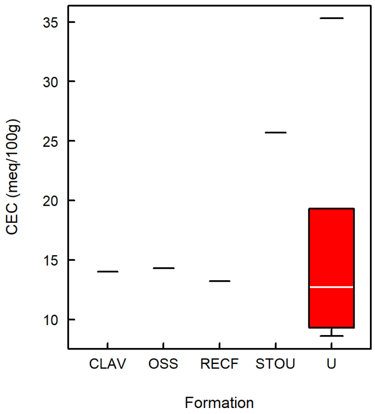




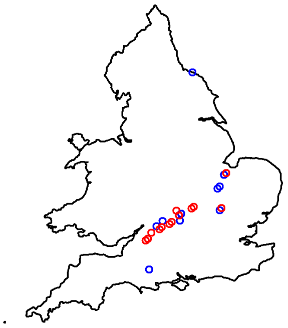
Great Oolite Group (GOG)

Cation Exchange Capacity (CEC)

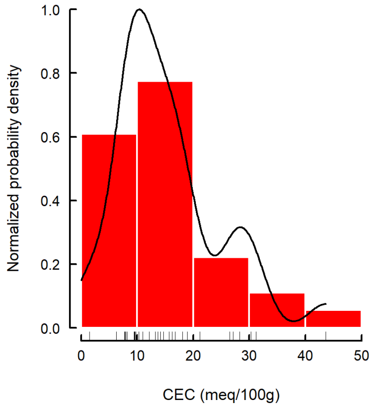
CEC (meq/100g)

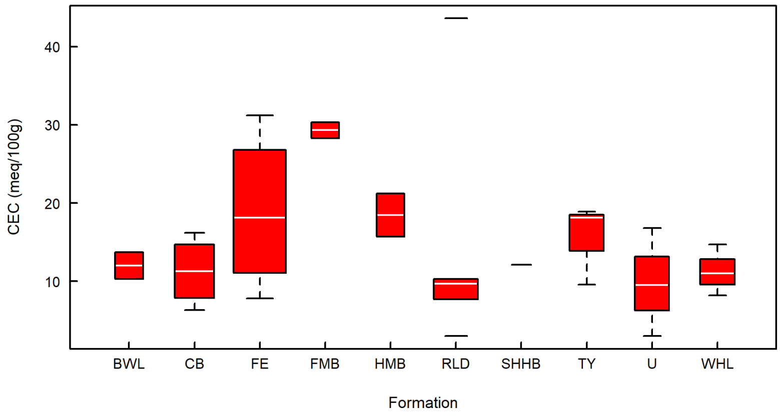
Min = 1.5
Median = 13.4
Mean = 15.3
Max = 43.6
Std dev = 9.3
n = 32

BWL	Blisworth Limestone Formation (2)
CB	Cornbrash Formation (4)
FE	Fuller'S Earth Formation (7)
FMB	Forest Marble Formation (2)
HMB	Hampen Formation (2)
RLD	Rutland Formation (5)
SHHB	Sharp'S Hill Formation (1)
TY	Taynton Limestone Formation (3)
U	Undifferentiated (3)
WHL	White Limestone Formation (3)



Blue points are below the median
Red points are at or above the median





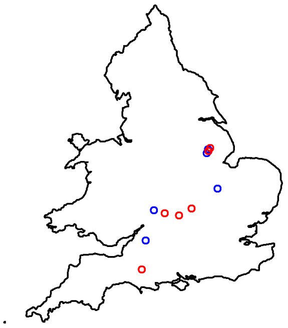
Inferior Oolite Group (INO)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 3.4
Median = 10.1
Mean = 9.79
Max = 15.4
Std dev = 4.46
n = 12

BLPL	Birdlip Limestone Formation (2)
GRF	Grantham Formation (2)
LL	Lincolnshire Limestone Formation (5)
NS	Northampton Sand Formation (1)
U	Undifferentiated (2)



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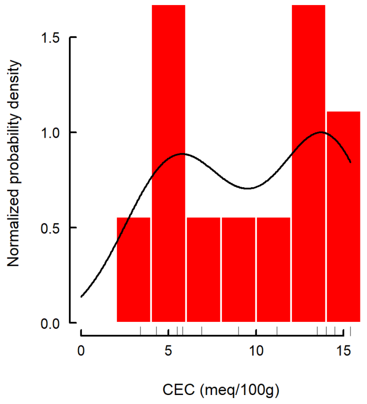
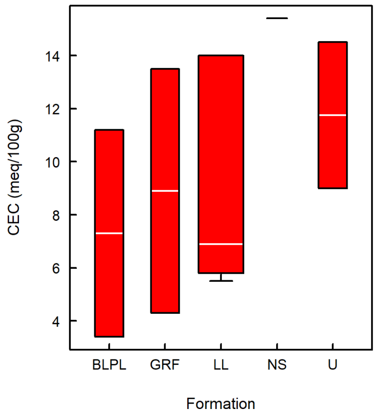




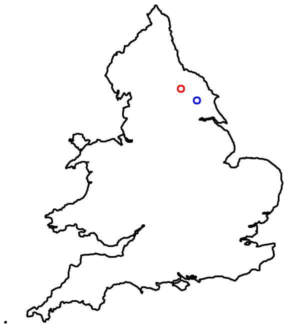
Ravenscar Group (RAG)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 1.5
Median = 9
Mean = 9
Max = 16.5
Std dev = 10.6
n = 2

SCY	Scalby Formation (1)
U	Undifferentiated (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

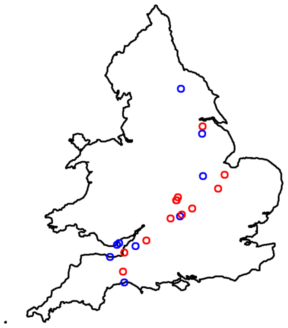
Lias Group (LI)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 9.7
Median = 23.6
Mean = 22.4
Max = 32.5
Std dev = 6.26
n = 24

BDS	Bridport Sand Formation (1)
BLI	Blue Lias Formation (8)
BNLS	Beacon Limestone Formation (1)
CHAM	Charmouth Mudstone Formation (3)
DYS	Dyrham Formation (1)
U	Undifferentiated (5)
WHM	Whitby Mudstone Formation (5)



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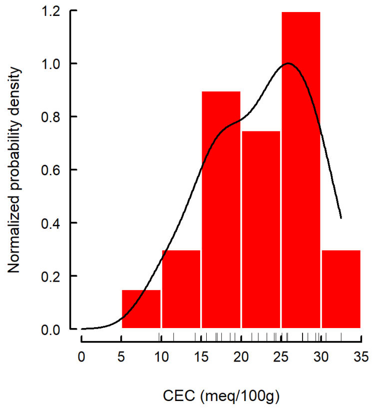
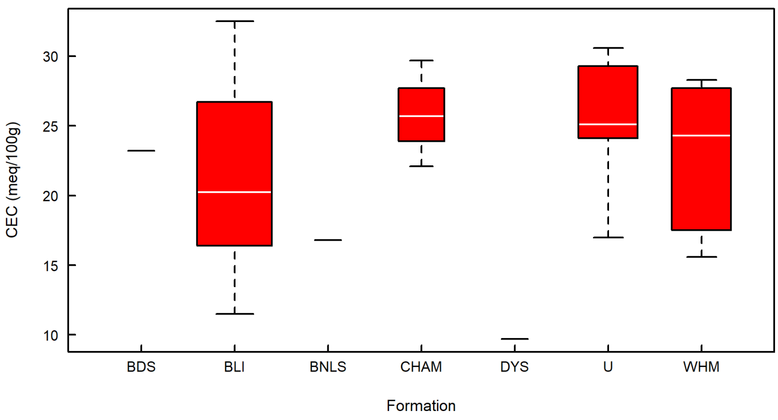




Other Jurassic (XJ)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 6.2
Median = 6.2
Mean = 6.2
Max = 6.2
Std dev = NA
n = 1

SAS Sandringham Sand Formation (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

5.4.4 Triassic

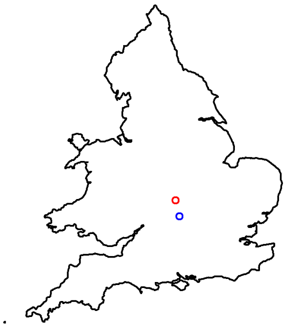
Penarth Group (PNG)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 33.1
Median = 35.8
Mean = 35.8
Max = 38.5
Std dev = 3.82
n = 2

U Undifferentiated (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

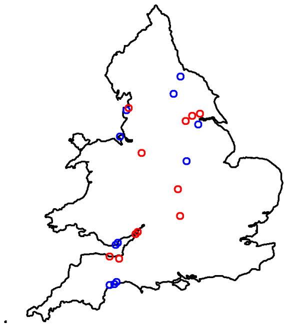
Mercia Mudstone Group (MMG)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 1.5
Median = 14.4
Mean = 15.2
Max = 35
Std dev = 8.85
n = 22

BAN	Blue Anchor Formation (3)
SIM	Sidmouth Mudstone Formation (2)
TPSF	Tarporley Siltstone Formation (1)
U	Undifferentiated (16)



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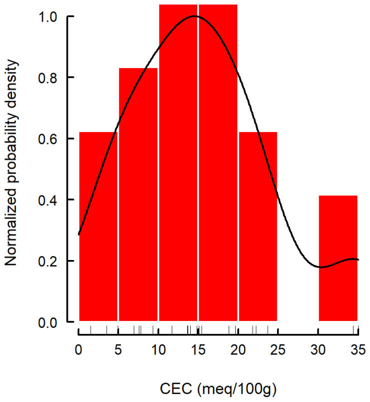
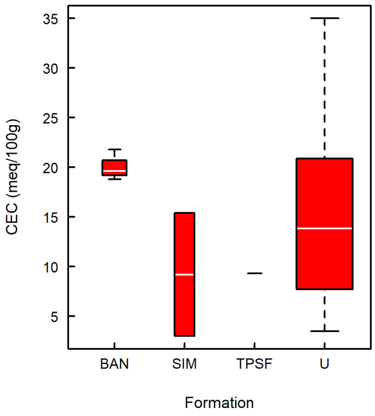




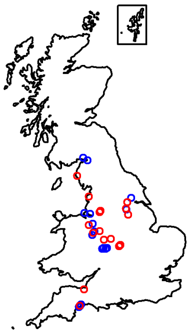
Sherwood Sandstone Group (SSG)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 1.5
Median = 5.25
Mean = 7.09
Max = 20.6
Std dev = 5.8
n = 34

BMS	Bromsgrove Sandstone Formation (4)
BSP	Budleigh Salterton Pebble Beds Formation (2
CPB	Chester Pebble Beds Formation (1)
HEY	Helsby Sandstone Formation (3)
KDM	Kidderminster Formation (1)
NTC	Nottingham Castle Sandstone Formation (2)
OS	Otter Sandstone Formation (3)
SBS	St Bees Sandstone Formation (1)
U	Undifferentiated (11)
WLSF	Wilmslow Sandstone Formation (5)
WRS	Wildmoor Sandstone Formation (1)



Blue points are below the median
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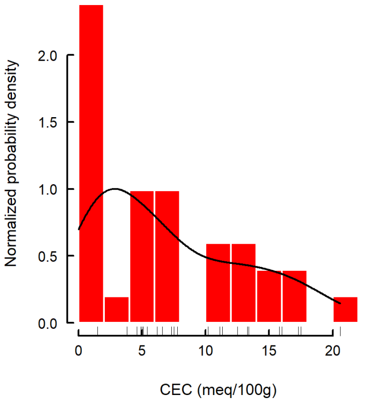
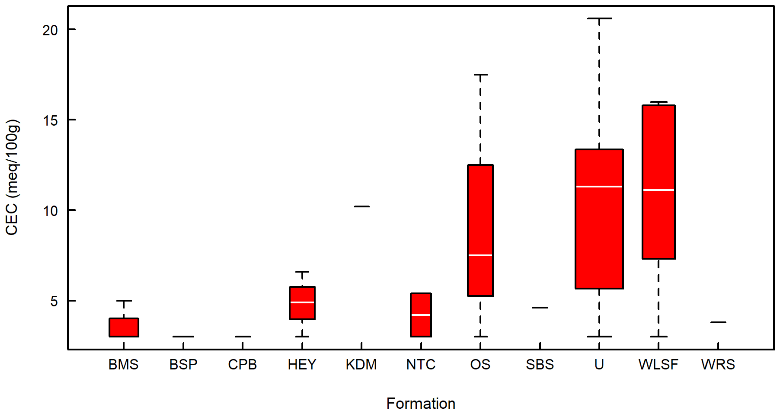




5.4.5 Permian

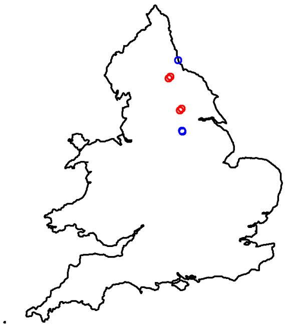
Zechstein Group (ZG)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 1.5
Median = 5.9
Mean = 10.7
Max = 25
Std dev = 8.98
n = 9

BTH	Brotherton Formation (1)
CDF	Cadeby Formation (2)
EDT	Edlington Formation (2)
RML	Raisby Formation (1)
U	Undifferentiated (3)



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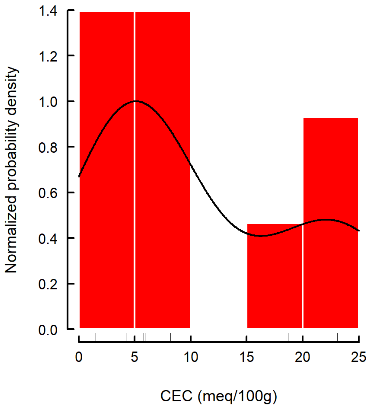
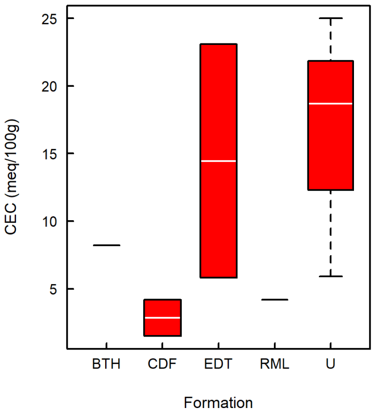
Red points are at or above the median





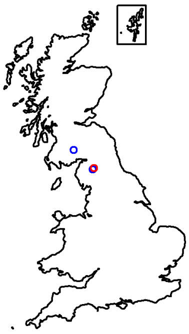
Appleby Group (APY)

Cation Exchange Capacity (CEC)

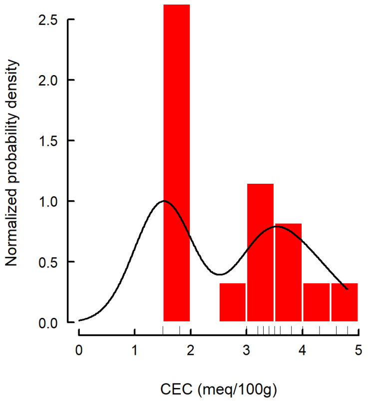
CEC (meq/100g)

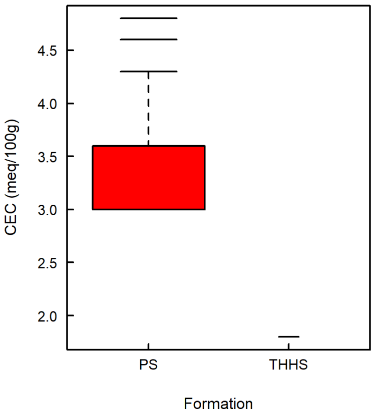
Min = 1.5
Median = 3
Mean = 2.67
Max = 4.8
Std dev = 1.17
n = 34

PS	Penrith Sandstone Formation (33)
THHS	Thornhill Sandstone Formation (1)



Blue points are below the median
Red points are at or above the median





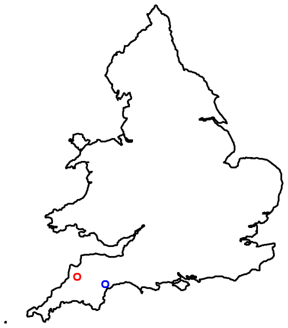
Exeter Group (EXE)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 4.9
Median = 5.9
Mean = 5.9
Max = 6.9
Std dev = 1.41
n = 2

BOB	Bow Breccia Formation (1)
HVBR	Heavitree Breccia Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

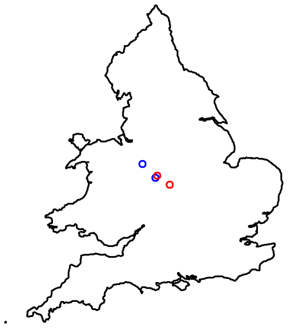
Warwickshire Group (WAWK)

Cation Exchange Capacity (CEC)

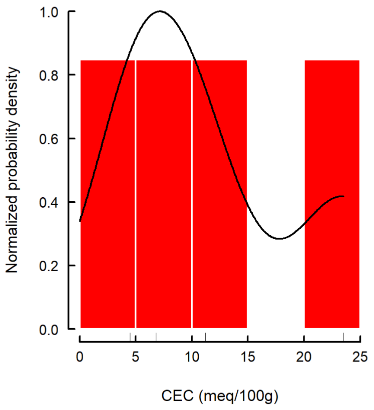
CEC (meq/100g)

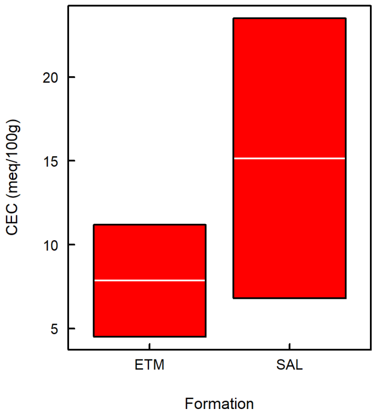
Min = 4.5
Median = 9
Mean = 11.5
Max = 23.5
Std dev = 8.47
n = 4

ETM	Etruria Formation (2)
SAL	Salop Formation (2)



Blue points are below the median
Red points are at or above the median





Other Permian (XP)

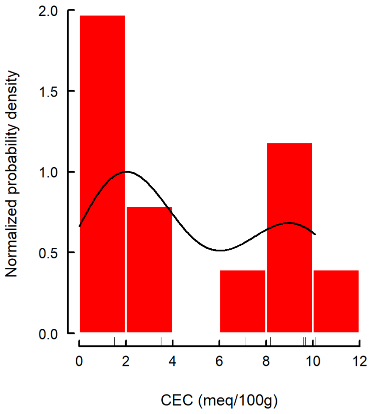
Cation Exchange Capacity (CEC)

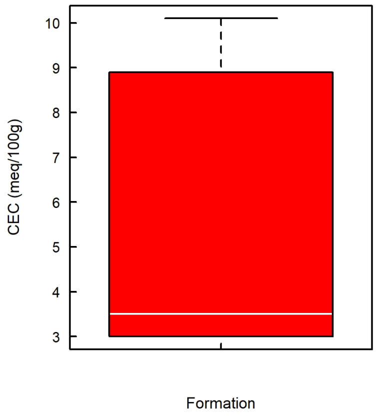
CEC (meq/100g)

Min = 1.5
Median = 3.5
Mean = 4.93
Max = 10.1
Std dev = 3.69
n = 12

BRI Bridgnorth Sandstone Formation (12)

Blue points are below the median
Red points are at or above the median





5.4.6 Carboniferous

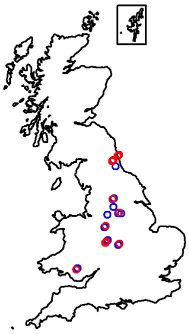
Pennine Coal Measures Group (PCM)

Cation Exchange Capacity (CEC)

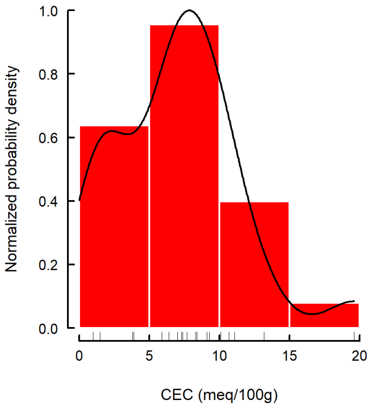
CEC (meq/100g)

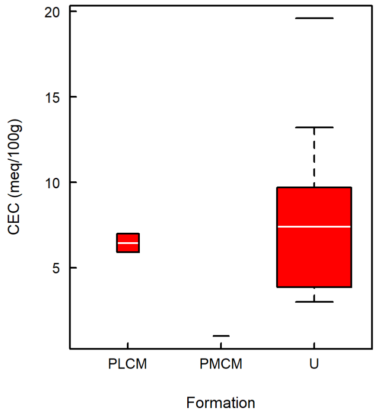
Min = 1
Median = 7.15
Mean = 6.95
Max = 19.6
Std dev = 4.34
n = 26

PLCM Pennine Lower Coal Measures Formation (2)
PMCM Pennine Middle Coal Measures Formation (1
U Undifferentiated (23)



Blue points are below the median
Red points are at or above the median





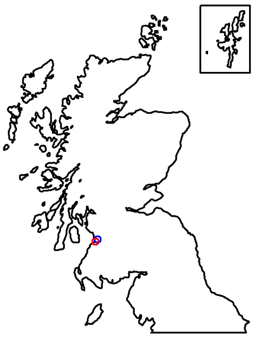
Scottish Coal Measures Group (CMSC)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 1.5
Median = 5.65
Mean = 5.65
Max = 9.8
Std dev = 5.87
n = 2

MCMS Scottish Middle Coal Measures Formation (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Holsworthy Group (HOWY)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 4.5
Median = 4.95
Mean = 4.95
Max = 5.4
Std dev = 0.636
n = 2

BF Bude Formation (2)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

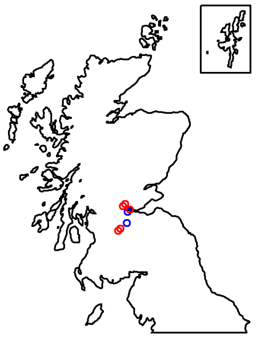
Clackmannan Group (CKN)

Cation Exchange Capacity (CEC)

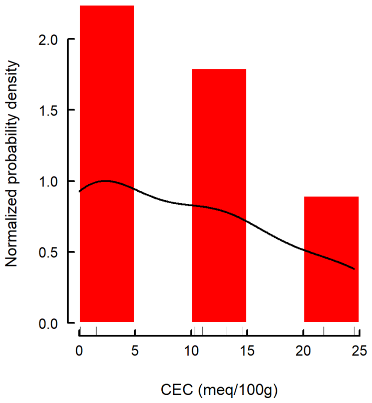
CEC (meq/100g)

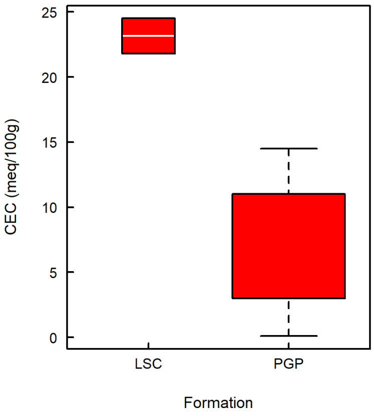
Min = 0.1
Median = 10.3
Mean = 9.21
Max = 24.5
Std dev = 8.72
n = 11

LSC	Limestone Coal Formation (2)
PGP	Passage Formation (9)



Blue points are below the median
Red points are at or above the median





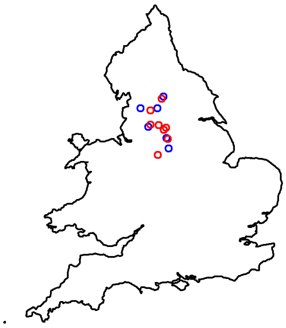
Millstone Grit Group (MG)

Cation Exchange Capacity (CEC)

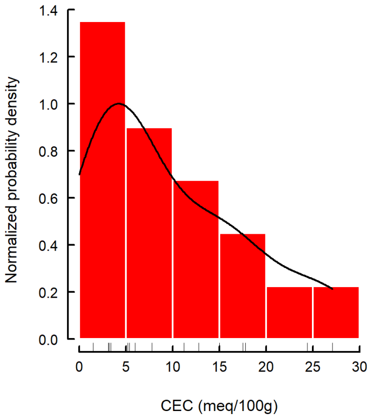
CEC (meq/100g)

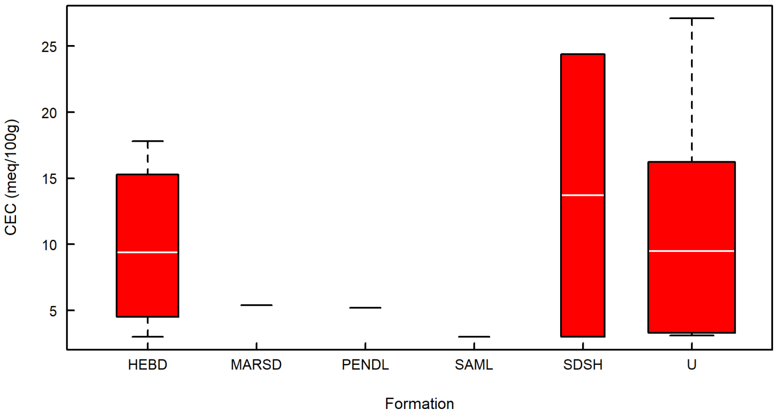
Min = 1.5
Median = 6
Mean = 9.67
Max = 27.1
Std dev = 8.17
n = 17

HEBD	Hebden Formation (4)
MARSD	Marsden Formation (1)
PENDL	Pendleton Formation (1)
SAML	Samlesbury Formation (1)
SDSH	Sabden Shales (2)
U	Undifferentiated (8)



Blue points are below the median
Red points are at or above the median





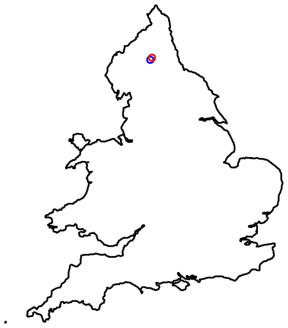
Yoredale Group (YORE)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 4.3
Median = 7.15
Mean = 7.15
Max = 10
Std dev = 4.03
n = 2

SMGP	Stainmore Formation (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

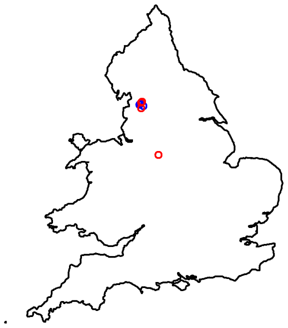
Craven Group (CRAV)

Cation Exchange Capacity (CEC)

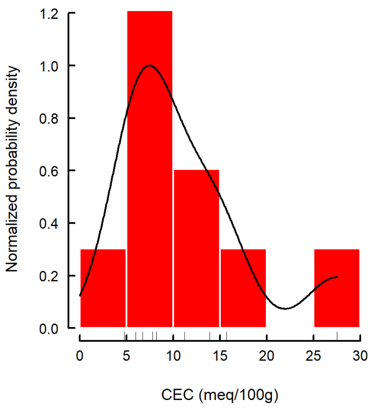
CEC (meq/100g)

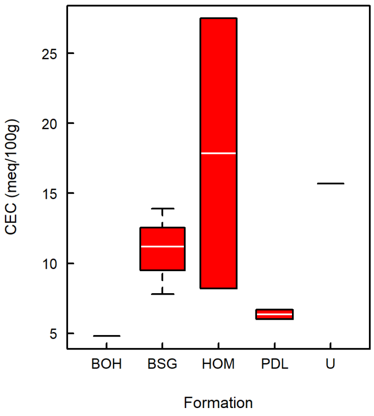
Min = 4.8
Median = 8.2
Mean = 11.3
Max = 27.5
Std dev = 7.09
n = 9

BOH	Hodderense Limestone Formation (1)
BSG	Bowland Shale Formation (3)
HOM	Hodder Mudstone Formation (2)
PDL	Pendleside Limestone Formation (2)
U	Undifferentiated (1)



Blue points are below the median
Red points are at or above the median





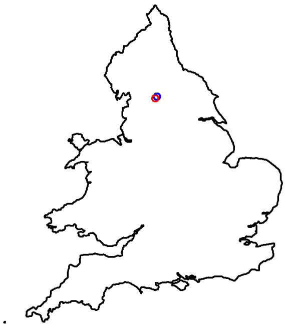
Great Scar Limestone Group (GSCL)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 3.4
Median = 3.8
Mean = 3.8
Max = 4.2
Std dev = 0.566
n = 2

KLSL Kilnsey Formation (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

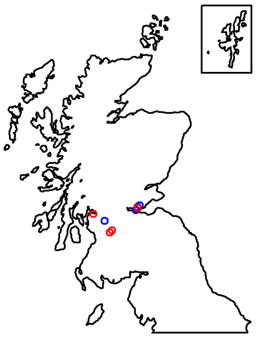
Strathclyde Group (SYG)

Cation Exchange Capacity (CEC)

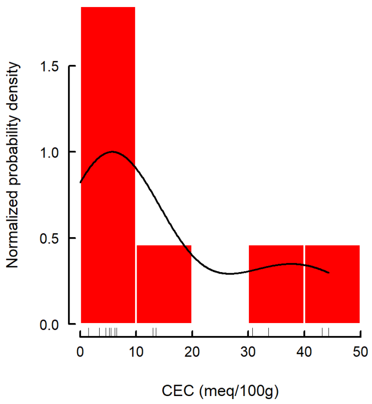
CEC (meq/100g)

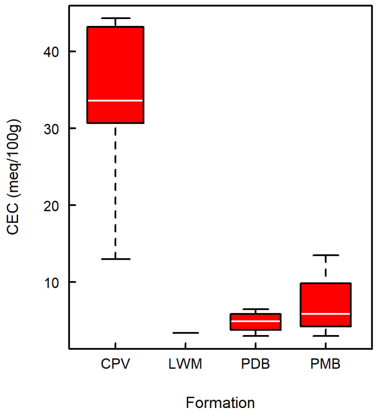
Min = 1.5
Median = 6.35
Mean = 15.2
Max = 44.3
Std dev = 15.7
n = 14

CPV Clyde Plateau Volcanic Formation (5)
LWM Lawmuir Formation (1)
PDB Pathhead Formation (4)
PMB Pittenweem Formation (4)



Blue points are below the median
Red points are at or above the median





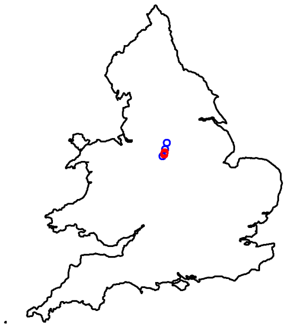
Peak Limestone Group (PKLM)

Cation Exchange Capacity (CEC)

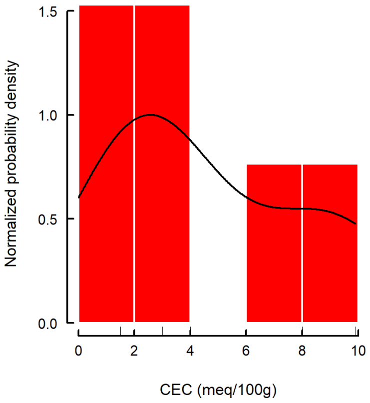
CEC (meq/100g)

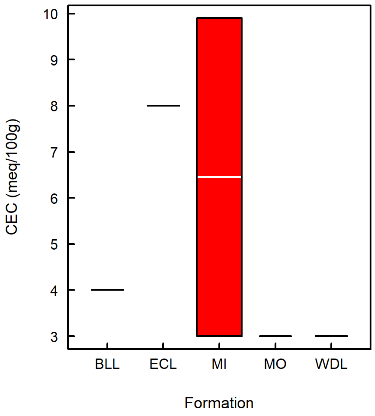
Min = 1.5
Median = 3.5
Mean = 4.65
Max = 9.9
Std dev = 3.52
n = 6

BLL	Bee Low Limestone Formation (1)
ECL	Ecton Limestone Formation (1)
MI	Milldale Limestone Formation (2)
MO	Monsal Dale Limestone Formation (1)
WDL	Woo Dale Limestone Formation (1)



Blue points are below the median
Red points are at or above the median





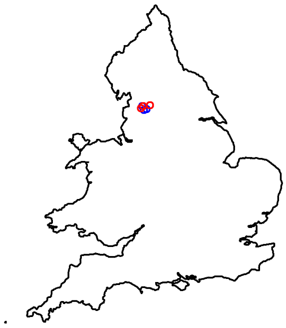
Bowland High Group (BOHI)

Cation Exchange Capacity (CEC)

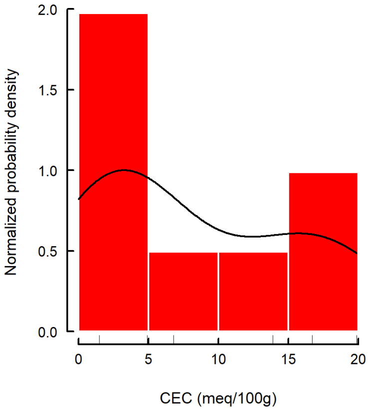
CEC (meq/100g)

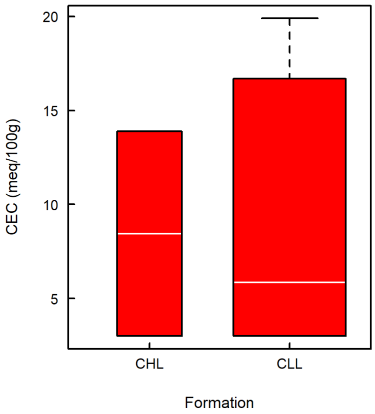
Min = 1.5
Median = 5.85
Mean = 8.34
Max = 19.9
Std dev = 7.46
n = 8

CHL	Chatburn Limestone Formation (2)
CLL	Clitheroe Limestone Formation (6)



Blue points are below the median
Red points are at or above the median





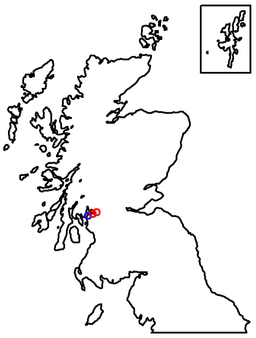
Inverclyde Group (INV)

Cation Exchange Capacity (CEC)

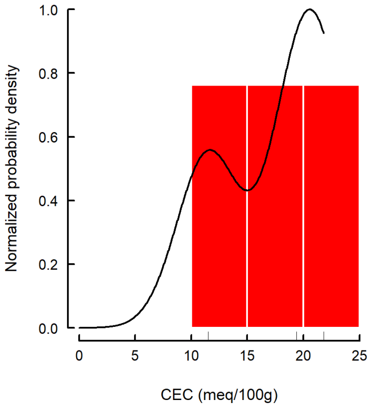
CEC (meq/100g)

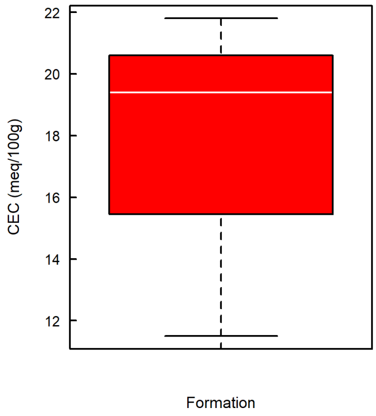
Min = 11.5
Median = 19.4
Mean = 17.6
Max = 21.8
Std dev = 5.39
n = 3

KNW Kinnesswood Formation (3)



Blue points are below the median
Red points are at or above the median





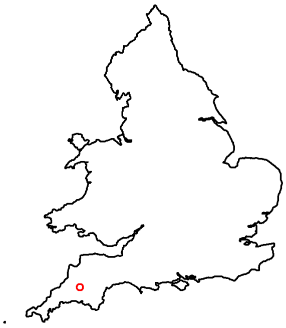
Transition Group (Devonian-Carboniferc

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 13.2
Median = 13.2
Mean = 13.2
Max = 13.2
Std dev = NA
n = 1

SBT South Brentor Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

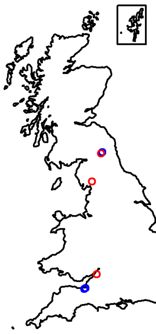
Other Carb. Limestone Supergroup (XC

Cation Exchange Capacity (CEC)

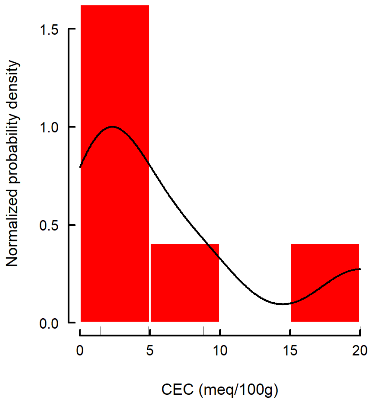
CEC (meq/100g)

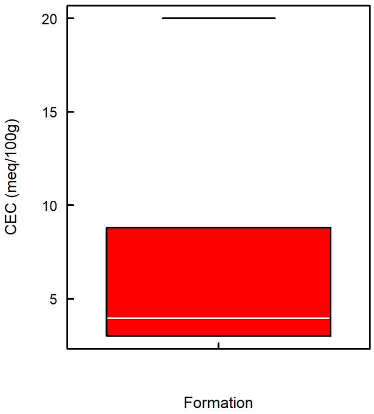
Min = 1.5
Median = 3.2
Mean = 6.37
Max = 20
Std dev = 7.28
n = 6

U Undifferentiated (6)



Blue points are below the median
Red points are at or above the median





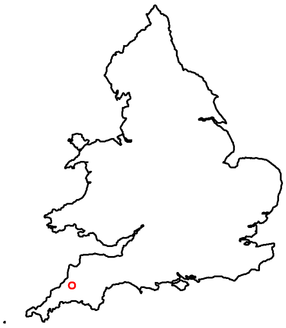
Other Culm Supergroup (XCU)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 1.5
Median = 1.5
Mean = 1.5
Max = 1.5
Std dev = NA
n = 1

U Undifferentiated (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

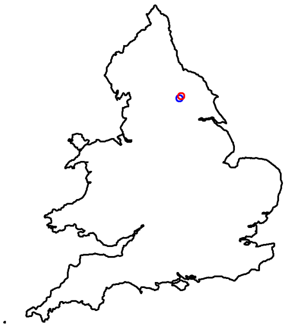
Other Carboniferous (XC)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 7.9
Median = 10.2
Mean = 10.2
Max = 12.6
Std dev = 3.32
n = 2

U Undifferentiated (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

5.4.7 Devonian

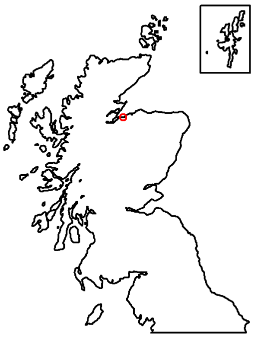
Forres Sandstone Group (FSA)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 7
Median = 7
Mean = 7
Max = 7
Std dev = NA
n = 1

U Undifferentiated (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Exmoor Group (EXM)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 3.2
Median = 3.2
Mean = 3.2
Max = 3.2
Std dev = NA
n = 1

PLT Pilton Mudstone Formation (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

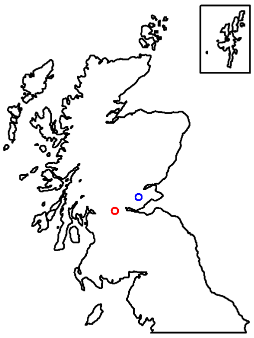
Stratheden Group (SAG)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 0.6
Median = 3.45
Mean = 3.45
Max = 6.3
Std dev = 4.03
n = 2

SCK Stockiemuir Sandstone Formation (1)
U Undifferentiated (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

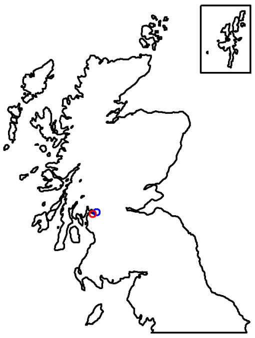
Fair Isle Group (FIL)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 7.3
Median = 21.6
Mean = 21.6
Max = 36
Std dev = 20.3
n = 2

BNG Bu Ness Sandstone Formation (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

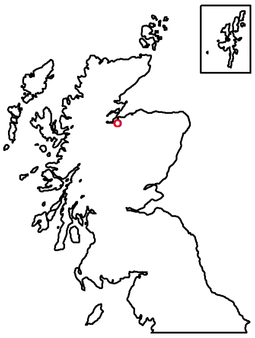
Inverness Sandstone Group (INS)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 3.6
Median = 4.15
Mean = 4.15
Max = 4.7
Std dev = 0.778
n = 2

DVC Daviot Conglomerate Formation (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Meadfoot Group (MDT)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 1.5
Median = 1.5
Mean = 1.5
Max = 1.5
Std dev = 0
n = 2

U Undifferentiated (2)


Blue points are below the median
Red points are at or above the median

Not enough data for plotting

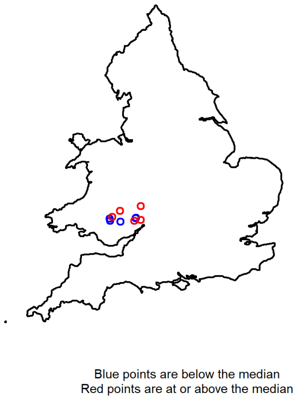
Lower Old Red Sandstone (LORS)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 1.5
Median = 8.35
Mean = 8.79
Max = 17.3
Std dev = 5.44
n = 10

BRS Brownstones Formation (8)
SMG St Maughans Formation (2)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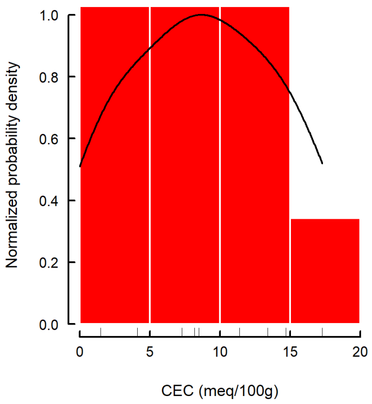
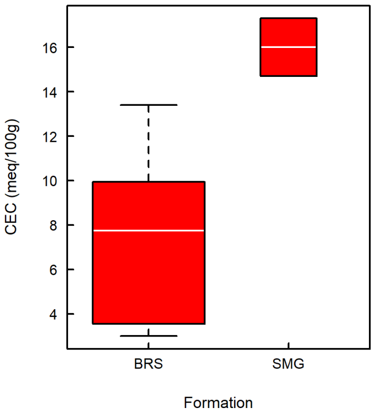




Downton Group (DOW)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 23.7
Median = 23.7
Mean = 23.7
Max = 23.7
Std dev = NA
n = 1

RG Raglan Mudstone Formation (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

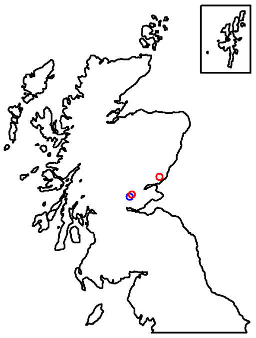
Arbuthnott-Garvock Group (ATGK)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 4.9
Median = 8.85
Mean = 8.6
Max = 11.8
Std dev = 3.07
n = 4

DEF Dundee Flagstone Formation (1)
OVF Ochil Volcanic Formation (3)



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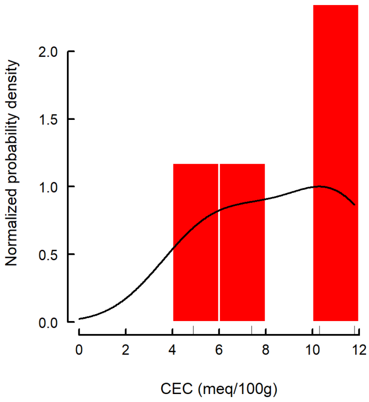
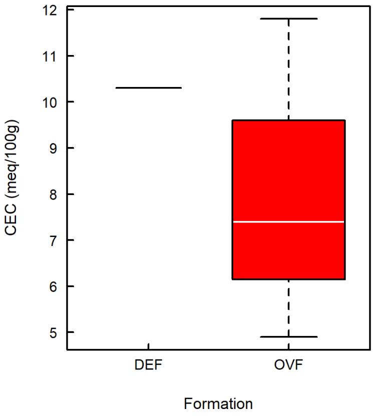




Other Devonian (XD)

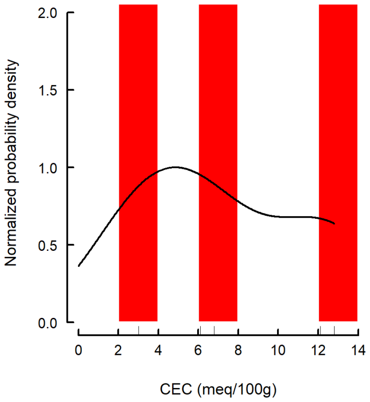
Cation Exchange Capacity (CEC)

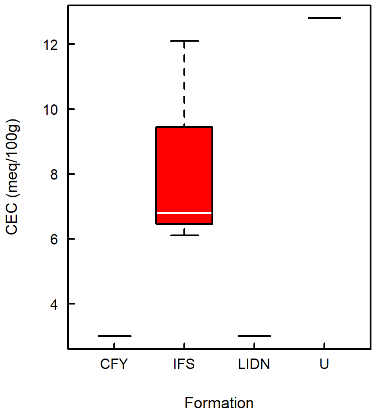
CEC (meq/100g)

Min = 3
Median = 6.45
Mean = 7.3
Max = 12.8
Std dev = 4.29
n = 6

CFY	Cnoc Fyrish Conglomerate Formation (1)
IFS	Ilfracombe Slates Formation (3)
LIDN	Liddaton Formation (1)
U	Undifferentiated (1)

Blue points are below the median
Red points are at or above the median





5.4.8 Pre-Devonian

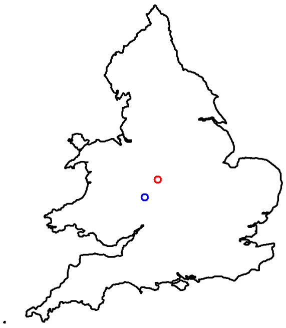
Lower Ludlow Shales Group (LLUS)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 14.7
Median = 15.4
Mean = 15.4
Max = 16
Std dev = 0.919
n = 2

U	Undifferentiated (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

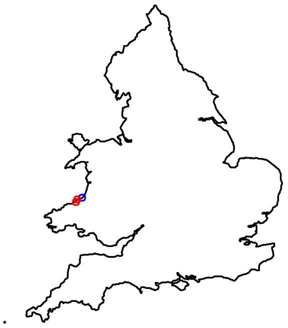
Aberystwyth Grits Group (AGF)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 3.2
Median = 4
Mean = 4.43
Max = 6.1
Std dev = 1.5
n = 3

MYBA	Mynydd Bach Formation (3)



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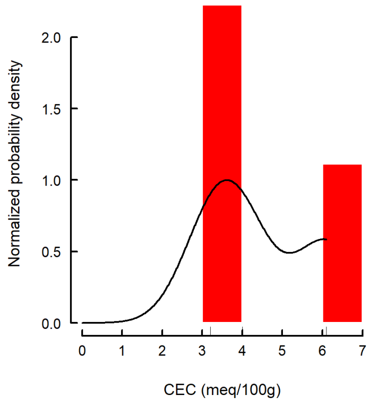
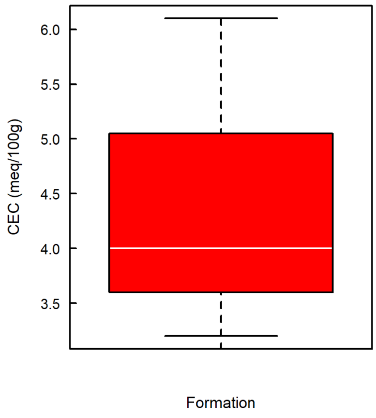
Red points are at or above the median





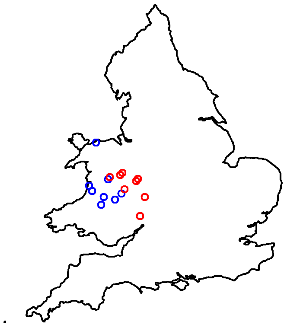
Other Silurian (XS)

Cation Exchange Capacity (CEC)

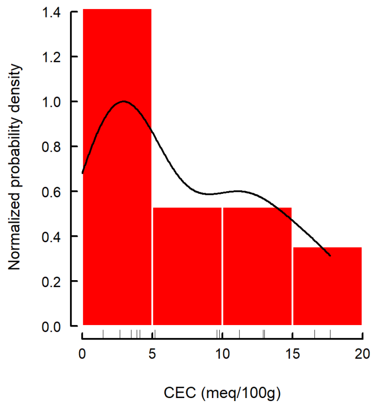
CEC (meq/100g)

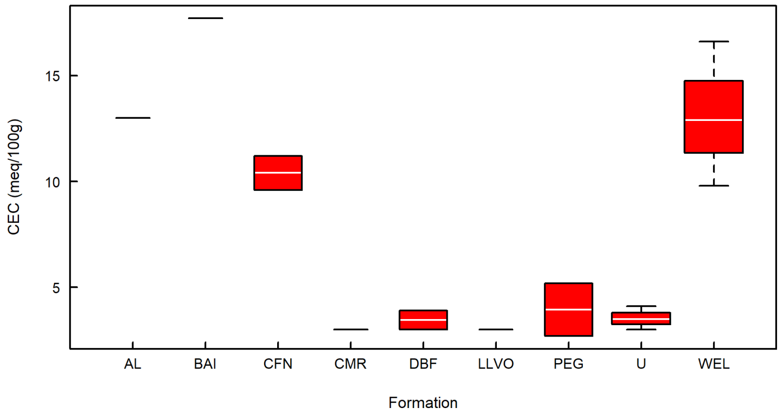
Min = 1.5
Median = 4.65
Mean = 7.26
Max = 17.7
Std dev = 5.67
n = 16

AL	Aymestry Limestone Formation (1)
BAI	Bailey Hill Formation (1)
CFN	Cefn Formation (2)
CMR	Cwmere Formation (1)
DBF	Devil'S Bridge Formation (2)
LLVO	Llanwrtyd Volcanic Formation (1)
PEG	Penstrowed Grits Formation (2)
U	Undifferentiated (3)
WEL	Much Wenlock Limestone Formation (3)



Blue points are below the median
Red points are at or above the median





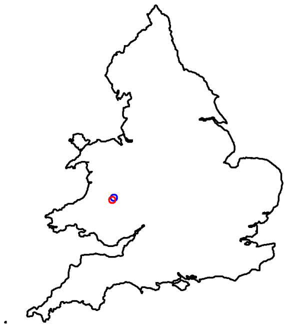
Builth Volcanic Group (BUVO)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 11.2
Median = 18.4
Mean = 18.4
Max = 25.7
Std dev = 10.3
n = 2

U Undifferentiated (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Mawddach Group (MWG)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 1.5
Median = 1.5
Mean = 1.5
Max = 1.5
Std dev = 0
n = 2

FF Ffestiniog Flags Formation (1)
MW Maentwrog Formation (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

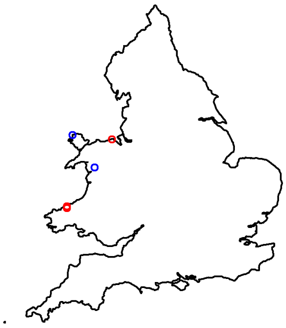
Other Ordovician (XO)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 1.5
Median = 5.7
Mean = 10.4
Max = 25.4
Std dev = 10.7
n = 5

DIIS	Dinas Island Formation (1)
I	(1)
PTRE	Pentre Formation (1)
U	Undifferentiated (2)



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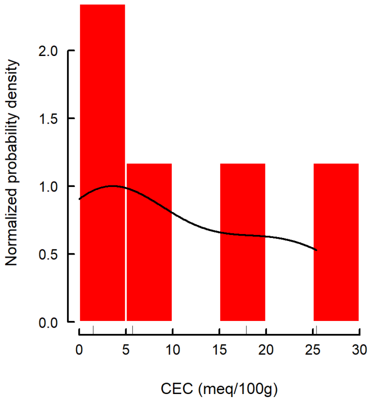
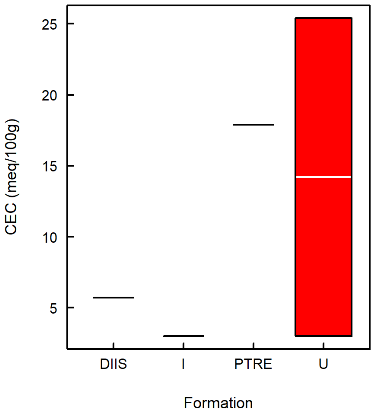




Mona Gneiss Suite (NMG)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 6
Median = 6
Mean = 6
Max = 6
Std dev = NA
n = 1

U	Undifferentiated (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

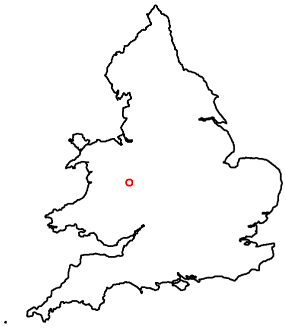
Stretton Group (YST)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 6.9
Median = 6.9
Mean = 6.9
Max = 6.9
Std dev = NA
n = 1

SYGP Synalds Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

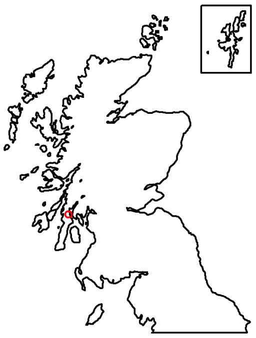
Argyll Group (ARGY)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 8.6
Median = 8.6
Mean = 8.6
Max = 8.6
Std dev = NA
n = 1

DBUE Upper Erins Quartzite Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

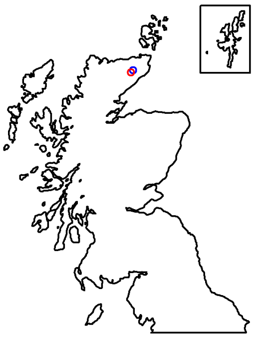
Loch Eil Group (LEIL)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 1.5
Median = 3.95
Mean = 3.95
Max = 6.4
Std dev = 3.46
n = 2

SUIS Suisgill Semipelite Formation (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Other Pre-Cambrian (XA)

Cation Exchange Capacity (CEC)

CEC (meq/100g)

Min = 1.5
Median = 1.5
Mean = 1.5
Max = 1.5
Std dev = NA
n = 1

U Undifferentiated (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

6 Organic and inorganic carbon

6.1 USE AND INTERPRETATION OF f_{OC} AND f_{IC}

The organic carbon fraction in aquifer materials exerts a major influence on the subsurface mobility of organic and organic-associated contaminants. The spatial distribution of total organic carbon (TOC) in aquifer materials must be determined before the transport of hydrophobic organic pollutants in aquifers can be modelled accurately. Solid carbon can occur in aquifer materials in inorganic and organic forms. The organic matter consists of plant, animal and microbial remains in various stages of decomposition along with their highly-altered derivatives (usually referred to as humic matter).

Organic carbon is found in virtually all superficial soils and sediments and is also found in many deeper-buried sediments and rocks to a varying extent. Natural organic matter is about 50% organic C by weight. The high organic content of soils (1-10% organic matter by weight) is one of their most distinguishing features.

Organic carbon is present in these earth materials in a variety of forms ranging from transient, soluble low molecular weight compounds such as fatty acids to the more recalcitrant solid humic compounds which have a molecular weight of several tens of thousand Daltons. Alkanes and amino acids are frequent structural elements. Carbon-14 analysis of such humic compounds in soils often suggests 'ages' of several thousand years. They are brown because they have no definite structure, and are known to be highly heterogeneous both from a structural (organic chemistry) point of view and from a behavioural (physical chemistry) point of view. Kerogen (bitumen), a solid, waxy, organic substance that forms when pressure and heat are applied to organic matter, is often found in small quantities in aquifer materials. For example, at the Borden research site, Ontario, Canada, the total fraction of organic carbon was low (f_{OC} = 0.021%), but the small amounts of kerogen (about 19% of the f_{OC}), identified by CPMAS ^{13}C NMR, were found to dominate the ability of the sands to adsorb organic compounds such as the PAHs, naphthalene and phenanthrene(Ran et al., 2003). Kerogens have also been identified in British Chalks. The humic acid content of the purest form of UK Chalk (upper White Chalk) is about 0.01% by weight. This increases to 0.1% in clayey and phosphatic facies and up to 1% in a sample of the Black Band Chalk (Pacey, 1989).

Occasionally, as in peats, these humic compounds become the dominant constituent. Coals contain quite a lot of humic acid but are predominantly 'pure' carbon.

These humic materials are important because they are highly reactive. When present in large quantity, their cation exchange properties may become important since they are invariably negatively charged (see above). However, of greater importance is their ability to specifically adsorb a large range of chemicals, especially trace organic compounds including many man-made pollutants. They also adsorb some trace metals such as Hg, Pb, Al and Cu very strongly and this may be important under acid conditions where the oxides become positively charged and are no longer able to adsorb these metals very strongly.

Organic matter provides a different type of surface and surface adsorption sites from the minerals that make up most of sediments and rocks bulk matter and is important for that reason. Hydrophobic ('water-hating') compounds are poorly sorbed by most minerals but are strongly adsorbed by humic compounds.

6.2 MEASUREMENT OF ORGANIC AND INORGANIC CARBON

6.2.1 Analytical approaches

ORGANIC CARBON CONTENT

There are number of approaches to the determination of organic C in soil:

(i) by determination of total C after removing inorganic carbon by acid treatment

(ii) by dry combustion in a furnace at moderate temperature with either the weight loss expressed as 'loss on ignition' or by quantification of the amount of carbon dioxide produced.

(iii)by organic carbon reduction of chromate ($Cr_2O_7^{2-}$) and subsequent titrimetric determination of the unreacted chromate with ferrous sulphate.

The first of these was evaluated specifically for aquifer materials by Caughey et al (Caughey et al., 1995). Sample replicates were digested with sulphurous acid, dried at 40°C, and then combusted at 950°C using proprietary instrumentation that measured the evolved carbon dioxide. For the three test materials that contained >2% TIC, incomplete acidification resulted in a systematic positive bias of TOC values reported by five of the six laboratories that used the test method. It was however anticipated that improvements in accuracy could be obtained with improved proficiency. The advantage of the approach is that carbonate C is removed before the analysis, reducing potential interference from the inorganic carbon, particularly in materials where organic carbon content is low compared to the inorganic carbon content. This was confirmed by Kerven et al (Kerven et al., 2000) who showed that a suitable acid pretreatment of alkaline soils followed by a drying step successfully eliminated the carbonate carbon prior to combustion.

The measurement of carbon in soils by this high temperature combustion in an oxygen atmosphere has been shown to be a rapid and reliable method capable of producing results in good agreement with established dichromate oxidation procedures. Nieuwenhuize et al. (1994) have also

Table 6.1. Organic carbon contents of various carbon-poor earth materials reported from several non-UK studies

Rock type	Location	f_{OC} (%)	Comments	Reference
Sandy aquifer material	Borden, Ontario, Canada	0.74%	Detailed studies of the sorption of non-ionic pollutants such as PAHs and chlorobenzenes	Ran et al. (2003)
Sandy soils	Superfund site New Jersey, USA	0.019 (i.e. v low)	Measured K_d of 11 VOC and SVOCs (chlorobenzenes etc). K_d not directly related to f_{OC}. Need site-specific measurements.	Carmichael et al. (1999)
Sand aquifer	Perth, Australia	avg 0.09%	Measured mobility of TCE through a column of sand	Benker et al. (1997)
Clay-rich till	Sarnia, Ontario, Canada	0.68% and 1.95%	Measured TCE sorption incl after heat treatment. Highly sorptive, perhaps related to residual kerogens. Just using f_{OC} underpredicts K_d to 2-3 orders of magnitude	Allenking et al. (1995)
Medium to coarse sand aquifer	Cape Cod, Massachusetts, USA	0.005–0.123% (finer grained greater)	Sorption of chlorobenzenes: sediment organic linearly adsorbs, mineral fraction is nonlinear	Barber (1994)
Beach and sand deposits	New Jersey and South Carolina, USA	0.057–0.109%	Column Kd's always much less than predicted from K_{oc}/f_{OC} suggesting some organics inaccessible for sorption	(Holmen and Gschwend, 1997)
Sandy aquifer	Tampa, Florida, USA	0.13%	Measured kinetics of sorption of a wide range of hydrophobic compounds	Brusseau (1991)

shown that this approach allows the determination of 60 samples per day by a single analyst and that extensive testing and application showed long-term precisions for organic carbon of about 3%. The accuracy was found to be excellent, irrespective of the calcium carbonate content of the sample.

Both CO_2 evolution and loss-on-ignition methods estimate total organic C without discrimination between humic material and elementary C, although this is probably not as important in aquifer material as it is in soil measurements. Loss on ignition, whilst very simple to carry out, may provide an overestimate of reactive organic material with samples containing high charcoal content or in certain clay soils where weight loss may be associated with loss of water or hydroxyl groups. In addition, it is necessary to convert the organic matter value obtained from the LOI measurement to an organic carbon content. In a recent study of sediments (Sutherland, 1998), examination of organic matter (OM) to organic carbon (OC) conversion factors for Manoa bed sediments indicated that values typically observed in the soils literature (1.7-2.2 mg/kg) are far too low. Values of OM/OC were found to increase with increasing grain size, and decrease with increasing LOI percentage. Conversion factors obtained for grouped data had a mean of 14.9, a coefficient of variation of 21%, and a range of values between 6.2 and 27.4 mg/kg. It is suggested that these high conversion factors reflect significant water loss by dehydration of Fe, Al, and Mn oxides at a muffle furnace temperature of 450°C. The authors suggested that the blind application of conversion factors developed from soils should be avoided when converting from OM to OC for fluvial bed sediments. This should also be a consideration in aquifer materials, which like sediment materials, have significantly different properties compared to soils.

The third approach to analysis of organic carbon, pioneered by Schollenberger (1927), involves a rapid titrimetric method whereby soil organic matter is oxidised by a saturated solution of potassium dichromate in concentrated sulphuric acid, with application of heat. The unreduced chromic acid is then back-titrated with ferrous ammonium sulphate solution. The method was later modified (e.g. Allison, 1960; Walkley, 1947; Walkley and Black, 1934) by omitting the heating step, using the heat generated on dilution of the sulphuric acid to provide sufficient energy for the reaction to take place. In soils the procedure is only partly efficient in recovering OC, depending on the sample type. Walkley and Black reported a mean recovery of 76% for a range of British and foreign soils, necessitating a multiplication factor of 1.32 to yield a result equivalent to OC by combustion methods. Other authors have suggested a much broader range of correction factors varying with soil group (Allison, 1965; Hefferman, 1985; Jackson, 1958; Kaira and Maynard, 1991; McKeague, 1978; Metson, 1956; Nelson and Sommers, 1962; Schumacher et al., 1995). However, in the absence of a specific recommended value the original Walkley and Black figure of 76% is frequently used. Details of the original Walkley and Black method have subsequently been modified by a number of authors (e.g. Matejovic, 1993; Wang and Anderson, 1998).

Recent trends in OC analysis are moving towards the use of dry combustion with CO_2 infra-red detection (Neal and Younglove, 1993; Wright and Bailey, 2001). In these methods, the combustion temperature and flow of oxygen are optimised to make the combustion specific for OC whilst leaving the IC unreacted. The method has been developed using a two-stage temperature programme to allow both OC and IC to be differentiated and quantified during a single-pass analysis (Chichester and Chaison, 1992). The procedure is potentially extremely cost-effective, offering a greater than 10-fold reduction in time required for sample preparation, analysis, and data acquisition. Results for a variety of soil types, with OC contents ranging from <1 to >4% and IC from <1 to >9%, were found to be correlated highly with results from more established methods (1997). Similarly, Matejovic (International Standards Organisation, 1995b) found the results by this method were in good agreement with those obtained by a laboratory proficiency test at the International Soil-Analytical Exchange, organized by Wageningen Agricultural University.

Although there is such a substantial body of work concerned with measurement of organic carbon, the multiple methods available have meant that there is no unequivocally established preferred method of analysis. Several standard methods have been published. There are ISO standard methods for both a version of the Walkley and Black wet oxidation method (International Standards Organisation, 1995a) and the dry oxidation method with acid pre-treatment (British Standards Institute, 1995a). A British standard method has only been published for the dry oxidation method with acid pre-treatment (Schumacher et al., 1995). The USEPA recommend the use of the Walkley and Black wet oxidation procedure (Cahill and Autrey, 1988; Jackson and Roof, 1992). Even these have to some extent been overtaken by developments in instrumentation.

A recent extensive review of OC measurement in aquifer materials recommended that the most accurate way of determining TOC was by high-temperature oxidation after carbonate removal with acid (Steventon-Barnes, 2000). This is the approach which has been adopted where possible in the acquisition of data for the Geochemical Properties Manual.

There are more reference materials available for OC than for CEC determination although the number and variety of samples is not very comprehensive. The NRCCRM, supplied through the Laboratory of the Government Chemist, lists a number of soils, sediments and rocks with certified or recommended values for OC. In addition, two recent publications have listed the organic carbon contents of 30 and 22 geological reference materials respectively (Nelson, 1982; Rowell, 1997). Of the laboratory proficiency schemes, while the NAPT scheme provides information on performance on total carbon and soil organic matter, the WEPAL scheme provides information only on the carbonate (not carbon) content of soils.

INORGANIC CARBON (CARBONATE) CONTENT

Carbonate carbon can also be determined by a number of methods, often broadly similar to those used for organic carbon. Traditionally, the simplest method involves the dissolution of carbonates in an excess of standard acid followed by back titration of the remaining acid (British Standards Institute, 1995b; International Standards Organisation, 1995b; Shapiro, 1975). Other methods measure the carbon dioxide evolved on acidification volumetrically (Peck, 1964), gravimetrically (Jones and Kaiteris, 1983), by pressure (Amundson et al., 1988; Weliky et al., 1983), thermal conductivity (Chan, 1986; Engleman et al., 1985) or by coulometric titration (Chichester and Chaison, 1992; Neal and Younglove, 1993; Wright and Bailey, 2001). Dry combustion methods with infra-red detection of carbon dioxide (as already discussed in relation to organic carbon analysis) have been developed using a two-stage temperature programme. This method has been used to allow both organic carbon and inorganic carbon to be differentiated and quantified (Krom and Berner, 1983). Finally, the carbonate content can be determined by difference where a total combustion method provides a value for the total carbon content and the organic carbon content is obtained either by ashing at a lower temperature (e.g. Snyder and Trofymow, 1984) or by removal of inorganic carbon by acidification prior to ashing (Engleman et al., 1985).

In general there is good agreement between most methods although some methods have been shown to have a higher precision and accuracy than others (Cahill and Autrey, 1988; Chan, 1986; Engleman et al., 1985; Jackson and Roof, 1992; Krom and Berner, 1983). The 'measurement by difference' methodology may also suffer from precision and accuracy problems when measuring a relatively low quantity of inorganic carbon in the presence of high organic carbon in which the result is calculated as a relatively small difference between two high values.

Published values for carbonate contents of soil and geological reference materials, analysed by various methods, are available from several sources (Lovley and Phillips, 1986b). In addition, the NRCCRM and NIST catalogues list a number of soil, sediment and rock samples with certified or recommended inorganic carbon data. Proficiency schemes also address carbonate content: the WEPAL scheme provides information on the carbonate content of soils and the GeoPT proficiency testing scheme, run by the International Association of Geoanalysts (IAG), include IC as one of the test determinands for rock samples. The NAPT scheme, on the other hand, provides information on total carbon and soil organic matter only.

6.2.2 Preferred method of analysis

There was a change in analytical protocol for analysis of organic and inorganic carbon during the course of the project. During the initial stages, BGS did not have in-house capability for inorganic and organic carbon analysis. Therefore, analysis for fraction of inorganic carbon, f_{IC}, and fraction of organic carbon, f_{OC} was subcontracted out to ALcontrol Geochem. Samples were first prepared at BGS by being dried at 40°C and then milled. At ALcontrol subsamples for f_{OC} determination were pre-treated with 10% HCl, followed by concentrated HCl, to remove any inorganic carbon, then washed in deionised water and dried at 80°C for 12 hours. The f_{OC} was determined on an Eltra Elemental Analyser, in which the sample is combusted at 2000°C and the resulting CO_2 detected by an infra-red detector. A portion of untreated (i.e. unacidified) sample was analysed in the same way to give a measurement of Total Carbon (TC). The f_{OC} value is subtracted from the TC value to give an estimate of f_{IC} present.

New equipment was installed and commissioned at BGS in the middle stages of the project. All subsequent carbon analysis was therefore carried out in-house at BGS. Although different instruments were therefore used, the technique applied in each case is essentially the same. The analytical precision which can be achieved by this method is good, and therefore the results from the two phases can be considered to form a consistent dataset.

For the later data, samples for f_{OC} determination were prepared by pre-drying for one hour at 110°C, followed by acidification with HCl (100-50% v/v) and further drying at 110°C for one hour. The prepared samples were analysed by combustion at 1050°C, using an 'Elementar Vario Max' C/N analyser. Total carbon (TC) was determined using the same method but without acidification. The fraction of inorganic carbon (f_{IC}) was calculated by difference (i.e. TC-f_{OC} = f_{IC}). The quality control samples from an international proficiency test analysed for f_{OC} and TC performed at the same time as the samples, gave excellent agreement for the consensus results (std. dev. = 0.16% bias = –0.55%), which gives good confidence in the BGS f_{OC} method. Procedural blanks were below instrumental response threshold. The LOD was 0.10-0.12% C in 1g of sample.

6.3 SUMMARY AND OVERVIEW OF f_{OC} AND f_{IC} DATA

Available data for measurement of f_{OC} and f_{IC} in rocks are presented in the following table for lithostratigraphical attributions at the Group level. For finer resolution showing data at Formation level please consult the figures in Sections 6.4 and 6.5.

Table 6.2 Overall summary statistical values for f_{OC} data (% organic carbon by weight), tabulated by lithostratigraphical Group.

LEX code	Group name	Min	P25	Median	Mean	P75	Max	n
	Quaternary							
GDU	Glacial Deposits	0.46	0.46	0.46	0.46	0.46	0.46	3
DUNW	Dunwich Group	0.03	0.03	0.03	0.03	0.03	0.03	1
CRAG	Crag Group	0.05	0.145	0.24	0.24	0.335	0.43	2
	Palaeogene							
BA	Barton Group	0.05	0.05	0.05	0.05	0.05	0.05	1
BRB	Bracklesham Group	0.41	0.45	0.49	0.49	0.53	0.57	2
THAM	Thames Group	0.05	0.225	0.42	0.359	0.53	0.6	11
LMBE	Lambeth Group	0.05	0.108	0.145	0.516	0.3	5.01	14
XG	Other Palaeogene	0.04	0.09	0.21	1.13	0.57	7.56	9
	Cretaceous							
CK	Chalk Group	0.04	0.05	0.06	0.108	0.09	0.96	61
SELB	Selborne Group	0.18	0.24	0.33	0.374	0.51	0.68	9
LGS	Lower Greensand Group	0.05	0.08	0.11	0.311	0.512	1.05	14
W	Wealden Group	0.05	0.19	0.3	0.567	0.69	2.81	17
PB	Purbeck Group	0.39	0.6	0.81	0.81	1.02	1.23	2
XK	Other Cretaceous	0.04	0.11	0.19	0.471	0.39	2.22	13
	Jurassic							
PL	Portland Group	0.05	0.29	0.41	0.45	0.57	0.93	4
AMG	Ancholme Group	0.66	0.83	1.2	3.32	3.17	14.4	13
CR	Corallian Group	0.07	0.21	0.43	0.454	0.48	1.34	9
GOG	Great Oolite Group	0.05	0.112	0.22	0.436	0.488	1.95	30
INO	Inferior Oolite Group	0.05	0.0875	0.14	0.412	0.38	1.6	12
RAG	Ravenscar Group	0.17	0.188	0.205	0.205	0.222	0.24	2
LI	Lias Group	0.05	0.41	0.675	1.02	1.4	3.28	22
XJ	Other Jurassic	0.11	0.11	0.11	0.11	0.11	0.11	1
	Triassic							
PNG	Penarth Group	0.51	0.585	0.66	0.66	0.735	0.81	2
MMG	Mercia Mudstone Group	0.01	0.05	0.05	0.0903	0.07	0.58	33
SSG	Sherwood Sandstone Group	0.01	0.02	0.05	0.0877	0.07	0.89	33
	Permian							
ZG	Zechstein Group	0.01	0.01	0.03	0.109	0.06	0.64	8
APY	Appleby Group	0.09	0.09	0.09	0.09	0.09	0.09	33
EXE	Exeter Group	0.02	0.035	0.05	0.05	0.065	0.08	2
WAWK	Warwickshire Group	0.05	0.06	0.07	0.07	0.08	0.09	2
XP	Other Permian	0.04	0.05	0.09	0.0825	0.09	0.17	12

LEX code	Group name	Min	P25	Median	Mean	P75	Max	n
	Carboniferous							
PCM	Pennine Coal Measures Group	0.05	0.12	0.425	6.51	1.38	60.8	24
CMSC	Scottish Coal Measures Group	0.09	0.15	0.21	0.21	0.27	0.33	2
HOWY	Holsworthy Group	0.21	0.375	0.54	0.54	0.705	0.87	2
CKN	Clackmannan Group	0.05	0.165	0.63	1.17	0.955	7.31	11
MG	Millstone Grit Group	0.05	0.15	0.545	1.03	1.43	4.57	16
YORE	Yoredale Group	0.08	0.205	0.33	0.33	0.455	0.58	2
CRAV	Craven Group	0.13	0.325	0.65	0.852	1.14	2.69	11
GSCL	Great Scar Limestone Group	0.04	0.045	0.05	0.05	0.055	0.06	2
SYG	Strathclyde Group	0.065	0.09	0.235	0.77	0.692	4.18	14
PKLM	Peak Limestone Group	0.01	0.05	0.07	0.078	0.08	0.18	5
BOHI	Bowland High Group	0.05	0.05	0.305	0.511	0.918	1.46	8
INV	Inverclyde Group	0.09	0.09	0.09	0.137	0.16	0.23	3
TRG	Transition Group (Devonian-Carboniferous)	0.02	0.02	0.02	0.02	0.02	0.02	1
XCL	Other Carb. Limestone Supergroup	0.01	0.053	0.075	0.25	0.428	0.75	6
XC	Other Carboniferous	0.02	0.315	0.61	0.61	0.905	1.2	2
XCU	Other Culm Supergroup	0.29	0.29	0.29	0.29	0.29	0.29	1
	Devonian							
EXM	Exmoor Group	0.07	0.07	0.07	0.07	0.07	0.07	1
SAG	Stratheden Group	0.05	0.05	0.05	0.05	0.05	0.05	1
FIL	Fair Isle Group	0.09	0.09	0.09	0.09	0.09	0.09	2
INS	Inverness Sandstone Group	0.05	0.06	0.07	0.07	0.08	0.09	2
MDT	Meadfoot Group	0.03	0.035	0.04	0.04	0.045	0.05	2
LORS	Lower Old Red Sandstone	0.05	0.05	0.05	0.05	0.05	0.05	9
DOW	Downton Group	0.03	0.03	0.03	0.03	0.03	0.03	1
ATGK	Arbuthnott-Garvock Group	0.09	0.09	0.09	0.117	0.13	0.17	3
XD	Other Devonian	0.03	0.04	0.29	0.192	0.29	0.31	5
EXM	Exmoor Group	0.07	0.07	0.07	0.07	0.07	0.07	1
	Pre-Devonian							
LLUS	Lower Ludlow Shales Group	0.05	0.06	0.07	0.07	0.08	0.09	2
AGF	Aberystwyth Grits Group	0.12	0.145	0.17	0.173	0.2	0.23	3
XS	Other Silurian	0.04	0.102	0.145	0.208	0.198	0.93	12
BUVO	Builth Volcanic Group	0.02	0.02	0.02	0.02	0.02	0.02	2
MWG	Mawddach Group	0.05	0.05	0.05	0.05	0.05	0.05	2
XO	Other Ordovician	0.05	0.05	0.45	0.658	0.78	1.96	5
XA	Other Pre-Cambrian	0.04	0.04	0.04	0.04	0.04	0.04	1
NMG	Mona Gneiss Suite	0.05	0.05	0.05	0.05	0.05	0.05	1
YST	Stretton Group	0.05	0.05	0.05	0.05	0.05	0.05	1
ARGY	Argyll Group	0.09	0.09	0.09	0.09	0.09	0.09	1
LEIL	Loch Eil Group	0.09	0.09	0.09	0.09	0.09	0.09	2

Table 6.3 Overall summary statistical values for f_{IC} data (as % inorganic carbon by weight), tabulated by lithostratigraphical Group.

LEX code	Group name	Min	P25	Median	Mean	P75	Max	n
	Quaternary							
GDU	Glacial Deposits	0.23	0.81	1.39	1.09	1.52	1.65	3
DUNW	Dunwich Group	0.05	0.05	0.05	0.05	0.05	0.05	1
CRAG	Crag Group	0.005	0.005	0.005	0.005	0.005	0.005	2
	Palaeogene							
BA	Barton Group	0.05	0.05	0.05	0.05	0.05	0.05	1
BRB	Bracklesham Group	0.03	0.0475	0.065	0.065	0.0825	0.1	2
THAM	Thames Group	0.005	0.005	0.05	0.0964	0.05	0.68	11
LMBE	Lambeth Group	0.005	0.005	0.0275	0.134	0.05	1.45	14
XG	Other Palaeogene	0.005	0.005	0.05	0.357	0.38	1.25	9
	Cretaceous							
CK	Chalk Group	0.05	10	11.5	10.2	11.8	12	61
SELB	Selborne Group	0.12	0.83	2.59	2.79	3.99	6.44	9
LGS	Lower Greensand Group	0.005	0.005	0.005	0.258	0.151	2.05	14
W	Wealden Group	0.005	0.05	0.05	0.371	0.05	3.77	17
PB	Purbeck Group	4.35	5.17	6	6	6.82	7.64	2
XK	Other Cretaceous	0.05	0.12	0.68	1.44	1.04	6.52	13
	Jurassic							
PL	Portland Group	2.65	4.32	8.04	7.56	11.3	11.5	4
AMG	Ancholme Group	0.005	0.23	1.26	1.95	3.05	8.12	13
CR	Corallian Group	0.005	1.93	8.88	5.95	9.49	10.7	9
GOG	Great Oolite Group	0.005	0.108	1.88	3.4	6.41	11.6	30
INO	Inferior Oolite Group	0.005	0.868	8.88	6.66	11.2	12	12
RAG	Ravenscar Group	0.05	0.05	0.05	0.05	0.05	0.05	2
LI	Lias Group	0.005	0.0138	0.59	2.37	3.65	9.87	22
XJ	Other Jurassic	2.67	2.67	2.67	2.67	2.67	2.67	1
	Triassic							
PNG	Penarth Group	0.005	0.005	0.005	0.005	0.005	0.005	2
MMG	Mercia Mudstone Group	0.005	0.33	0.9	2.25	2.5	10.8	33
SSG	Sherwood Sandstone Group	0.005	0.05	0.09	0.767	0.63	11.3	33
	Permian							
ZG	Zechstein Group	0.13	0.528	2.19	3.46	4.79	11.9	8
APY	Appleby Group	0.045	0.045	0.045	0.045	0.045	0.045	33
EXE	Exeter Group	0.2	0.202	0.205	0.205	0.208	0.21	2
WAWK	Warwickshire Group	0.67	0.99	1.31	1.31	1.63	1.95	2
XP	Other Permian	0.05	0.05	0.09	0.25	0.472	0.68	12

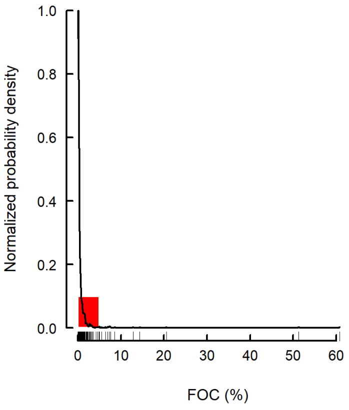
LEX code	Group name	Min	P25	Median	Mean	P75	Max	n
	Carboniferous							
PCM	Pennine Coal Measures Group	0.005	0.005	0.335	1.24	1.5	6.65	24
CMSC	Scottish Coal Measures Group	0.09	0.138	0.185	0.185	0.232	0.28	2
HOWY	Holsworthy Group	0.05	0.05	0.05	0.05	0.05	0.05	2
CKN	Clackmannan Group	0.09	0.09	0.09	0.696	0.395	3.98	11
MG	Millstone Grit Group	0.005	0.005	0.05	0.367	0.725	1.39	16
YORE	Yoredale Group	0.08	0.268	0.455	0.455	0.642	0.83	2
CRAV	Craven Group	0.3	1.28	9.14	6.75	10.7	11.4	11
GSCL	Great Scar Limestone Group	4.48	5.84	7.19	7.19	8.54	9.9	2
SYG	Strathclyde Group	0.09	0.09	0.295	0.872	1.01	4.22	14
PKLM	Peak Limestone Group	8.21	10.1	10.8	10.6	11.8	11.9	5
BOHI	Bowland High Group	5.44	5.89	10.8	9.22	11.6	11.8	8
INV	Inverclyde Group	2.84	3.1	3.36	4.23	4.92	6.48	3
TRG	Transition Group (Devonian-Carboniferous)	2.94	2.94	2.94	2.94	2.94	2.94	1
XCL	Other Carb. Limestone Supergroup	0.005	0.352	1.56	4.29	7.95	12.6	6
XC	Other Carboniferous	0.005	0.0812	0.158	0.158	0.234	0.31	2
XCU	Other Culm Supergroup	1.25	1.25	1.25	1.25	1.25	1.25	1
	Devonian							
EXM	Exmoor Group	0.05	0.05	0.05	0.05	0.05	0.05	1
SAG	Stratheden Group	0.09	0.09	0.09	0.09	0.09	0.09	1
FIL	Fair Isle Group	1.84	1.9	1.96	1.96	2.02	2.08	2
INS	Inverness Sandstone Group	0.09	0.09	0.09	0.09	0.09	0.09	2
MDT	Meadfoot Group	0.005	0.005	0.005	0.005	0.005	0.005	2
LORS	Lower Old Red Sandstone	0.05	0.05	1.65	1.31	2.14	3.05	9
DOW	Downton Group	1.31	1.31	1.31	1.31	1.31	1.31	1
ATGK	Arbuthnott-Garvock Group	0.09	0.09	0.09	0.09	0.09	0.09	3
XD	Other Devonian	0.77	1.64	2.13	3.73	4.46	9.65	5
EXM	Exmoor Group	0.05	0.05	0.05	0.05	0.05	0.05	1
	Pre-Devonian							
LLUS	Lower Ludlow Shales Group	1.26	1.6	1.93	1.93	2.26	2.6	2
AGF	Aberystwyth Grits Group	0.05	0.05	0.05	0.05	0.05	0.05	3
XS	Other Silurian	0.005	0.05	0.245	2.31	4.14	10.3	12
BUVO	Builth Volcanic Group	0.005	0.005	0.005	0.005	0.005	0.005	2
MWG	Mawddach Group	0.05	0.262	0.475	0.475	0.688	0.9	2
XO	Other Ordovician	0.05	0.05	0.42	1.2	1.43	4.03	5
XA	Other Pre-Cambrian	0.05	0.05	0.05	0.05	0.05	0.05	1
NMG	Mona Gneiss Suite	1.92	1.92	1.92	1.92	1.92	1.92	1
YST	Stretton Group	0.05	0.05	0.05	0.05	0.05	0.05	1
ARGY	Argyll Group	0.62	0.62	0.62	0.62	0.62	0.62	1
LEIL	Loch Eil Group	0.09	0.09	0.09	0.09	0.09	0.09	2

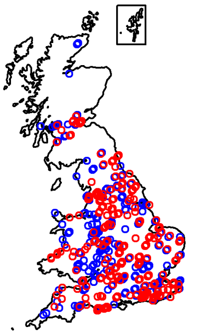
6.4 GEOLOGICAL ATLAS OF DATA FOR f_{OC}

All Groups (All)

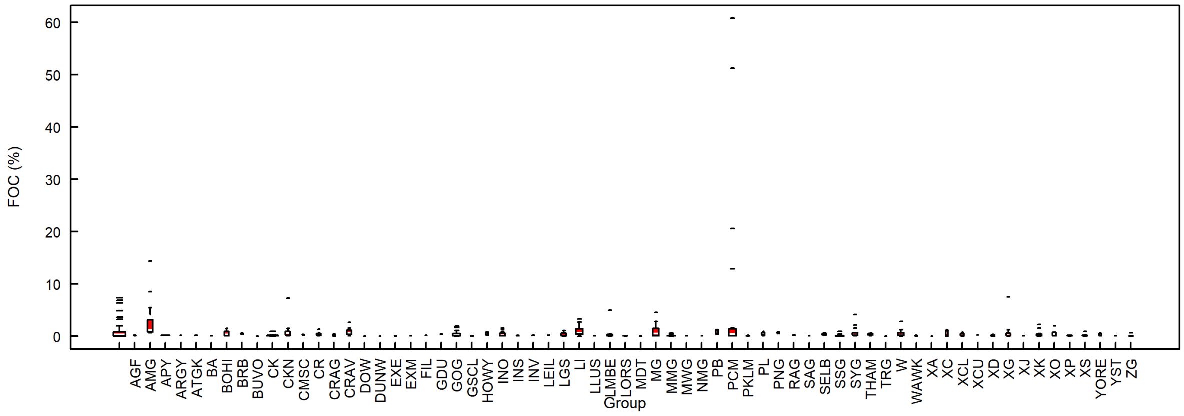
Carbon - fraction of organic (fOC)

FOC (%)





Blue points are below the median
Red points are at or above the median



6.4.1 Quaternary and Neogene

Glacial Deposits (GDU)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.46
Median = 0.46
Mean = 0.46
Max = 0.46
Std dev = 0
n = 3

U Undifferentiated (3)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Dunwich Group (DUNW)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.03
Median = 0.03
Mean = 0.03
Max = 0.03
Std dev = NA
n = 1

KGCA Kesgrave Catchment Subgroup (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

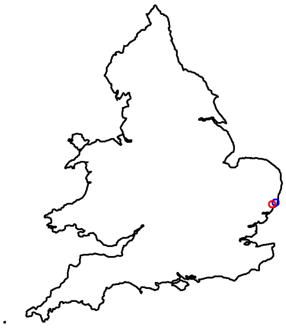
Crag Group (CRAG)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.05
Median = 0.24
Mean = 0.24
Max = 0.43
Std dev = 0.269
n = 2

NCG Norwich Crag Formation (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Palaeogene

Barton Group (BA)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.05
Median = 0.05
Mean = 0.05
Max = 0.05
Std dev = NA
n = 1

BECH Becton Sand and Chama Sand Fms (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

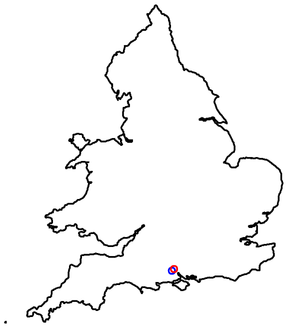
Bracklesham Group (BRB)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.41
Median = 0.49
Mean = 0.49
Max = 0.57
Std dev = 0.113
n = 2

WTT Wittering Formation (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

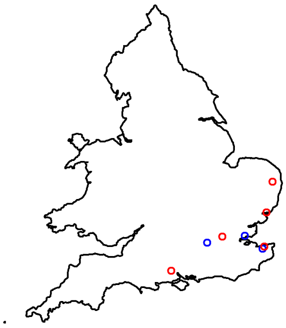
Thames Group (THAM)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.05
Median = 0.42
Mean = 0.359
Max = 0.6
Std dev = 0.203
n = 11

HWH Harwich Formation (2)
LC London Clay Formation (9)



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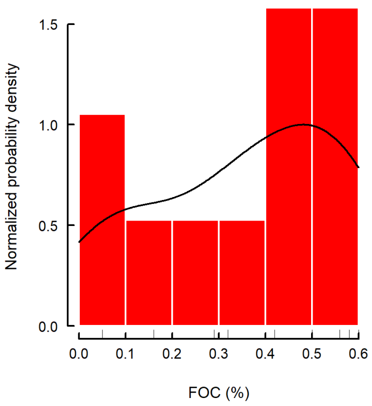
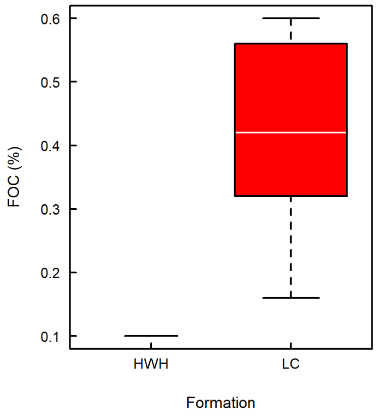




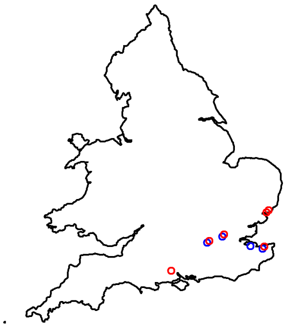
Lambeth Group (LMBE)

Carbon - fraction of organic (fOC)

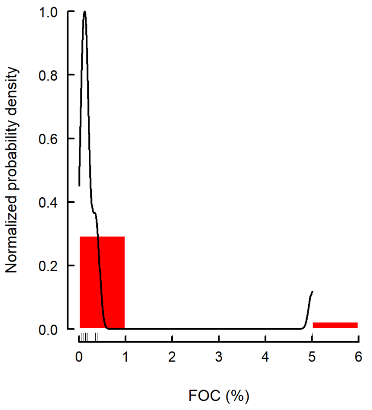
FOC (%)

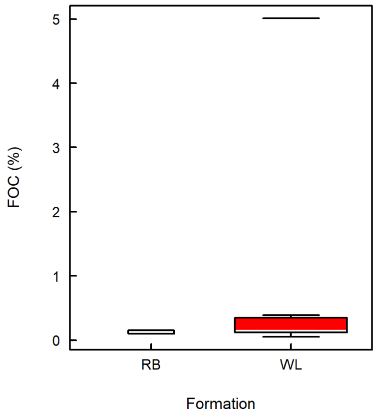
Min = 0.05
Median = 0.145
Mean = 0.516
Max = 5.01
Std dev = 1.3
n = 14

RB Reading Formation (2)
WL Woolwich Formation (12)



Blue points are below the median
Red points are at or above the median





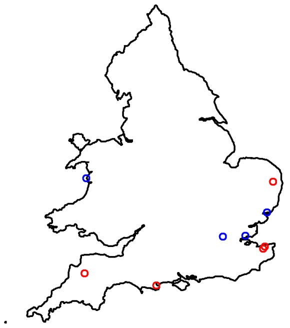
Other Palaeogene (XG)

Carbon - fraction of organic (fOC)

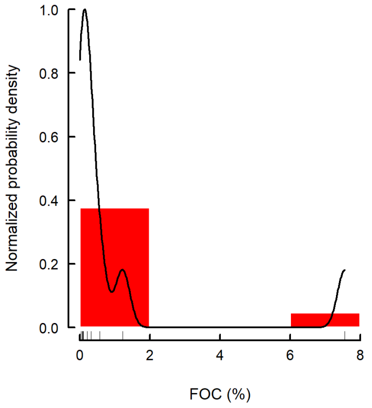
FOC (%)

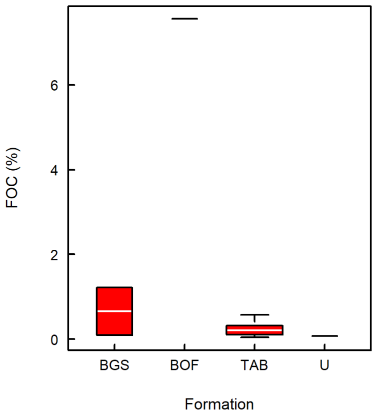
Min = 0.04
Median = 0.21
Mean = 1.13
Max = 7.56
Std dev = 2.44
n = 9

BGS	Bagshot Formation (2)
BOF	Bovey Formation (1)
TAB	Thanet Formation (5)
U	Undifferentiated (1)



Blue points are below the median
Red points are at or above the median





6.4.2 Cretaceous

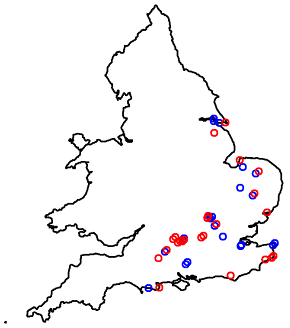
Chalk Group (CK)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.04
Median = 0.06
Mean = 0.108
Max = 0.96
Std dev = 0.131
n = 61

BCK	Burnham Chalk Formation (2)
CUCK	Culver Chalk Formation (1)
FCK	Flamborough Chalk Formation (2)
FYCK	Ferriby Chalk Formation (3)
HCK	Holywell Nodular Chalk Formation (6)
LECH	Lewes Nodular Chalk Formation (5)
NCK	Newhaven Chalk Formation (6)
NPCH	New Pit Chalk Formation (6)
SECK	Seaford Chalk Formation (17)
U	Undifferentiated (1)
WMCH	West Melbury Marly Chalk Formation (4)
ZZCH	Zig Zag Chalk Formation (8)



Blue points are below the median
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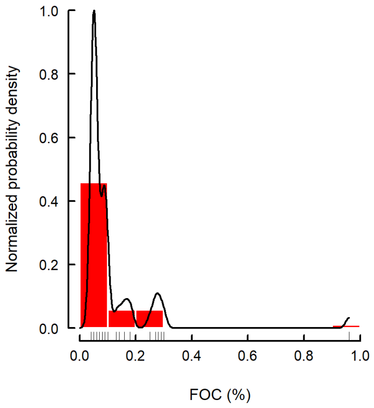
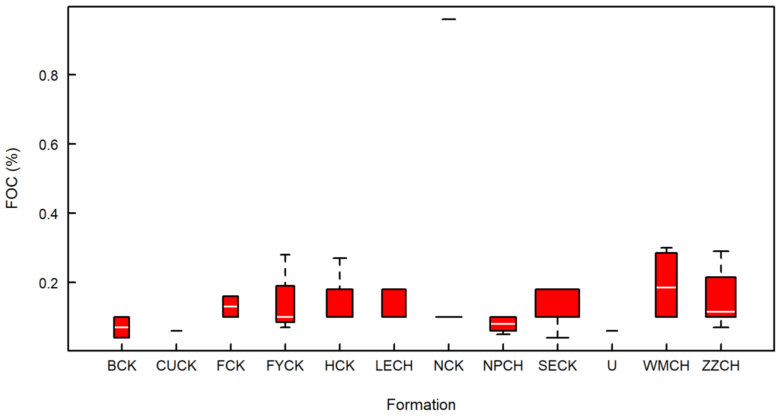




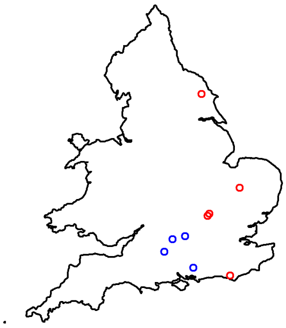
Selborne Group (SELB)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.18
Median = 0.33
Mean = 0.374
Max = 0.68
Std dev = 0.17
n = 9

GLT	Gault Formation (4)
UGS	Upper Greensand Formation (5)



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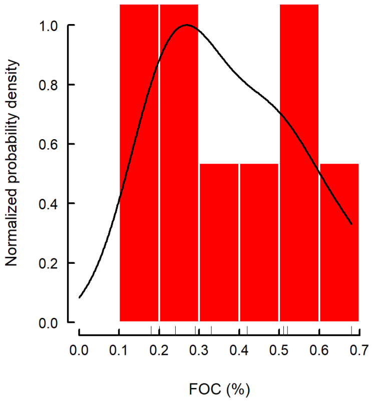
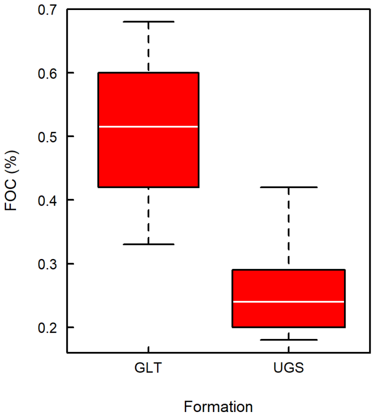




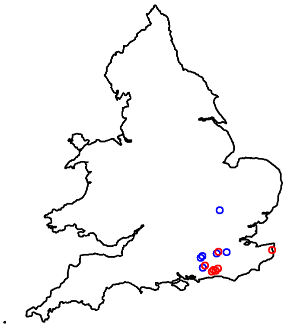
Lower Greensand Group (LGS)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.05
Median = 0.11
Mean = 0.311
Max = 1.05
Std dev = 0.33
n = 14

FO	Folkestone Formation (5)
HY	Hythe Formation (4)
SAB	Sandgate Formation (4)
U	Undifferentiated (1)



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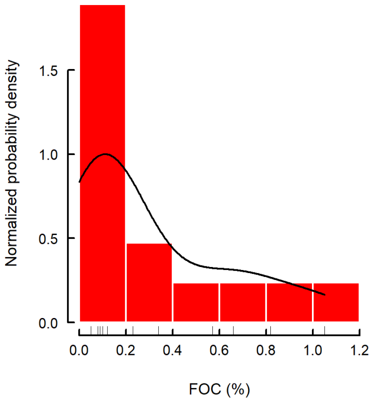
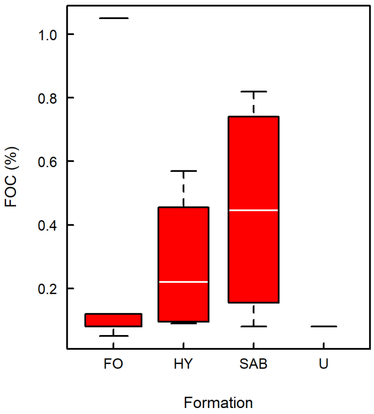




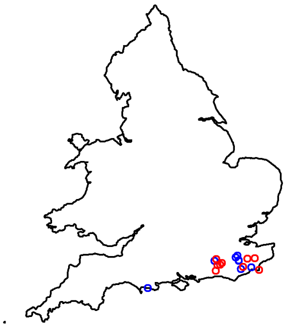
Wealden Group (W)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.05
Median = 0.3
Mean = 0.567
Max = 2.81
Std dev = 0.676
n = 17

ASD	Ashdown Formation (4)
HAS	Hastings Beds (Subgroup) (1)
TWS	Tunbridge Wells Sand Formation (4)
U	Undifferentiated (1)
WC	Weald Clay Formation (7)



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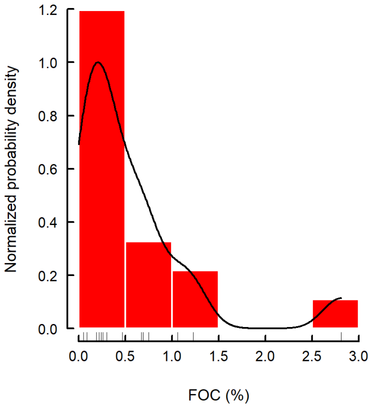
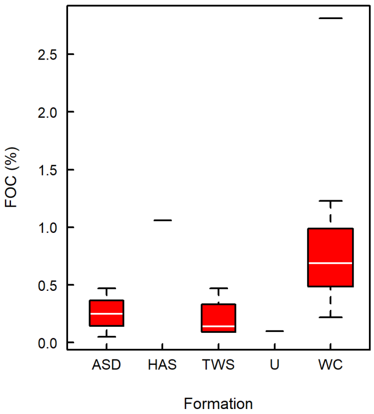




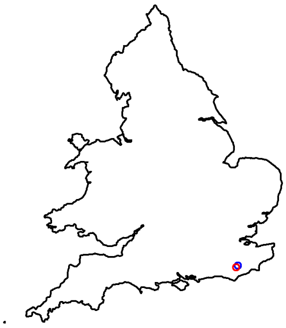
Purbeck Group (PB)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.39
Median = 0.81
Mean = 0.81
Max = 1.23
Std dev = 0.594
n = 2

DURN	Durlston Formation (1)
LULW	Lulworth Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

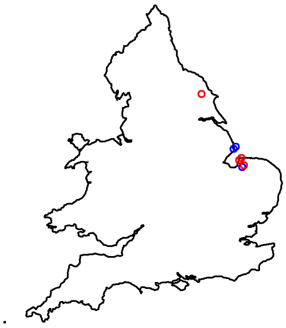
Other Cretaceous (XK)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.04
Median = 0.19
Mean = 0.471
Max = 2.22
Std dev = 0.667
n = 13

CA	Carstone Formation (2)
DEB	Dersingham Formation (2)
HUCK	Hunstanton Formation (3)
ROH	Roach Formation (2)
SAS	Sandringham Sand Formation (3)
SPC	Speeton Clay Formation (1)



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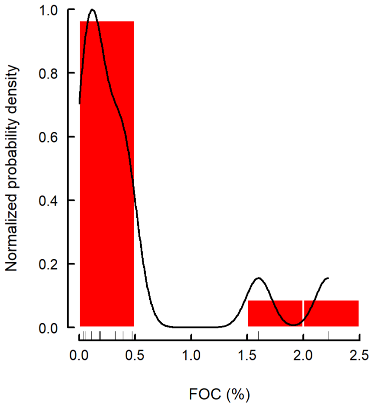
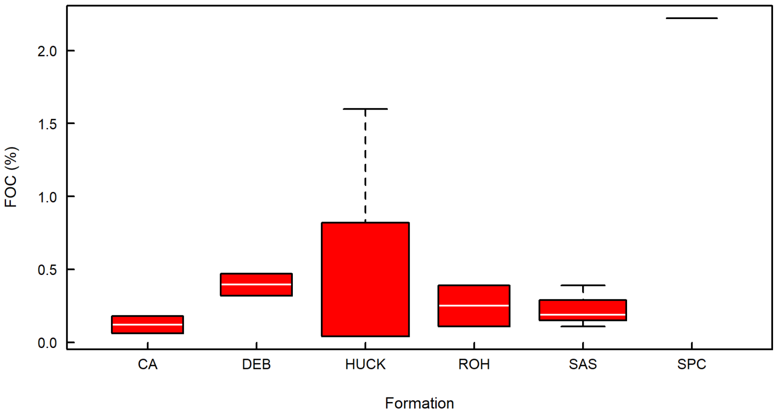




6.4.3 Jurassic

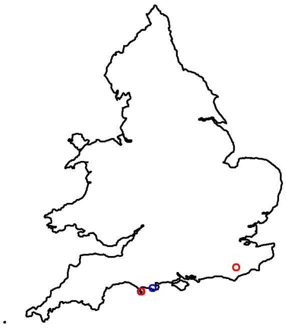
Portland Group (PL)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.05
Median = 0.41
Mean = 0.45
Max = 0.93
Std dev = 0.364
n = 4

POST	Portland Stone Formation (3)
U	Undifferentiated (1)



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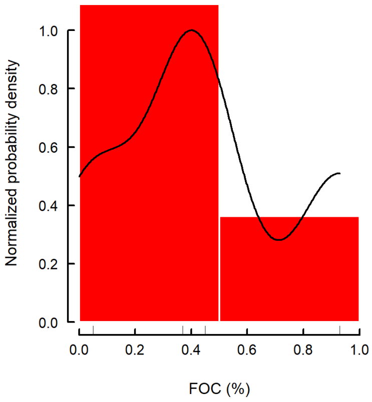
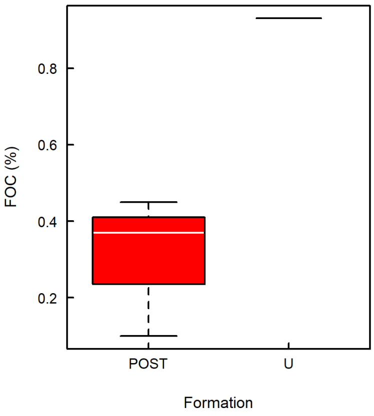




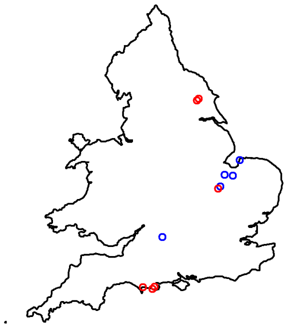
Ancholme Group (AMG)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.66
Median = 1.2
Mean = 3.32
Max = 14.4
Std dev = 4.05
n = 13

AMC	Ampthill Clay Formation (2)
KC	Kimmeridge Clay Formation (5)
KLB	Kellaways Formation (2)
OXC	Oxford Clay Formation (4)



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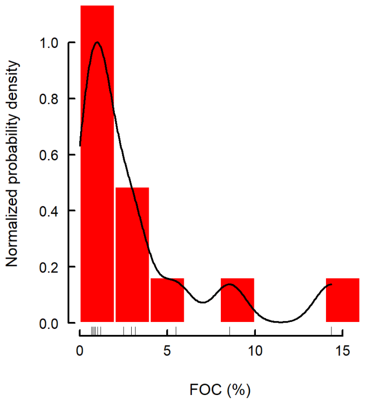
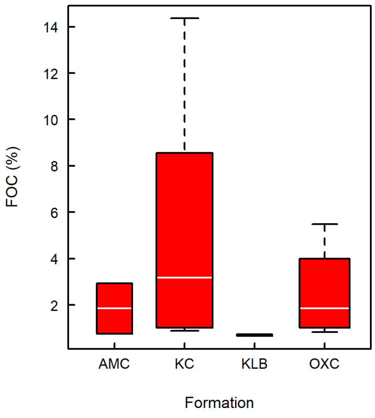




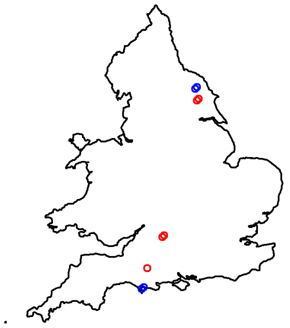
Corallian Group (CR)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.07
Median = 0.43
Mean = 0.454
Max = 1.34
Std dev = 0.373
n = 9

CLAV	Clavellata Formation (1)
OSS	Osmington Oolite Formation (1)
RECF	Redcliff Formation (1)
STOU	Stour Formation (1)
U	Undifferentiated (5)



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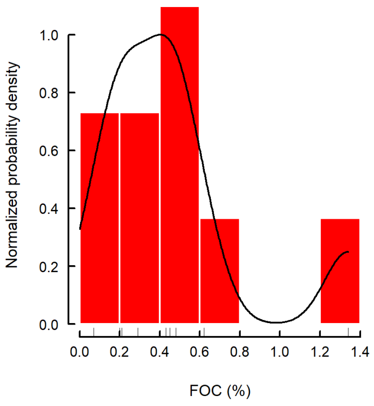
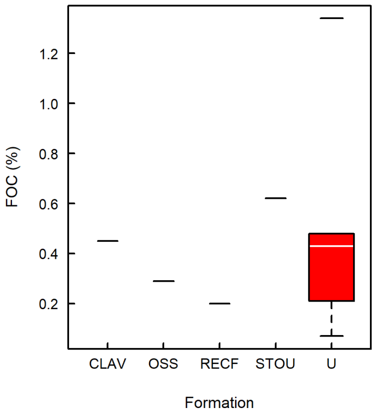




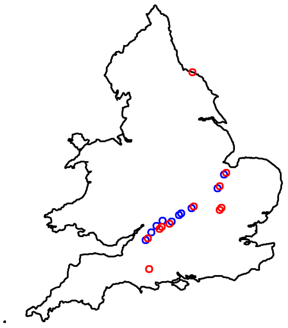
Great Oolite Group (GOG)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.05
Median = 0.22
Mean = 0.436
Max = 1.95
Std dev = 0.491
n = 30

BWL	Blisworth Limestone Formation (2)
CB	Cornbrash Formation (3)
FE	Fuller'S Earth Formation (7)
FMB	Forest Marble Formation (2)
HMB	Hampen Formation (2)
RLD	Rutland Formation (5)
SHHB	Sharp'S Hill Formation (1)
TY	Taynton Limestone Formation (3)
U	Undifferentiated (2)
WHL	White Limestone Formation (3)



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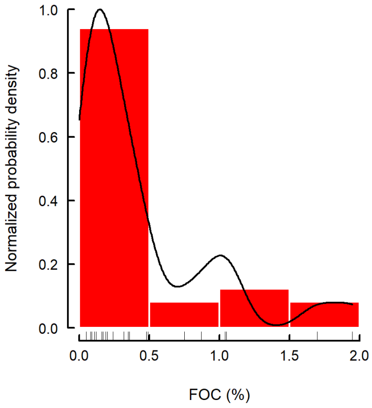
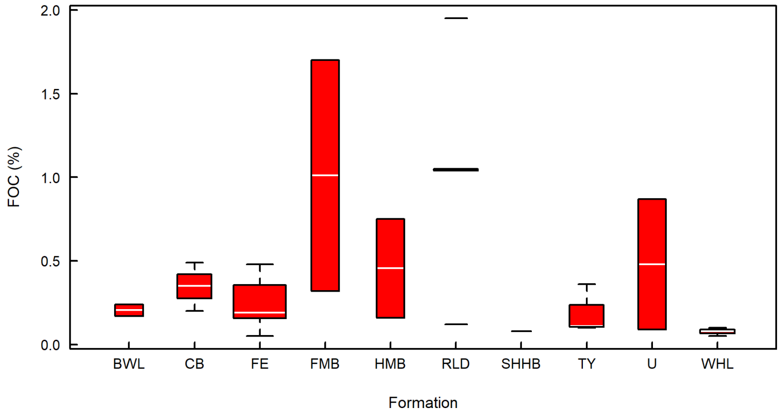




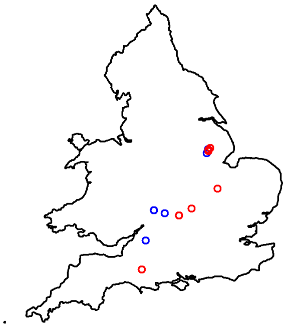
Inferior Oolite Group (INO)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.05
Median = 0.14
Mean = 0.413
Max = 1.6
Std dev = 0.555
n = 12

BLPL	Birdlip Limestone Formation (2)
GRF	Grantham Formation (2)
LL	Lincolnshire Limestone Formation (5)
NS	Northampton Sand Formation (1)
U	Undifferentiated (2)



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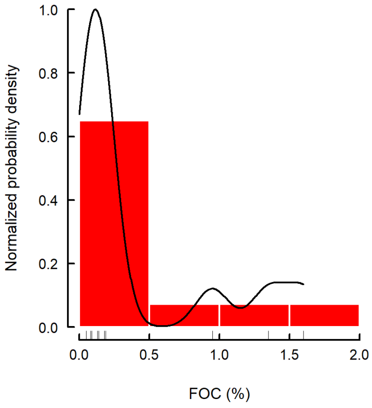
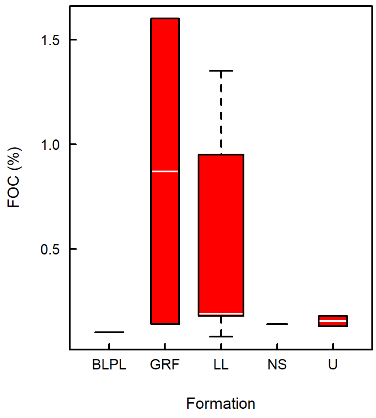




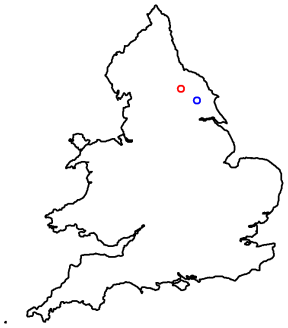
Ravenscar Group (RAG)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.17
Median = 0.205
Mean = 0.205
Max = 0.24
Std dev = 0.049
n = 2

SCY	Scalby Formation (1)
U	Undifferentiated (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

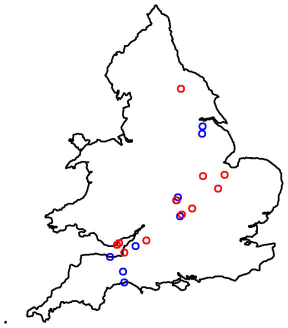
Lias Group (LI)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.05
Median = 0.675
Mean = 1.02
Max = 3.28
Std dev = 0.899
n = 22

BDS	Bridport Sand Formation (1)
BLI	Blue Lias Formation (7)
BNLS	Beacon Limestone Formation (1)
CHAM	Charmouth Mudstone Formation (3)
DYS	Dyrham Formation (1)
U	Undifferentiated (5)
WHM	Whitby Mudstone Formation (4)



Blue points are below the median
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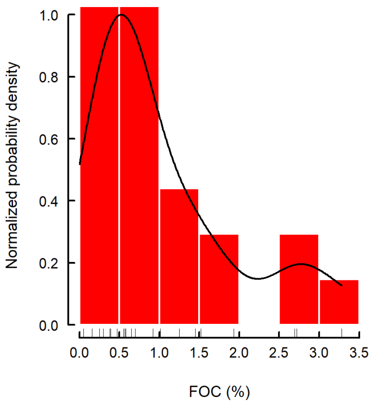
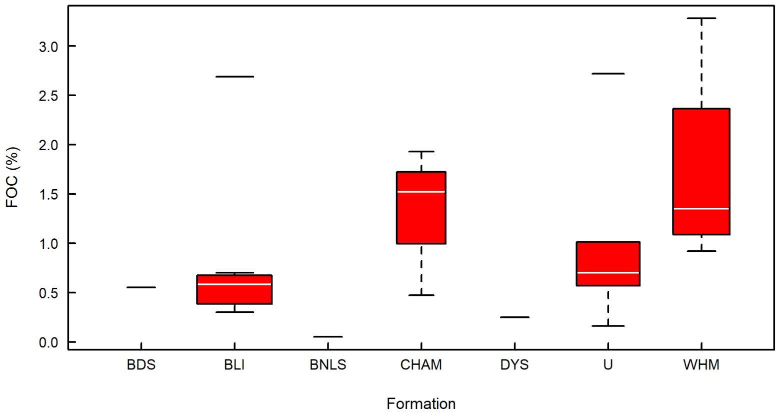




Other Jurassic (XJ)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.11
Median = 0.11
Mean = 0.11
Max = 0.11
Std dev = NA
n = 1

SAS Sandringham Sand Formation (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

6.4.4 Triassic

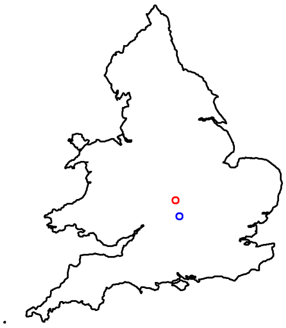
Penarth Group (PNG)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.51
Median = 0.66
Mean = 0.66
Max = 0.81
Std dev = 0.212
n = 2

U Undifferentiated (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

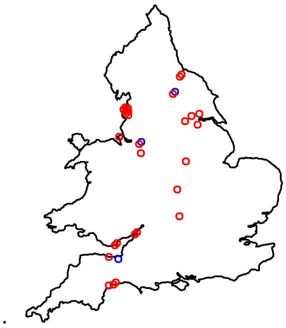
Mercia Mudstone Group (MMG)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.01
Median = 0.05
Mean = 0.0903
Max = 0.58
Std dev = 0.102
n = 33

BAN	Blue Anchor Formation (3)
SIM	Sidmouth Mudstone Formation (7)
TPSF	Tarporley Siltstone Formation (1)
U	Undifferentiated (22)



Blue points are below the median
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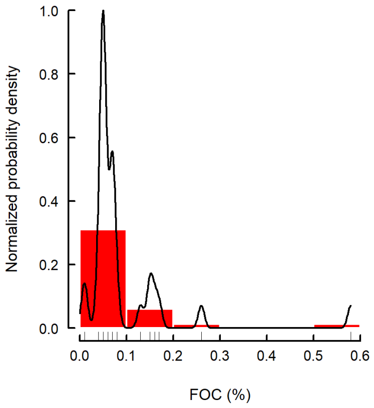
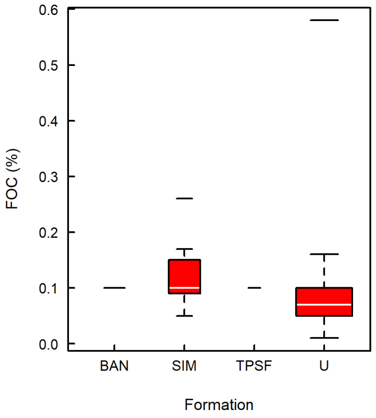




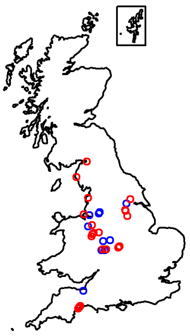
Sherwood Sandstone Group (SSG)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.01
Median = 0.05
Mean = 0.0877
Max = 0.89
Std dev = 0.164
n = 33

BMS	Bromsgrove Sandstone Formation (4)
BSP	Budleigh Salterton Pebble Beds Formation (2
CPB	Chester Pebble Beds Formation (1)
HEY	Helsby Sandstone Formation (3)
KDM	Kidderminster Formation (1)
NTC	Nottingham Castle Sandstone Formation (2)
OS	Otter Sandstone Formation (3)
U	Undifferentiated (11)
WLSF	Wilmslow Sandstone Formation (5)
WRS	Wildmoor Sandstone Formation (1)



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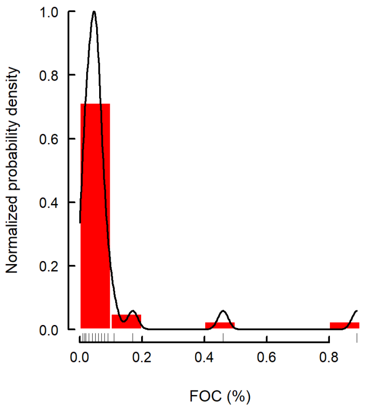
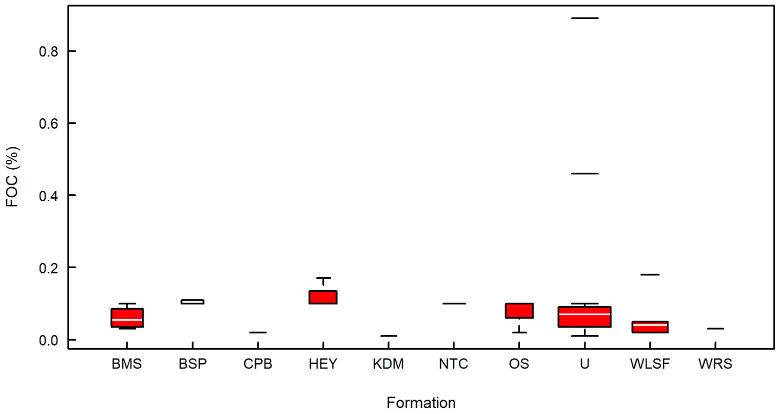




6.4.5 Permian

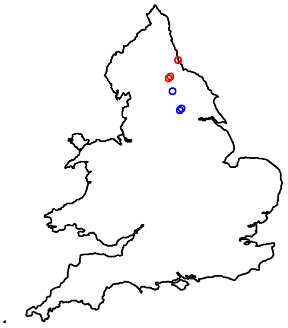
Zechstein Group (ZG)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.01
Median = 0.03
Mean = 0.109
Max = 0.64
Std dev = 0.216
n = 8

BTH	Brotherton Formation (1)
CDF	Cadeby Formation (1)
EDT	Edlington Formation (1)
RML	Raisby Formation (1)
ROX	Roxby Formation (1)
U	Undifferentiated (3)



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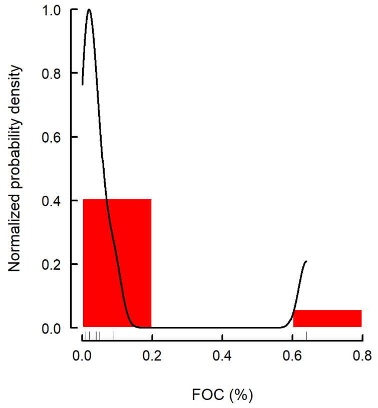
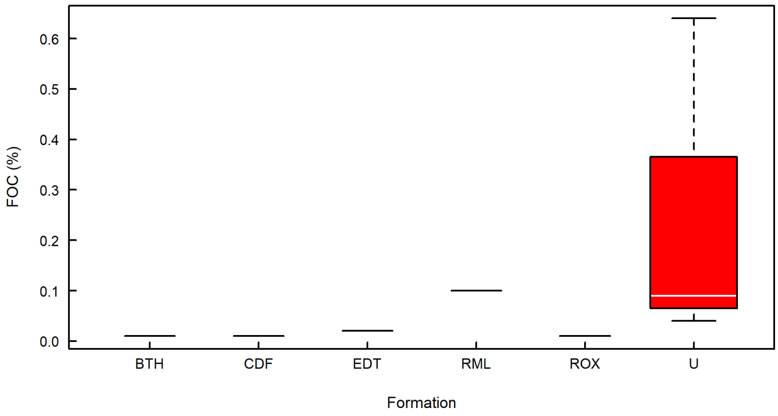




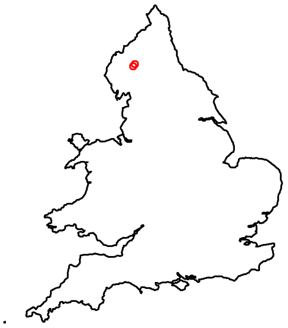
Appleby Group (APY)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.09
Median = 0.09
Mean = 0.09
Max = 0.09
Std dev = 0
n = 33

PS	Penrith Sandstone Formation (33)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

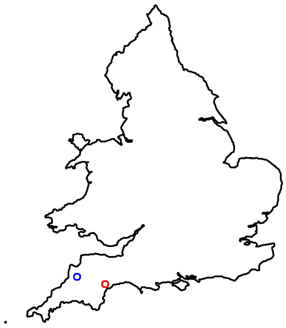
Exeter Group (EXE)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.02
Median = 0.05
Mean = 0.05
Max = 0.08
Std dev = 0.042
n = 2

BOB	Bow Breccia Formation (1)
HVBR	Heavitree Breccia Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

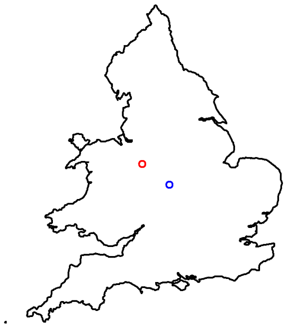
Warwickshire Group (WAWK)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.05
Median = 0.07
Mean = 0.07
Max = 0.09
Std dev = 0.028
n = 2

SAL	Salop Formation (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Other Permian (XP)

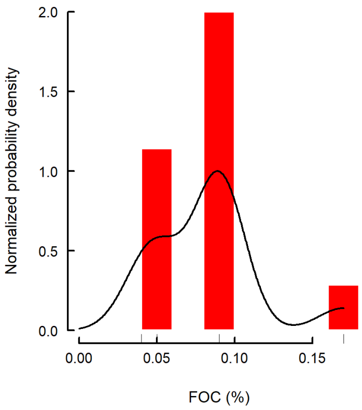
Carbon - fraction of organic (fOC)

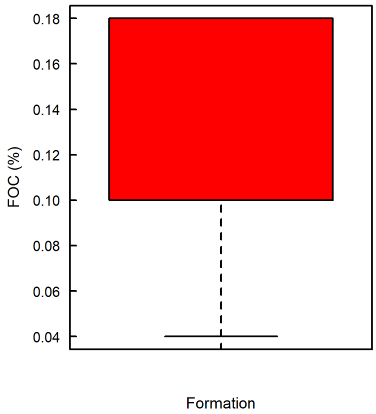
FOC (%)

Min = 0.04
Median = 0.09
Mean = 0.0825
Max = 0.17
Std dev = 0.034
n = 12

BRI Bridgnorth Sandstone Formation (12)

Blue points are below the median
Red points are at or above the median





6.4.6 Carboniferous

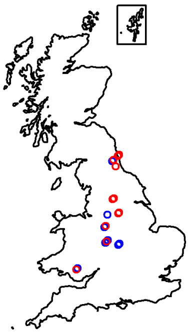
Pennine Coal Measures Group (PCM)

Carbon - fraction of organic (fOC)

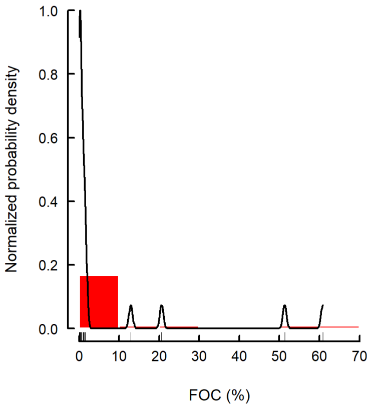
FOC (%)

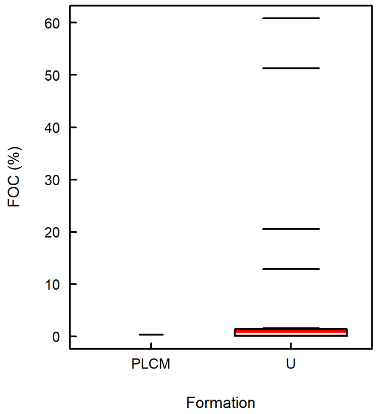
Min = 0.05
Median = 0.425
Mean = 6.51
Max = 60.8
Std dev = 16
n = 24

PLCM Pennine Lower Coal Measures Formation (1)
U Undifferentiated (23)



Blue points are below the median
Red points are at or above the median





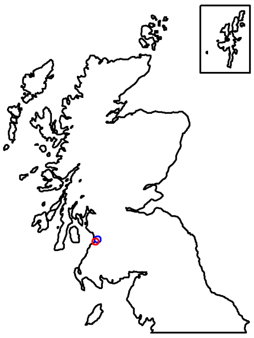
Scottish Coal Measures Group (CMSC)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.09
Median = 0.21
Mean = 0.21
Max = 0.33
Std dev = 0.17
n = 2

MCMS Scottish Middle Coal Measures Formation (2



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Holsworthy Group (HOWY)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.21
Median = 0.54
Mean = 0.54
Max = 0.87
Std dev = 0.467
n = 2

BF Bude Formation (2)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

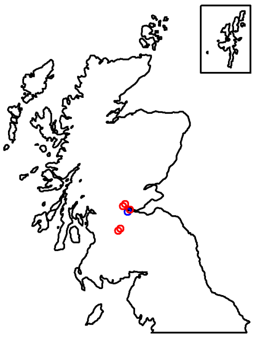
Clackmannan Group (CKN)

Carbon - fraction of organic (fOC)

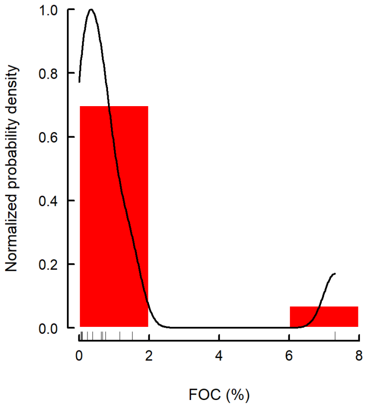
FOC (%)

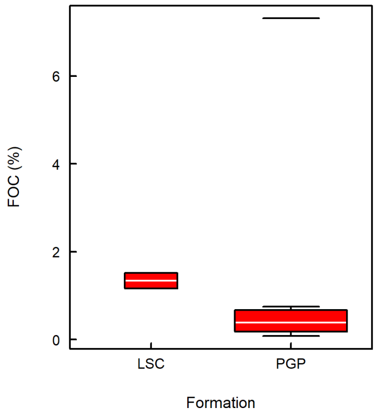
Min = 0.05
Median = 0.63
Mean = 1.17
Max = 7.31
Std dev = 2.09
n = 11

LSC	Limestone Coal Formation (2)
PGP	Passage Formation (9)



Blue points are below the median
Red points are at or above the median





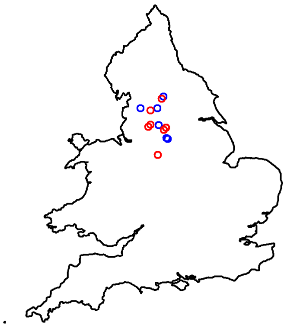
Millstone Grit Group (MG)

Carbon - fraction of organic (fOC)

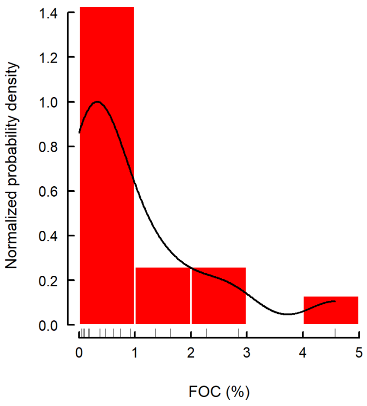
FOC (%)

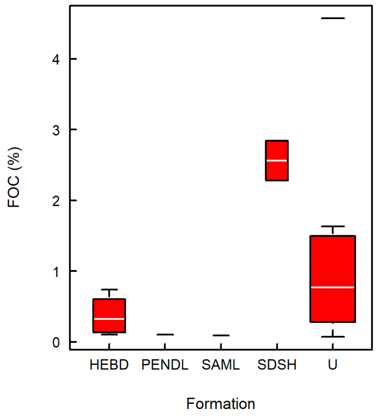
Min = 0.05
Median = 0.545
Mean = 1.03
Max = 4.57
Std dev = 1.27
n = 16

HEBD	Hebden Formation (4)
PENDL	Pendleton Formation (1)
SAML	Samlesbury Formation (1)
SDSH	Sabden Shales (2)
U	Undifferentiated (8)



Blue points are below the median
Red points are at or above the median





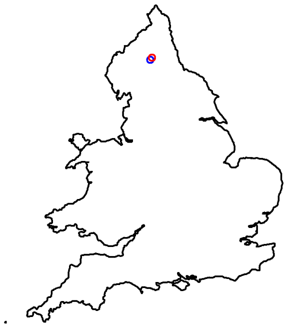
Yoredale Group (YORE)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.08
Median = 0.33
Mean = 0.33
Max = 0.58
Std dev = 0.354
n = 2

SMGP	Stainmore Formation (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

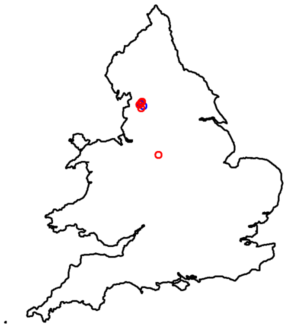
Craven Group (CRAV)

Carbon - fraction of organic (fOC)

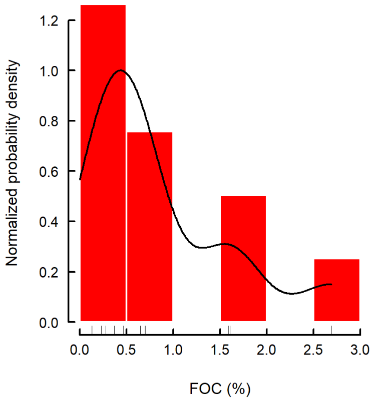
FOC (%)

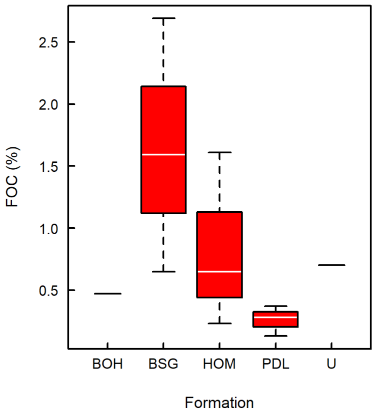
Min = 0.13
Median = 0.65
Mean = 0.852
Max = 2.69
Std dev = 0.788
n = 11

BOH	Hodderense Limestone Formation (1)
BSG	Bowland Shale Formation (3)
HOM	Hodder Mudstone Formation (3)
PDL	Pendleside Limestone Formation (3)
U	Undifferentiated (1)



Blue points are below the median
Red points are at or above the median





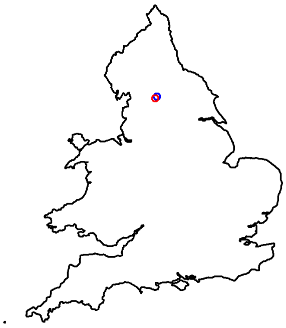
Great Scar Limestone Group (GSCL)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.04
Median = 0.05
Mean = 0.05
Max = 0.06
Std dev = 0.014
n = 2

KLSL	Kilnsey Formation (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

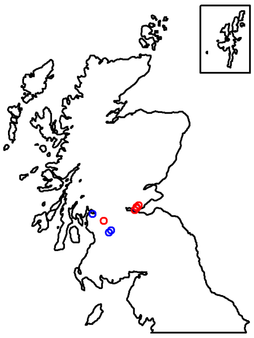
Strathclyde Group (SYG)

Carbon - fraction of organic (fOC)

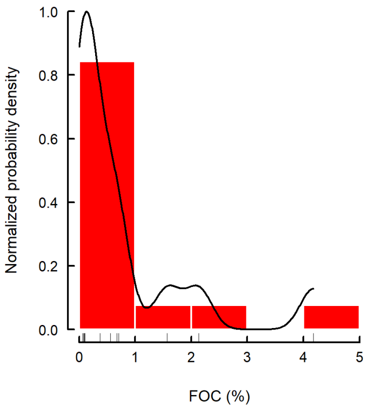
FOC (%)

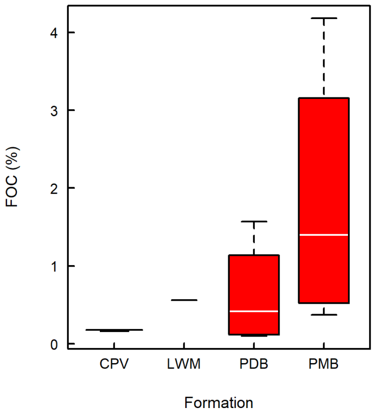
Min = 0.065
Median = 0.235
Mean = 0.77
Max = 4.18
Std dev = 1.16
n = 14

CPV	Clyde Plateau Volcanic Formation (5)
LWM	Lawmuir Formation (1)
PDB	Pathhead Formation (4)
PMB	Pittenweem Formation (4)



Blue points are below the median
Red points are at or above the median





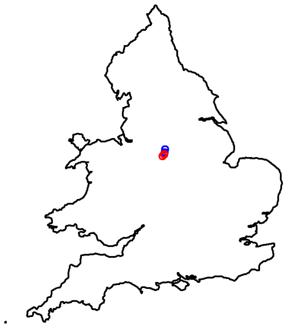
Peak Limestone Group (PKLM)

Carbon - fraction of organic (fOC)

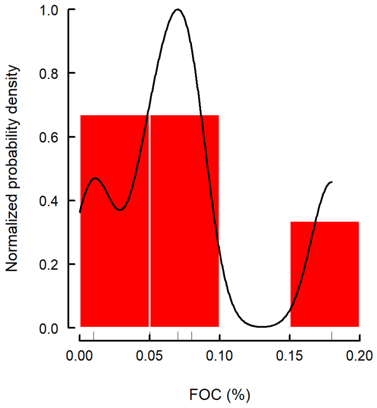
FOC (%)

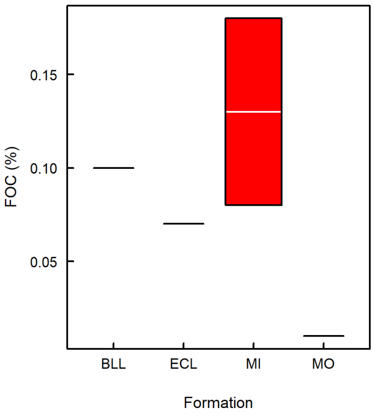
Min = 0.01
Median = 0.07
Mean = 0.078
Max = 0.18
Std dev = 0.063
n = 5

BLL	Bee Low Limestone Formation (1)
ECL	Ecton Limestone Formation (1)
MI	Milldale Limestone Formation (2)
MO	Monsal Dale Limestone Formation (1)



Blue points are below the median
Red points are at or above the median





Bowland High Group (BOHI)

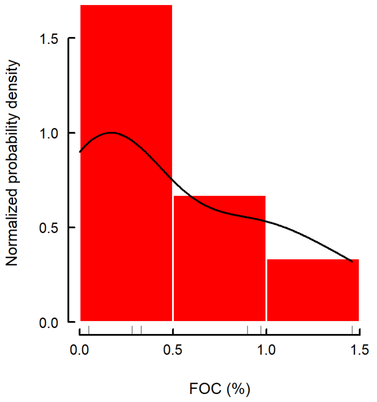
Carbon - fraction of organic (fOC)

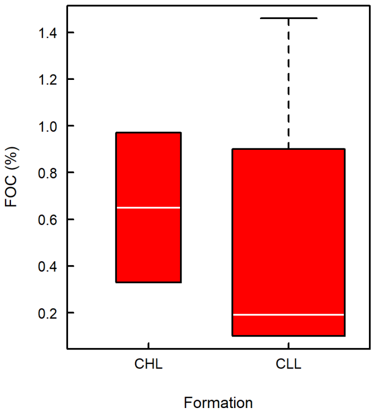
FOC (%)

Min = 0.05
Median = 0.305
Mean = 0.511
Max = 1.46
Std dev = 0.533
n = 8

CHL	Chatburn Limestone Formation (2)
CLL	Clitheroe Limestone Formation (6)

Blue points are below the median
Red points are at or above the median





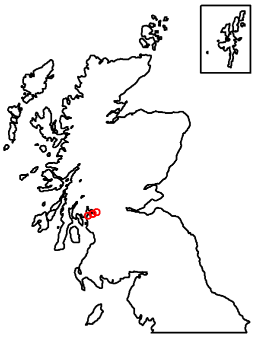
Inverclyde Group (INV)

Carbon - fraction of organic (fOC)

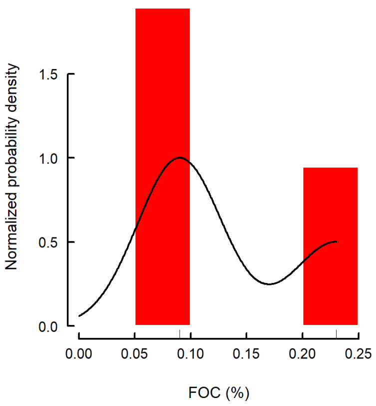
FOC (%)

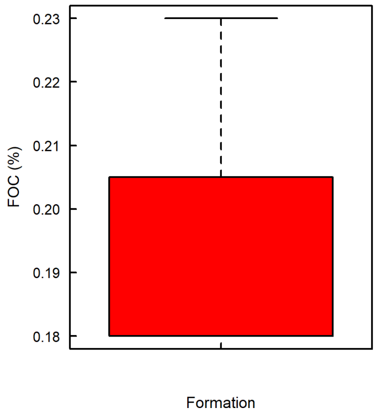
Min = 0.09
Median = 0.09
Mean = 0.137
Max = 0.23
Std dev = 0.081
n = 3

KNW Kinnesswood Formation (3)



Blue points are below the median
Red points are at or above the median





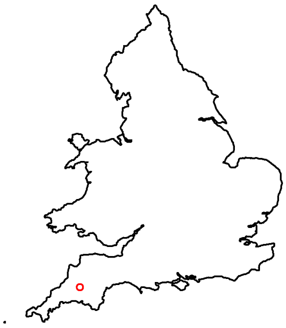
Transition Group (Devonian-Carboniferc

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.02
Median = 0.02
Mean = 0.02
Max = 0.02
Std dev = NA
n = 1

SBT South Brentor Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Other Carb. Limestone Supergroup (XC

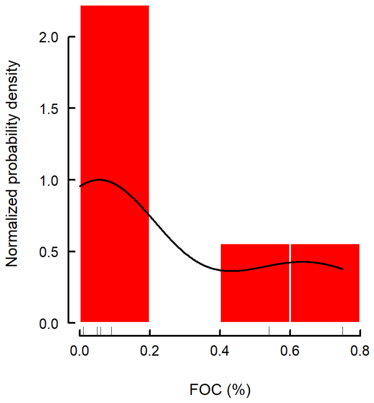
Carbon - fraction of organic (fOC)

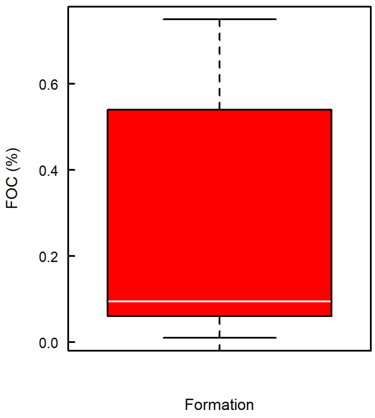
FOC (%)

Min = 0.01
Median = 0.075
Mean = 0.25
Max = 0.75
Std dev = 0.314
n = 6

U Undifferentiated (6)

Blue points are below the median
Red points are at or above the median





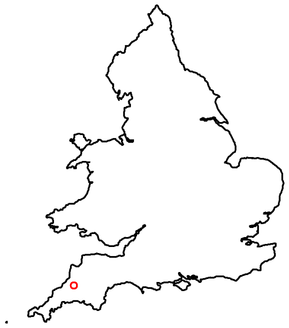
Other Culm Supergroup (XCU)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.29
Median = 0.29
Mean = 0.29
Max = 0.29
Std dev = NA
n = 1

U Undifferentiated (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

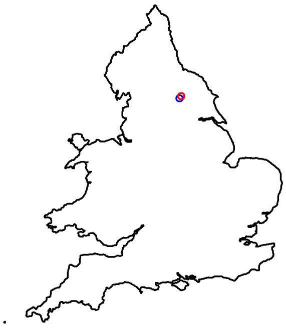
Other Carboniferous (XC)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.02
Median = 0.61
Mean = 0.61
Max = 1.2
Std dev = 0.834
n = 2

U Undifferentiated (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

6.4.7 Devonian

Exmoor Group (EXM)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.07
Median = 0.07
Mean = 0.07
Max = 0.07
Std dev = NA
n = 1

PLT Pilton Mudstone Formation (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Stratheden Group (SAG)

Carbon - fraction of organic (fOC)

FOC (%)

Min	=	0.05
Median	=	0.05
Mean	=	0.05
Max	=	0.05
Std dev	=	NA
n	=	1

SCK Stockiemuir Sandstone Formation (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

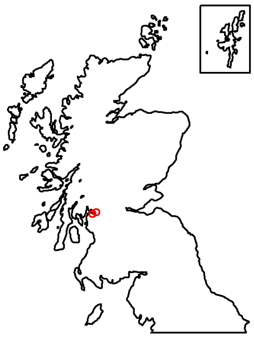
Fair Isle Group (FIL)

Carbon - fraction of organic (fOC)

FOC (%)

Min	=	0.09
Median	=	0.09
Mean	=	0.09
Max	=	0.09
Std dev	=	0
n	=	2

BNG Bu Ness Sandstone Formation (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

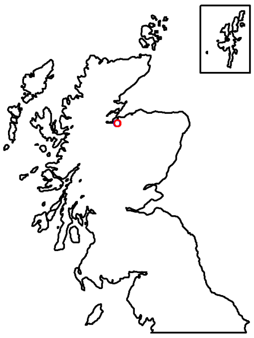
Inverness Sandstone Group (INS)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.05
Median = 0.07
Mean = 0.07
Max = 0.09
Std dev = 0.028
n = 2

DVC Daviot Conglomerate Formation (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

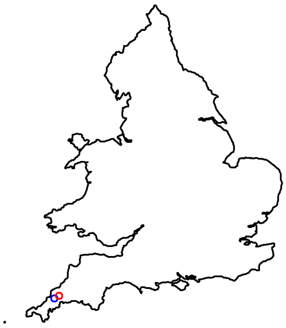
Meadfoot Group (MDT)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.03
Median = 0.04
Mean = 0.04
Max = 0.05
Std dev = 0.014
n = 2

U Undifferentiated (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

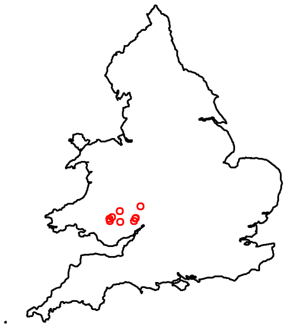
Lower Old Red Sandstone (LORS)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.05
Median = 0.05
Mean = 0.05
Max = 0.05
Std dev = 0
n = 9

BRS	Brownstones Formation (7)
SMG	St Maughans Formation (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Downton Group (DOW)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.03
Median = 0.03
Mean = 0.03
Max = 0.03
Std dev = NA
n = 1

RG	Raglan Mudstone Formation (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

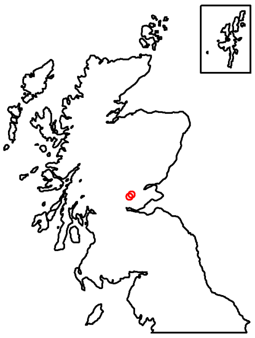
Arbuthnott-Garvock Group (ATGK)

Carbon - fraction of organic (fOC)

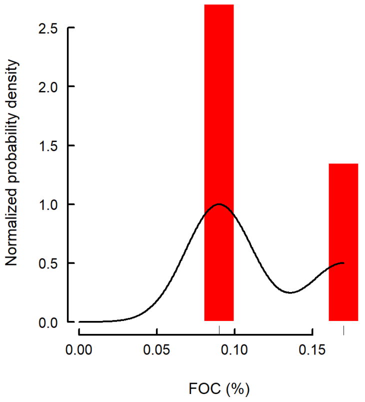
FOC (%)

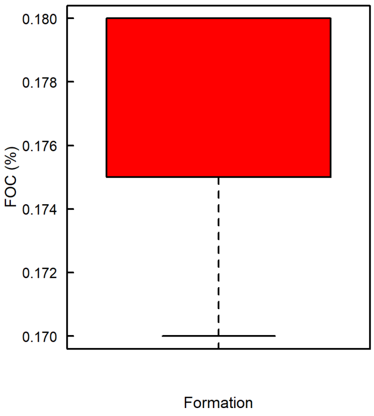
Min = 0.09
Median = 0.09
Mean = 0.117
Max = 0.17
Std dev = 0.046
n = 3

OVF Ochil Volcanic Formation (3)



Blue points are below the median
Red points are at or above the median





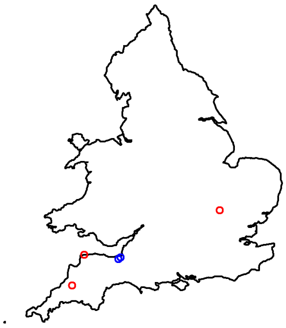
Other Devonian (XD)

Carbon - fraction of organic (fOC)

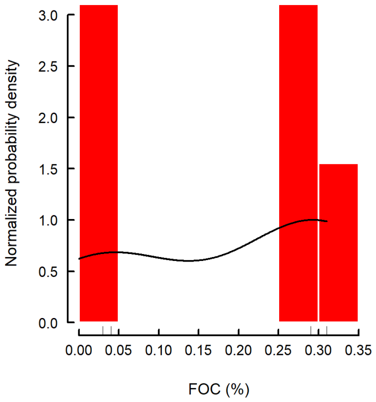
FOC (%)

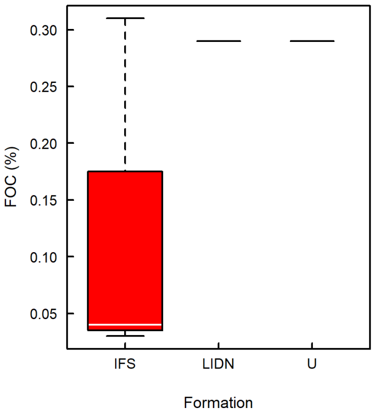
Min = 0.03
Median = 0.29
Mean = 0.192
Max = 0.31
Std dev = 0.144
n = 5

IFS	Ilfracombe Slates Formation (3)
LIDN	Liddaton Formation (1)
U	Undifferentiated (1)



Blue points are below the median
Red points are at or above the median





6.4.8 Pre-Devonian

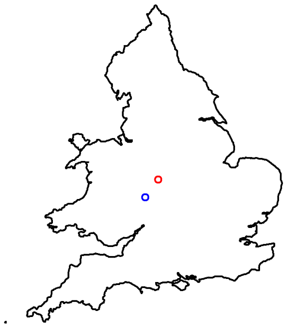
Lower Ludlow Shales Group (LLUS)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.05
Median = 0.07
Mean = 0.07
Max = 0.09
Std dev = 0.028
n = 2

U Undifferentiated (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

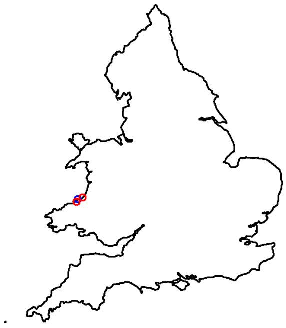
Aberystwyth Grits Group (AGF)

Carbon - fraction of organic (fOC)

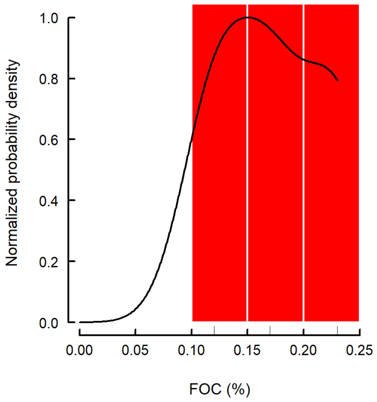
FOC (%)

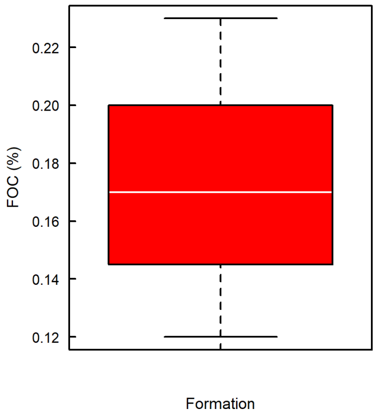
Min = 0.12
Median = 0.17
Mean = 0.173
Max = 0.23
Std dev = 0.055
n = 3

MYBA Mynydd Bach Formation (3)



Blue points are below the median
Red points are at or above the median





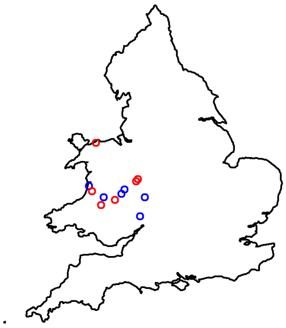
Other Silurian (XS)

Carbon - fraction of organic (fOC)

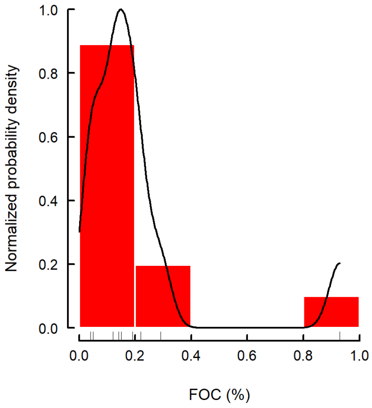
FOC (%)

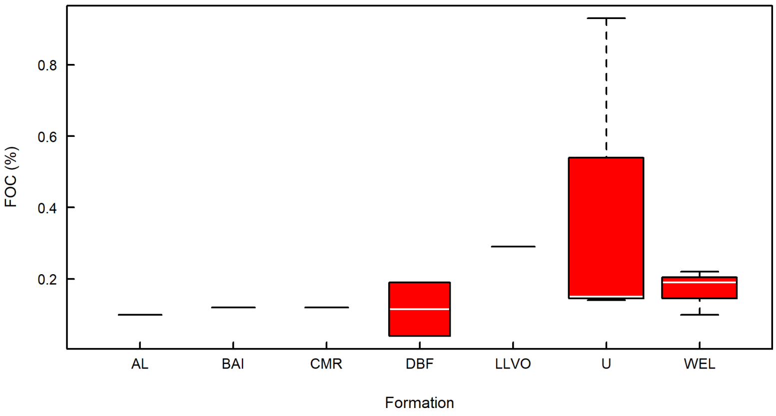
Min = 0.04
Median = 0.145
Mean = 0.208
Max = 0.93
Std dev = 0.239
n = 12

AL	Aymestry Limestone Formation (1)
BAI	Bailey Hill Formation (1)
CMR	Cwmere Formation (1)
DBF	Devil'S Bridge Formation (2)
LLVO	Llanwrtyd Volcanic Formation (1)
U	Undifferentiated (3)
WEL	Much Wenlock Limestone Formation (3)



Blue points are below the median
Red points are at or above the median





Builth Volcanic Group (BUVO)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.02
Median = 0.02
Mean = 0.02
Max = 0.02
Std dev = 0
n = 2

U Undifferentiated (2)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Mawddach Group (MWG)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.05
Median = 0.05
Mean = 0.05
Max = 0.05
Std dev = 0
n = 2

FF	Ffestiniog Flags Formation (1)
MW	Maentwrog Formation (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

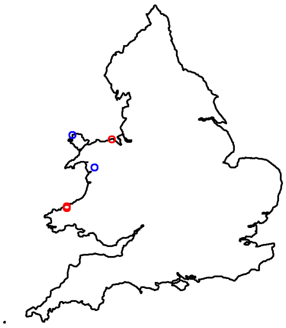
Other Ordovician (XO)

Carbon - fraction of organic (fOC)

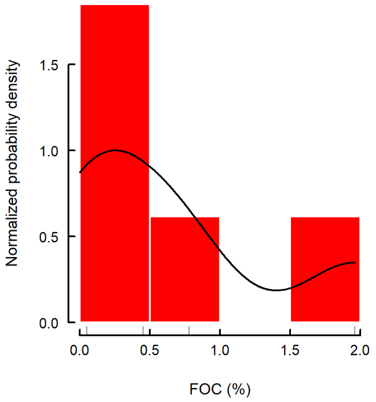
FOC (%)

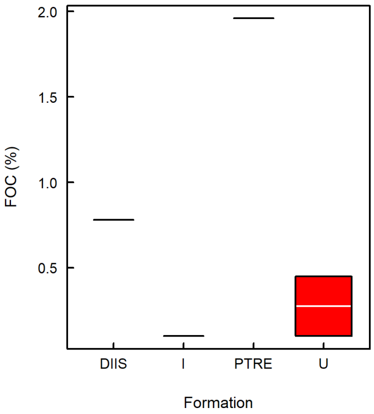
Min = 0.05
Median = 0.45
Mean = 0.658
Max = 1.96
Std dev = 0.789
n = 5

DIIS	Dinas Island Formation (1)
I	(1)
PTRE	Pentre Formation (1)
U	Undifferentiated (2)



Blue points are below the median
Red points are at or above the median





Mona Gneiss Suite (NMG)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.05
Median = 0.05
Mean = 0.05
Max = 0.05
Std dev = NA
n = 1

U Undifferentiated (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

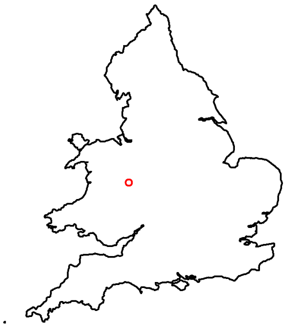
Stretton Group (YST)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.05
Median = 0.05
Mean = 0.05
Max = 0.05
Std dev = NA
n = 1

SYGP Synalds Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

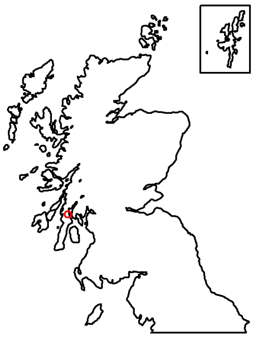
Argyll Group (ARGY)

Carbon - fraction of organic (fOC)

FOC (%)

Min	=	0.09
Median	=	0.09
Mean	=	0.09
Max	=	0.09
Std dev	=	NA
n	=	1

DBUE Upper Erins Quartzite Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

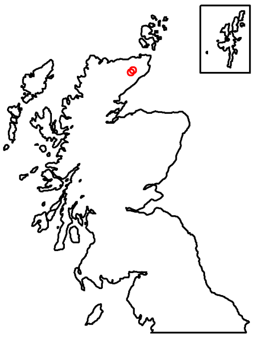
Loch Eil Group (LEIL)

Carbon - fraction of organic (fOC)

FOC (%)

Min	=	0.09
Median	=	0.09
Mean	=	0.09
Max	=	0.09
Std dev	=	0
n	=	2

SUIS Suisgill Semipelite Formation (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Other Pre-Cambrian (XA)

Carbon - fraction of organic (fOC)

FOC (%)

Min = 0.04
Median = 0.04
Mean = 0.04
Max = 0.04
Std dev = NA
n = 1

U Undifferentiated (1)

Blue points are below the median
Red points are at or above the median

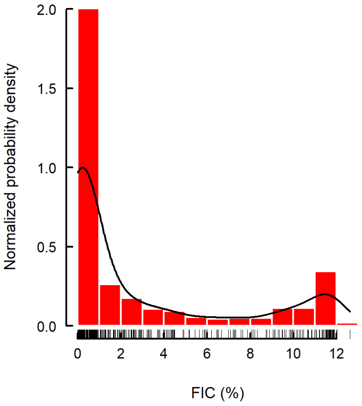
Not enough data for plotting

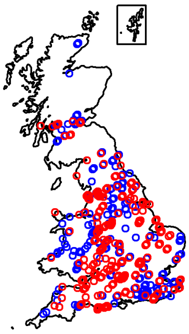
6.5 GEOLOGICAL ATLAS OF DATA FOR f_{IC}

All Groups (All)

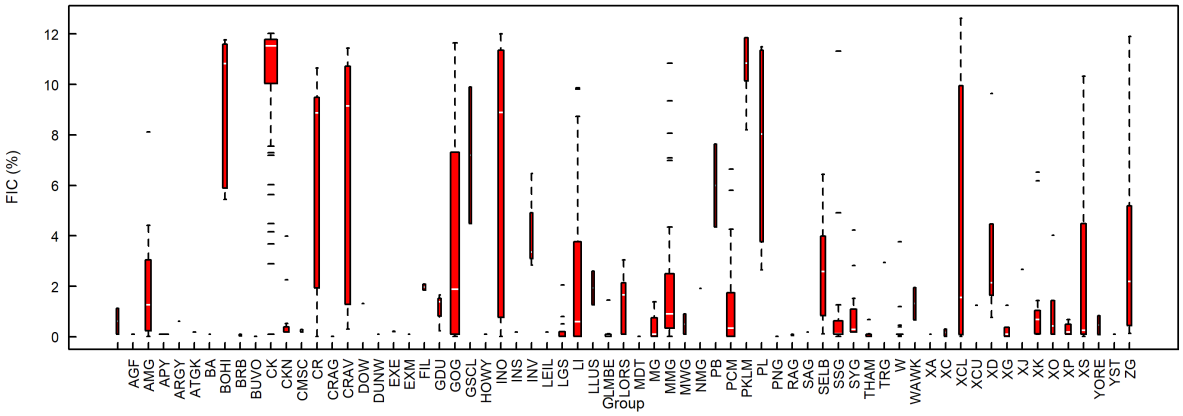
Carbon - fraction of inorganic (fIC)

FIC (%)





Blue points are below the median
Red points are at or above the median



6.5.1 Quaternary and Neogene

Glacial Deposits (GDU)

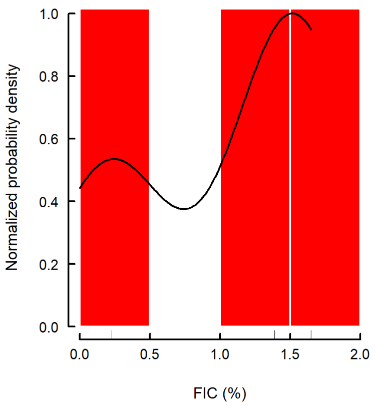
Carbon - fraction of inorganic (fIC)

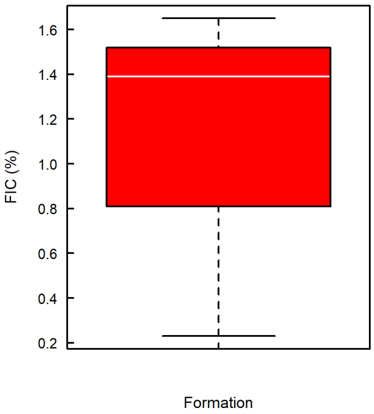
FIC (%)

Min = 0.23
Median = 1.39
Mean = 1.09
Max = 1.65
Std dev = 0.756
n = 3

U Undifferentiated (3)

Blue points are below the median
Red points are at or above the median





Dunwich Group (DUNW)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 0.05
Median = 0.05
Mean = 0.05
Max = 0.05
Std dev = NA
n = 1

KGCA Kesgrave Catchment Subgroup (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Crag Group (CRAG)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 0.005
Median = 0.005
Mean = 0.005
Max = 0.005
Std dev = 0
n = 2

NCG Norwich Crag Formation (2)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Palaeogene

Barton Group (BA)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 0.05
Median = 0.05
Mean = 0.05
Max = 0.05
Std dev = NA
n = 1

BECH Becton Sand and Chama Sand Fms (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

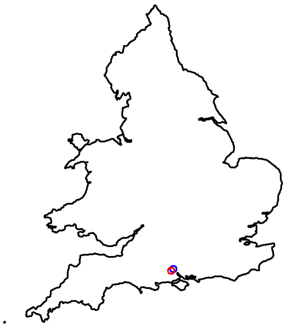
Bracklesham Group (BRB)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 0.03
Median = 0.065
Mean = 0.065
Max = 0.1
Std dev = 0.049
n = 2

WTT	Wittering Formation (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

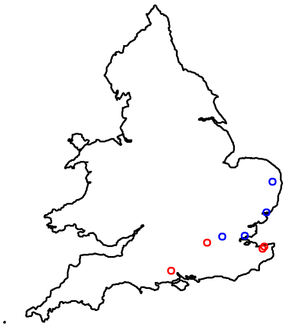
Thames Group (THAM)

Carbon - fraction of inorganic (fIC)

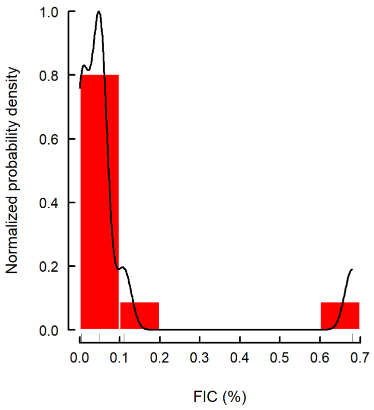
FIC (%)

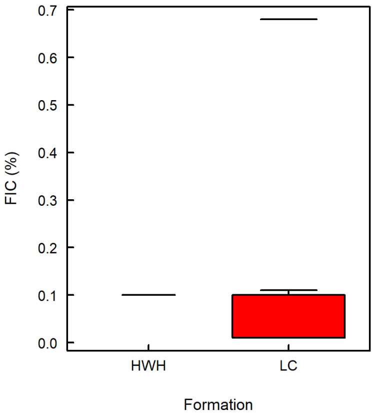
Min = 0.005
Median = 0.05
Mean = 0.0964
Max = 0.68
Std dev = 0.196
n = 11

HWH	Harwich Formation (2)
LC	London Clay Formation (9)



Blue points are below the median
Red points are at or above the median





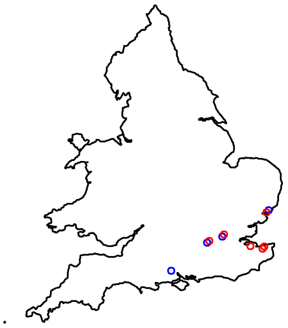
Lambeth Group (LMBE)

Carbon - fraction of inorganic (fIC)

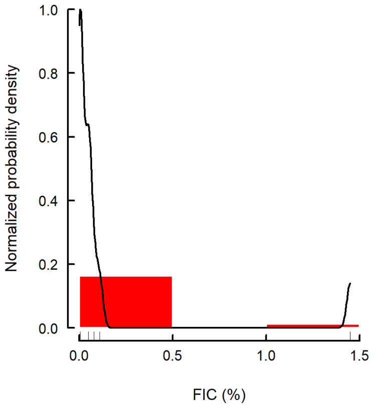
FIC (%)

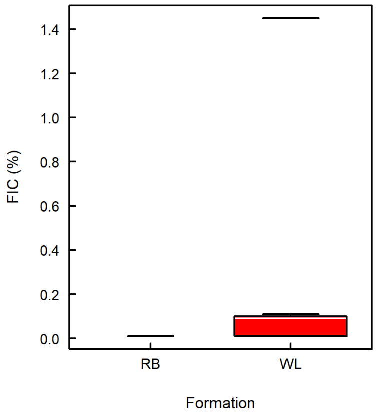
Min = 0.005
Median = 0.0275
Mean = 0.134
Max = 1.45
Std dev = 0.38
n = 14

RB	Reading Formation (2)
WL	Woolwich Formation (12)



Blue points are below the median
Red points are at or above the median





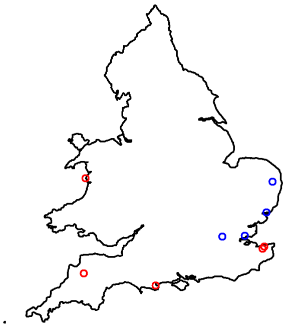
Other Palaeogene (XG)

Carbon - fraction of inorganic (fIC)

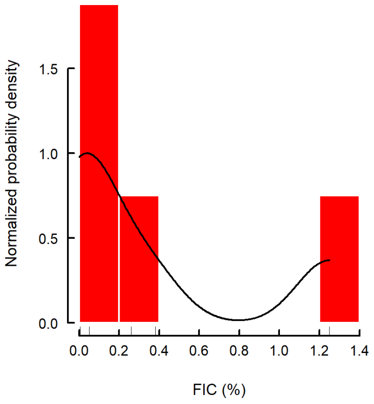
FIC (%)

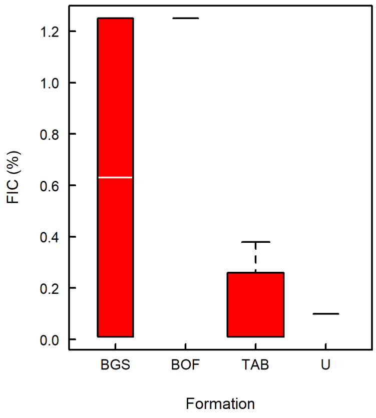
Min = 0.005
Median = 0.05
Mean = 0.357
Max = 1.25
Std dev = 0.524
n = 9

BGS	Bagshot Formation (2)
BOF	Bovey Formation (1)
TAB	Thanet Formation (5)
U	Undifferentiated (1)



Blue points are below the median
Red points are at or above the median





6.5.2 Cretaceous

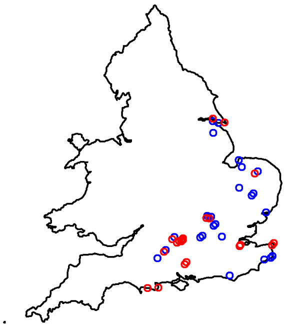
Chalk Group (CK)

Carbon - fraction of inorganic (fIC)

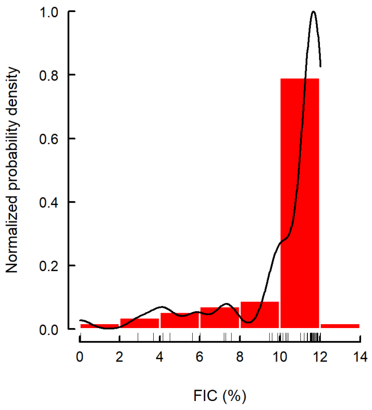
FIC (%)

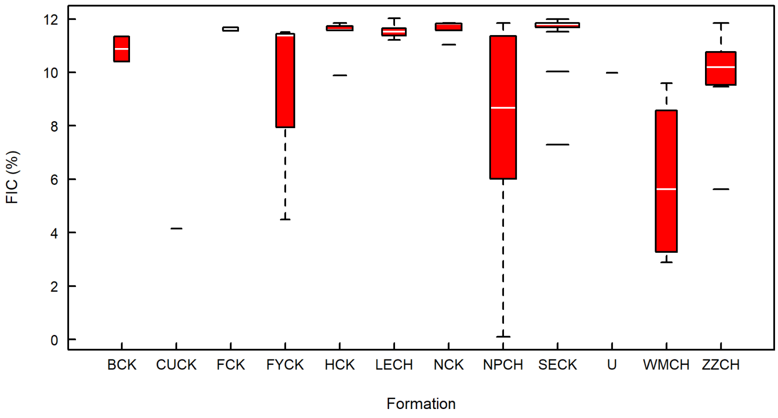
Min = 0.05
Median = 11.5
Mean = 10.3
Max = 12
Std dev = 2.64
n = 61

BCK	Burnham Chalk Formation (2)
CUCK	Culver Chalk Formation (1)
FCK	Flamborough Chalk Formation (2)
FYCK	Ferriby Chalk Formation (3)
HCK	Holywell Nodular Chalk Formation (6)
LECH	Lewes Nodular Chalk Formation (5)
NCK	Newhaven Chalk Formation (6)
NPCH	New Pit Chalk Formation (6)
SECK	Seaford Chalk Formation (17)
U	Undifferentiated (1)
WMCH	West Melbury Marly Chalk Formation (4)
ZZCH	Zig Zag Chalk Formation (8)



Blue points are below the median
Red points are at or above the median





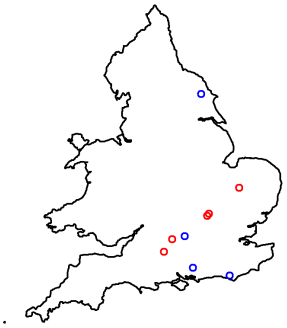
Selborne Group (SELB)

Carbon - fraction of inorganic (fIC)

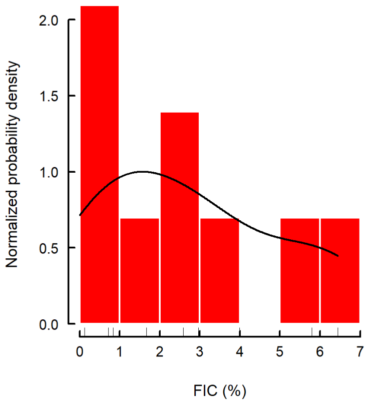
FIC (%)

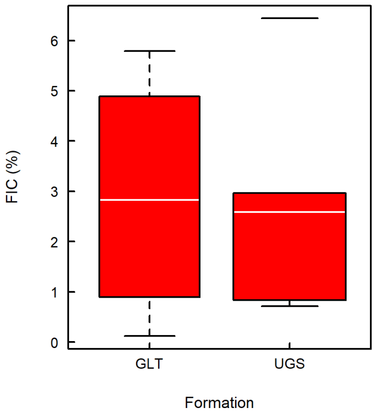
Min = 0.12
Median = 2.59
Mean = 2.79
Max = 6.44
Std dev = 2.25
n = 9

GLT	Gault Formation (4)
UGS	Upper Greensand Formation (5)



Blue points are below the median
Red points are at or above the median





Lower Greensand Group (LGS)

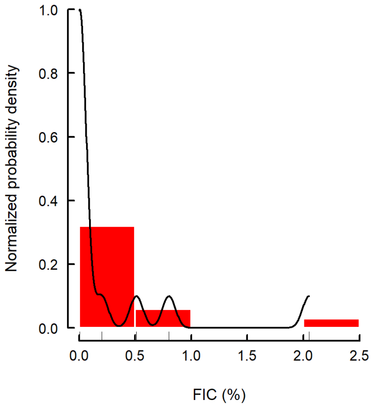
Carbon - fraction of inorganic (fIC)

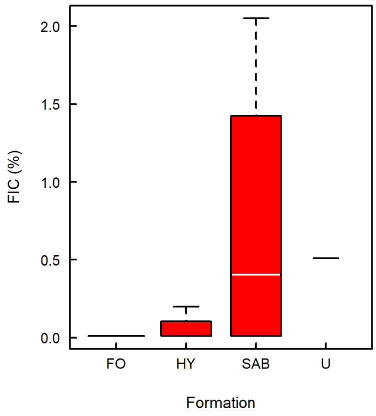
FIC (%)

Min = 0.005
Median = 0.005
Mean = 0.258
Max = 2.05
Std dev = 0.569
n = 14

FO	Folkestone Formation (5)
HY	Hythe Formation (4)
SAB	Sandgate Formation (4)
U	Undifferentiated (1)

Blue points are below the median
Red points are at or above the median





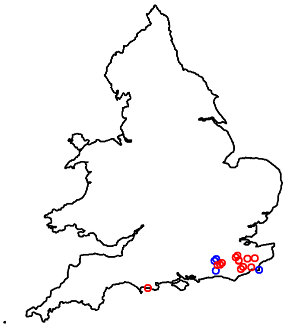
Wealden Group (W)

Carbon - fraction of inorganic (fIC)

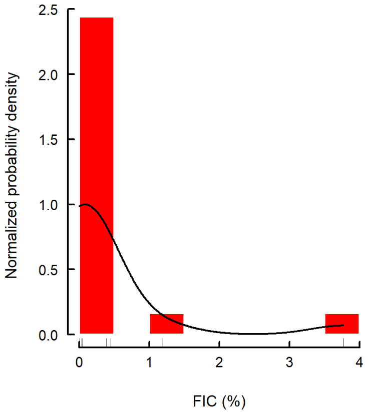
FIC (%)

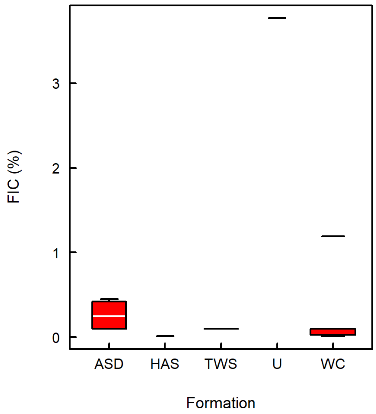
Min = 0.005
Median = 0.05
Mean = 0.371
Max = 3.77
Std dev = 0.924
n = 17

ASD	Ashdown Formation (4)
HAS	Hastings Beds (Subgroup) (1)
TWS	Tunbridge Wells Sand Formation (4)
U	Undifferentiated (1)
WC	Weald Clay Formation (7)



Blue points are below the median
Red points are at or above the median





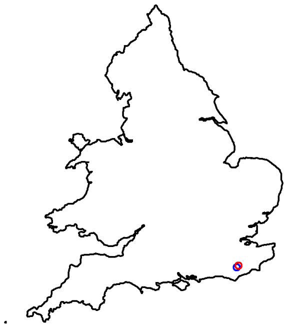
Purbeck Group (PB)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 4.35
Median = 5.99
Mean = 5.99
Max = 7.64
Std dev = 2.33
n = 2

DURN	Durlston Formation (1)
LULW	Lulworth Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Other Cretaceous (XK)

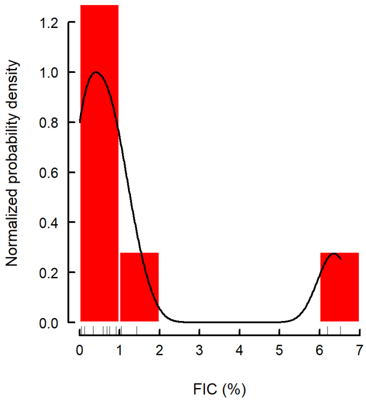
Carbon - fraction of inorganic (fIC)

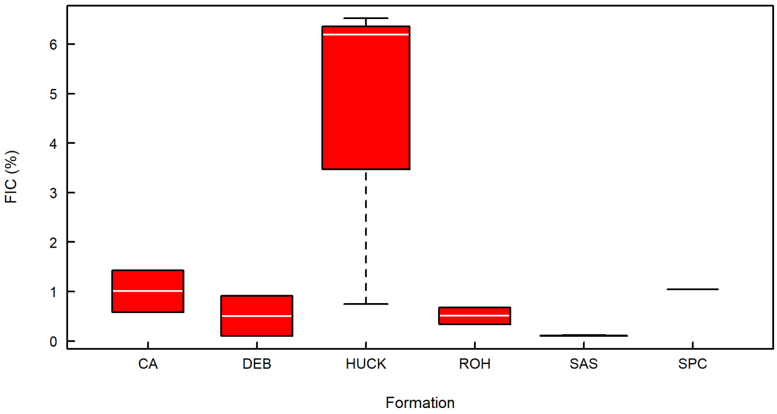
FIC (%)

Min = 0.05
Median = 0.68
Mean = 1.44
Max = 6.52
Std dev = 2.22
n = 13

CA	Carstone Formation (2)
DEB	Dersingham Formation (2)
HUCK	Hunstanton Formation (3)
ROH	Roach Formation (2)
SAS	Sandringham Sand Formation (3)
SPC	Speeton Clay Formation (1)

Blue points are below the median
Red points are at or above the median





6.5.3 Jurassic

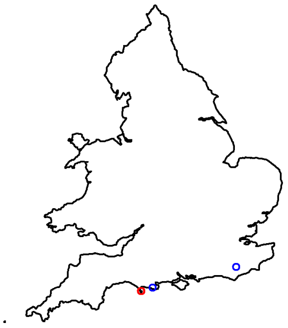
Portland Group (PL)

Carbon - fraction of inorganic (fIC)

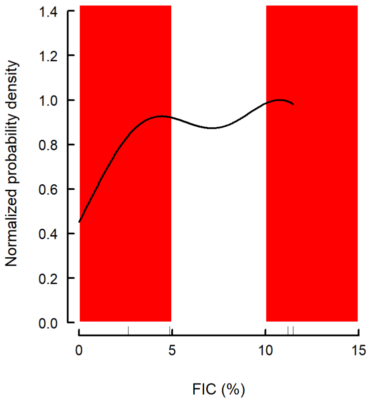
FIC (%)

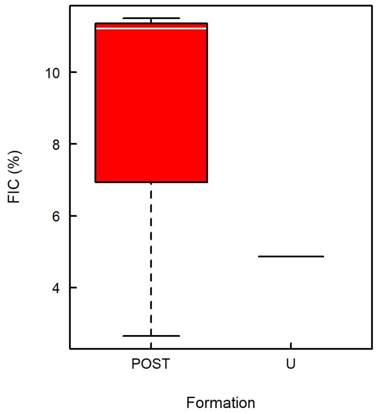
Min = 2.65
Median = 8.04
Mean = 7.56
Max = 11.5
Std dev = 4.48
n = 4

POST Portland Stone Formation (3)
U Undifferentiated (1)



Blue points are below the median
Red points are at or above the median





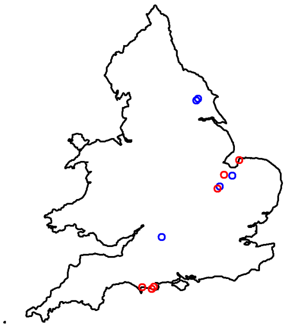
Ancholme Group (AMG)

Carbon - fraction of inorganic (fIC)

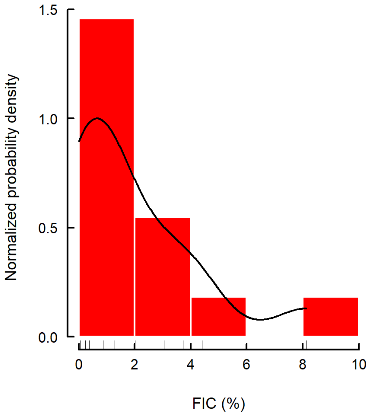
FIC (%)

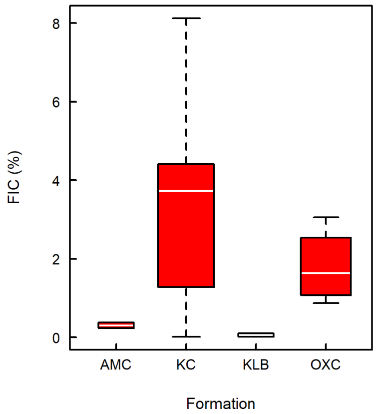
Min = 0.005
Median = 1.26
Mean = 1.95
Max = 8.12
Std dev = 2.37
n = 13

AMC Ampthill Clay Formation (2)
KC Kimmeridge Clay Formation (5)
KLB Kellaways Formation (2)
OXC Oxford Clay Formation (4)



Blue points are below the median
Red points are at or above the median





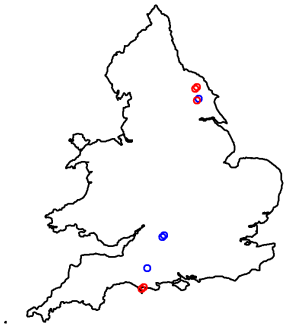
Corallian Group (CR)

Carbon - fraction of inorganic (fIC)

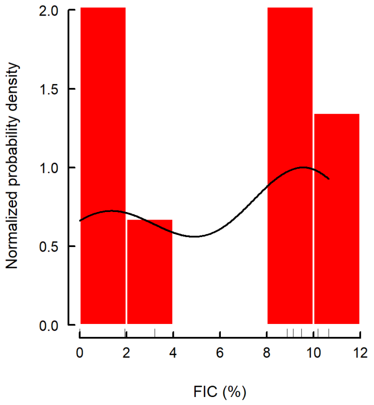
FIC (%)

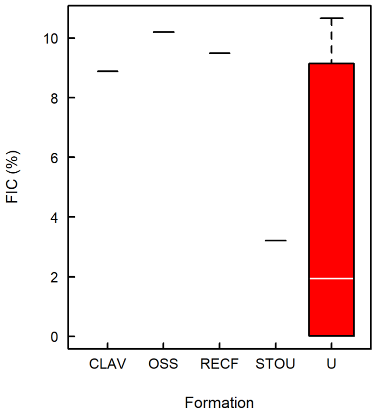
Min = 0.005
Median = 8.88
Mean = 5.95
Max = 10.7
Std dev = 4.55
n = 9

CLAV	Clavellata Formation (1)
OSS	Osmington Oolite Formation (1)
RECF	Redcliff Formation (1)
STOU	Stour Formation (1)
U	Undifferentiated (5)



Blue points are below the median
Red points are at or above the median





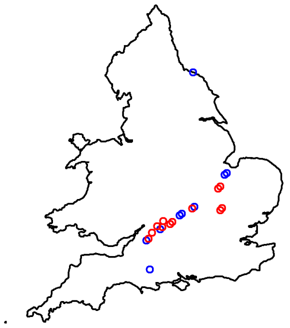
Great Oolite Group (GOG)

Carbon - fraction of inorganic (fIC)

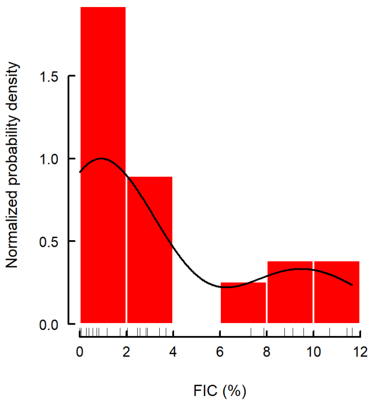
FIC (%)

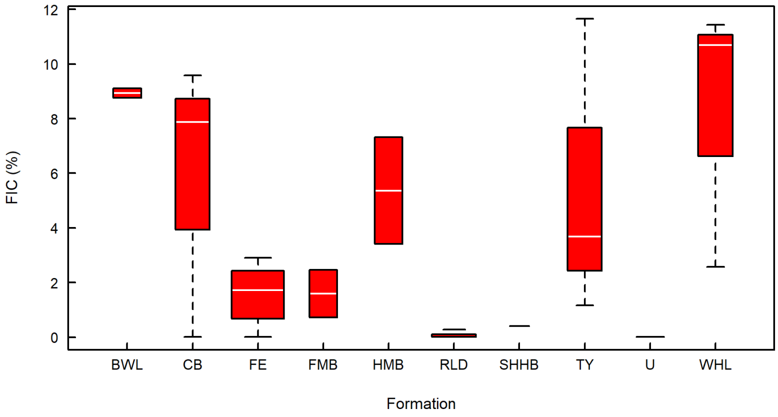
Min = 0.005
Median = 1.88
Mean = 3.4
Max = 11.6
Std dev = 4.01
n = 30

BWL	Blisworth Limestone Formation (2)
CB	Cornbrash Formation (3)
FE	Fuller'S Earth Formation (7)
FMB	Forest Marble Formation (2)
HMB	Hampen Formation (2)
RLD	Rutland Formation (5)
SHHB	Sharp'S Hill Formation (1)
TY	Taynton Limestone Formation (3)
U	Undifferentiated (2)
WHL	White Limestone Formation (3)



Blue points are below the median
Red points are at or above the median





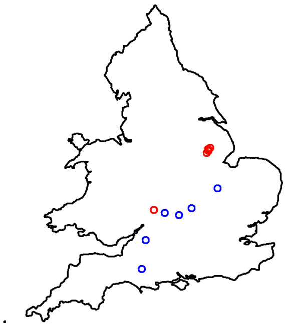
Inferior Oolite Group (INO)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 0.005
Median = 8.89
Mean = 6.66
Max = 12
Std dev = 5.08
n = 12

BLPL	Birdlip Limestone Formation (2)
GRF	Grantham Formation (2)
LL	Lincolnshire Limestone Formation (5)
NS	Northampton Sand Formation (1)
U	Undifferentiated (2)



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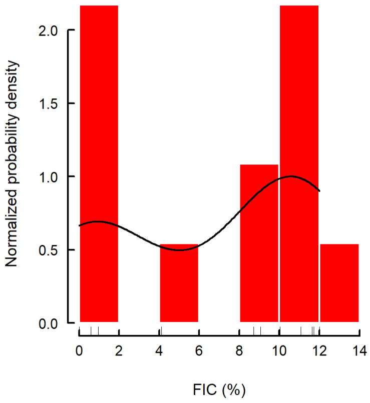
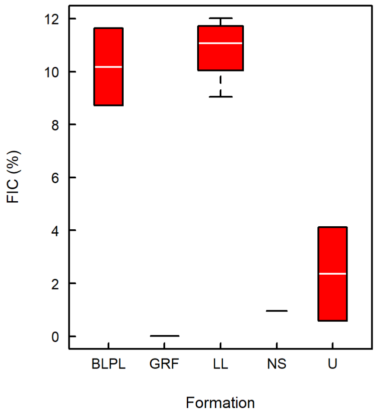
Red points are at or above the median





Ravenscar Group (RAG)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 0.05
Median = 0.05
Mean = 0.05
Max = 0.05
Std dev = 0
n = 2

SCY	Scalby Formation (1)
U	Undifferentiated (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

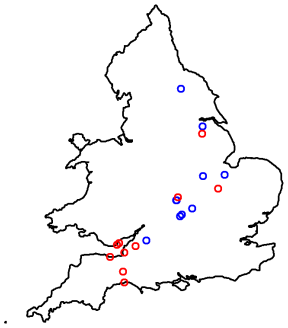
Lias Group (LI)

Carbon - fraction of inorganic (fIC)

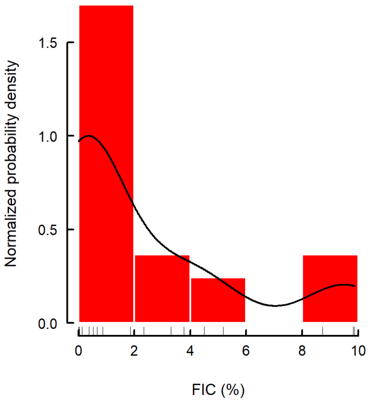
FIC (%)

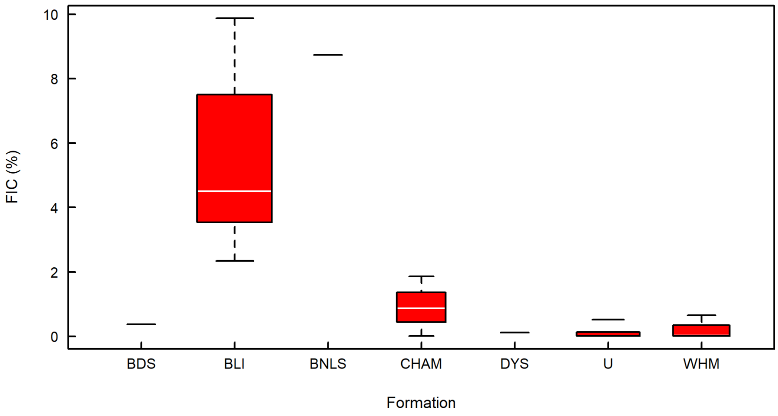
Min = 0.005
Median = 0.59
Mean = 2.37
Max = 9.87
Std dev = 3.3
n = 22

BDS	Bridport Sand Formation (1)
BLI	Blue Lias Formation (7)
BNLS	Beacon Limestone Formation (1)
CHAM	Charmouth Mudstone Formation (3)
DYS	Dyrham Formation (1)
U	Undifferentiated (5)
WHM	Whitby Mudstone Formation (4)



Blue points are below the median
Red points are at or above the median





Other Jurassic (XJ)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 2.67
Median = 2.67
Mean = 2.67
Max = 2.67
Std dev = NA
n = 1

SAS	Sandringham Sand Formation (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

6.5.4 Triassic

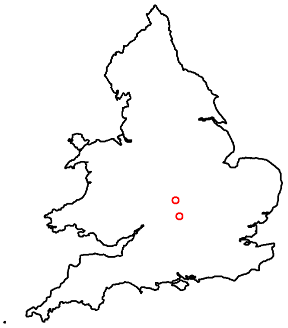
Penarth Group (PNG)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 0.005
Median = 0.005
Mean = 0.005
Max = 0.005
Std dev = 0
n = 2

U	Undifferentiated (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

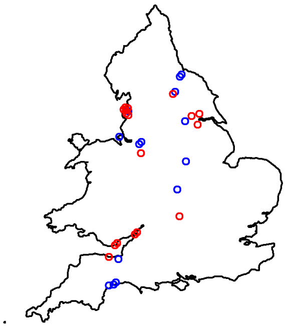
Mercia Mudstone Group (MMG)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 0.005
Median = 0.9
Mean = 2.25
Max = 10.8
Std dev = 2.92
n = 33

BAN	Blue Anchor Formation (3)
SIM	Sidmouth Mudstone Formation (7)
TPSF	Tarporley Siltstone Formation (1)
U	Undifferentiated (22)



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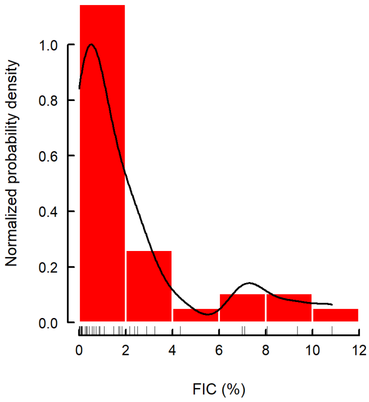
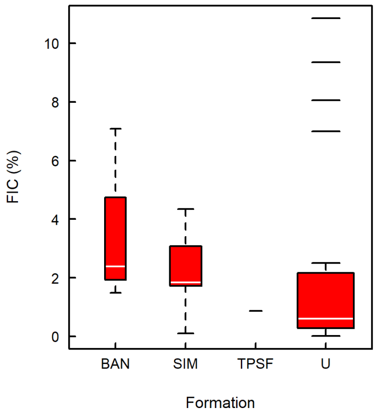




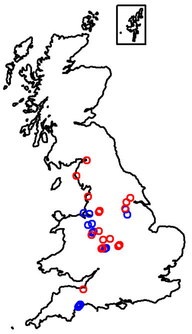
Sherwood Sandstone Group (SSG)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 0.005
Median = 0.09
Mean = 0.767
Max = 11.3
Std dev = 2.09
n = 33

BMS	Bromsgrove Sandstone Formation (4)
BSP	Budleigh Salterton Pebble Beds Formation (2
CPB	Chester Pebble Beds Formation (1)
HEY	Helsby Sandstone Formation (3)
KDM	Kidderminster Formation (1)
NTC	Nottingham Castle Sandstone Formation (2)
OS	Otter Sandstone Formation (3)
U	Undifferentiated (11)
WLSF	Wilmslow Sandstone Formation (5)
WRS	Wildmoor Sandstone Formation (1)



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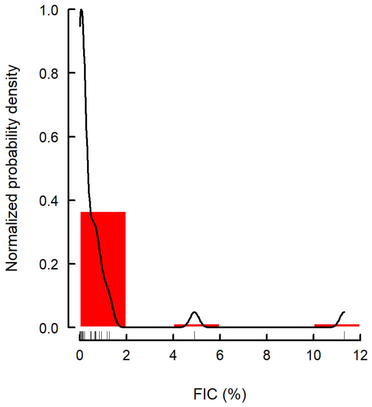
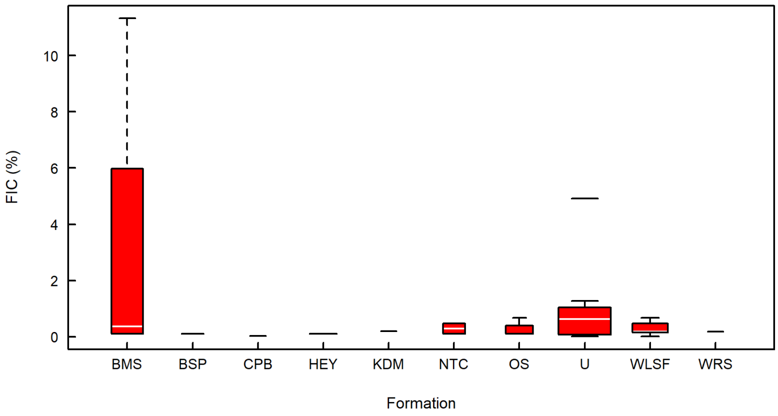
Red points are at or above the median





6.5.5 Permian

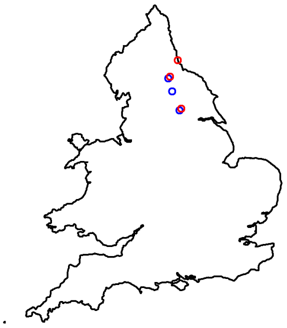
Zechstein Group (ZG)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 0.13
Median = 2.19
Mean = 3.46
Max = 11.9
Std dev = 4.03
n = 8

BTH	Brotherton Formation (1)
CDF	Cadeby Formation (1)
EDT	Edlington Formation (1)
RML	Raisby Formation (1)
ROX	Roxby Formation (1)
U	Undifferentiated (3)



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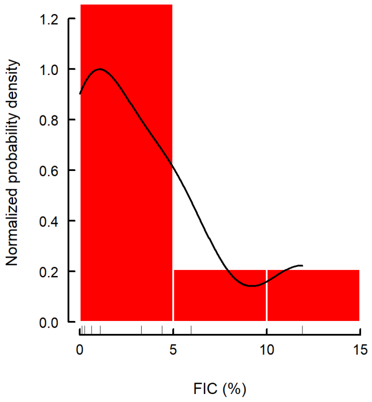
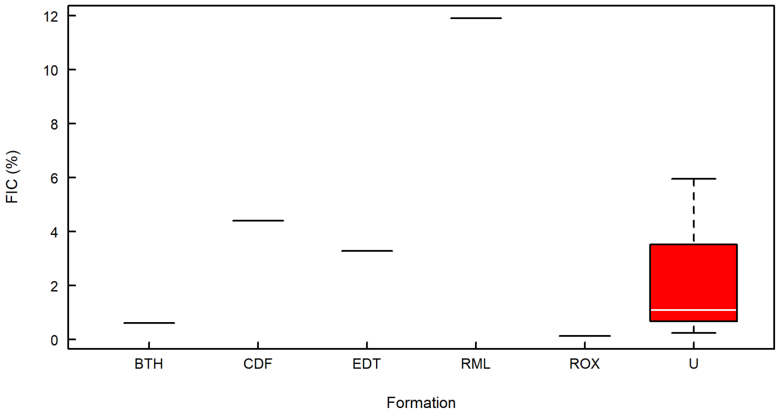




Appleby Group (APY)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 0.045
Median = 0.045
Mean = 0.045
Max = 0.045
Std dev = 0
n = 33

PS	Penrith Sandstone Formation (33)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

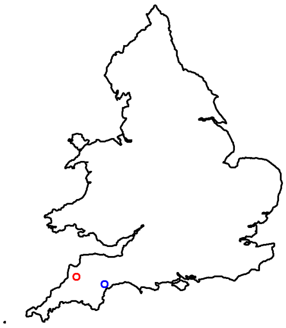
Exeter Group (EXE)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 0.2
Median = 0.205
Mean = 0.205
Max = 0.21
Std dev = 0.007
n = 2

BOB	Bow Breccia Formation (1)
HVBR	Heavitree Breccia Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

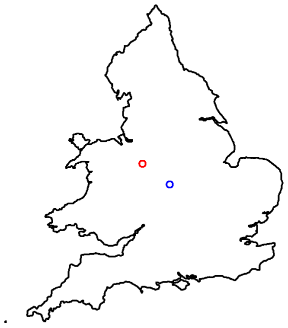
Warwickshire Group (WAWK)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 0.67
Median = 1.31
Mean = 1.31
Max = 1.95
Std dev = 0.905
n = 2

SAL Salop Formation (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

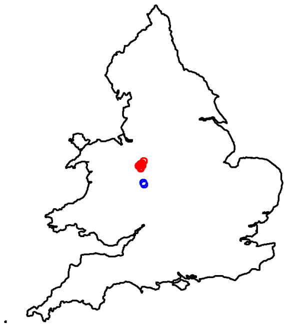
Other Permian (XP)

Carbon - fraction of inorganic (fIC)

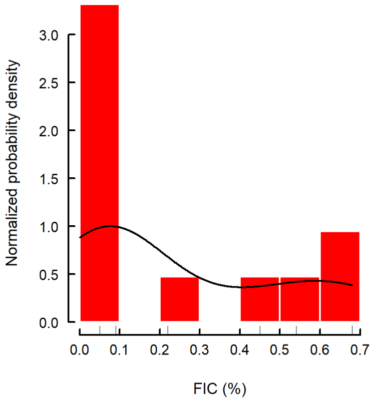
FIC (%)

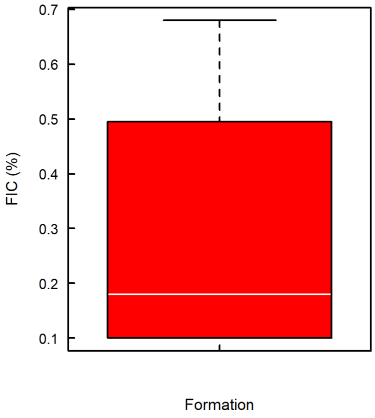
Min = 0.05
Median = 0.09
Mean = 0.25
Max = 0.68
Std dev = 0.26
n = 12

BRI Bridgnorth Sandstone Formation (12)



Blue points are below the median
Red points are at or above the median





6.5.6 Carboniferous

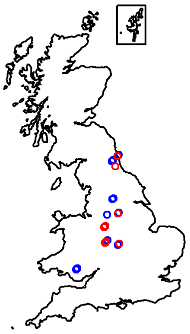
Pennine Coal Measures Group (PCM)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 0.005
Median = 0.335
Mean = 1.24
Max = 6.65
Std dev = 1.98
n = 24

PLCM	Pennine Lower Coal Measures Formation (1)
U	Undifferentiated (23)



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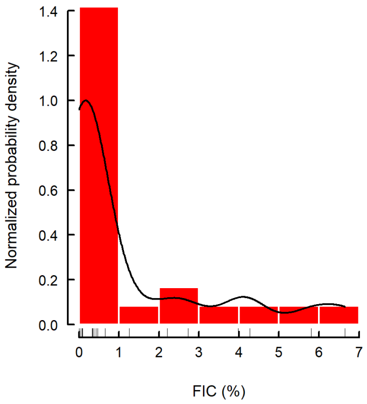
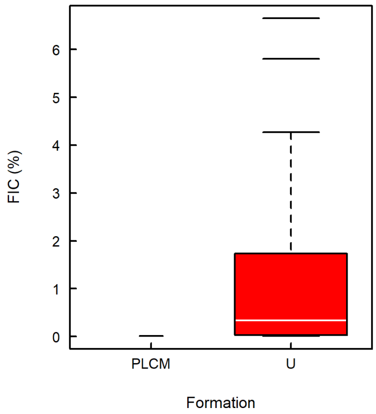




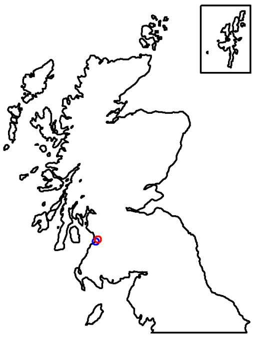
Scottish Coal Measures Group (CMSC)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 0.09
Median = 0.185
Mean = 0.185
Max = 0.28
Std dev = 0.134
n = 2

MCMS	Scottish Middle Coal Measures Formation (2



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Holsworthy Group (HOWY)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 0.05
Median = 0.05
Mean = 0.05
Max = 0.05
Std dev = 0
n = 2

BF Bude Formation (2)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Clackmannan Group (CKN)

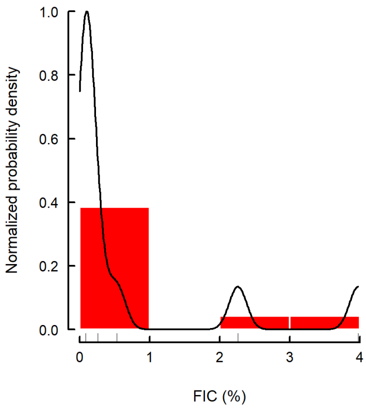
Carbon - fraction of inorganic (fIC)

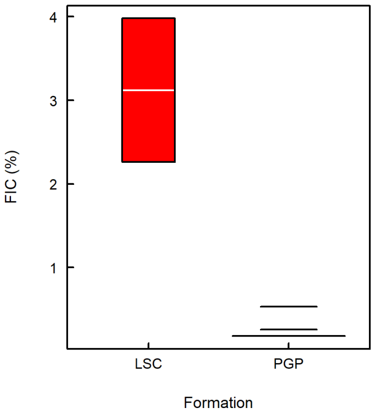
FIC (%)

Min = 0.09
Median = 0.09
Mean = 0.696
Max = 3.98
Std dev = 1.27
n = 11

LSC Limestone Coal Formation (2)
PGP Passage Formation (9)

Blue points are below the median
Red points are at or above the median





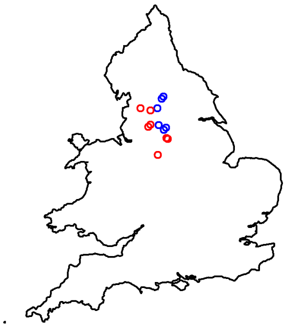
Millstone Grit Group (MG)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 0.005
Median = 0.05
Mean = 0.367
Max = 1.39
Std dev = 0.463
n = 16

HEBD	Hebden Formation (4)
PENDL	Pendleton Formation (1)
SAML	Samlesbury Formation (1)
SDSH	Sabden Shales (2)
U	Undifferentiated (8)



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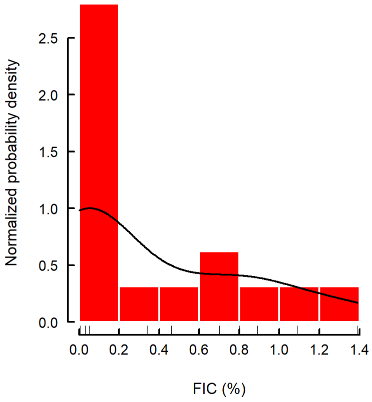
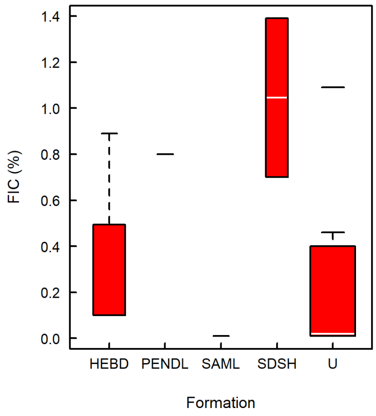




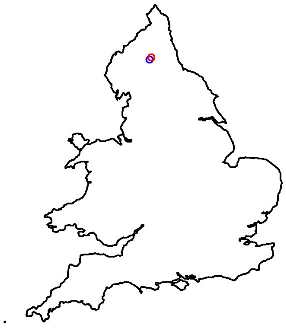
Yoredale Group (YORE)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 0.08
Median = 0.455
Mean = 0.455
Max = 0.83
Std dev = 0.53
n = 2

SMGP	Stainmore Formation (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

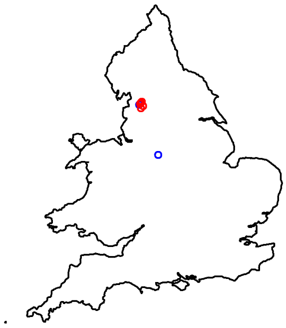
Craven Group (CRAV)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 0.3
Median = 9.14
Mean = 6.75
Max = 11.4
Std dev = 4.82
n = 11

BOH	Hodderense Limestone Formation (1)
BSG	Bowland Shale Formation (3)
HOM	Hodder Mudstone Formation (3)
PDL	Pendleside Limestone Formation (3)
U	Undifferentiated (1)



Blue points are below the median
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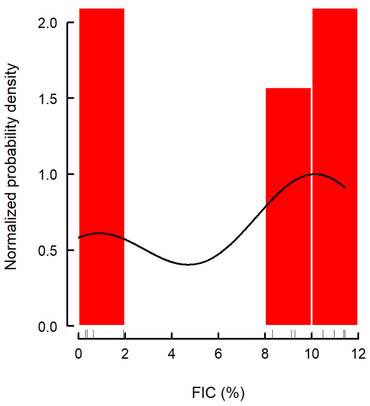
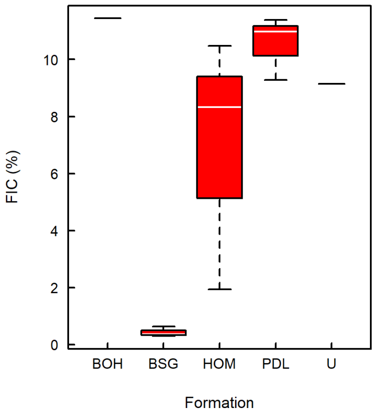




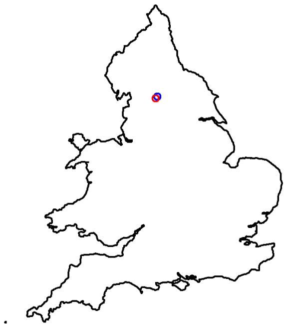
Great Scar Limestone Group (GSCL)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 4.48
Median = 7.19
Mean = 7.19
Max = 9.9
Std dev = 3.83
n = 2

KLSL	Kilnsey Formation (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

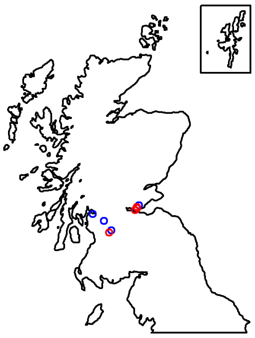
Strathclyde Group (SYG)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 0.09
Median = 0.295
Mean = 0.872
Max = 4.22
Std dev = 1.24
n = 14

CPV	Clyde Plateau Volcanic Formation (5)
LWM	Lawmuir Formation (1)
PDB	Pathhead Formation (4)
PMB	Pittenweem Formation (4)



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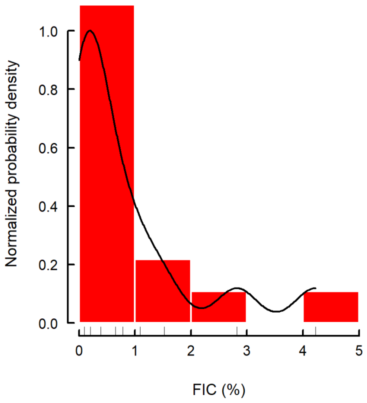
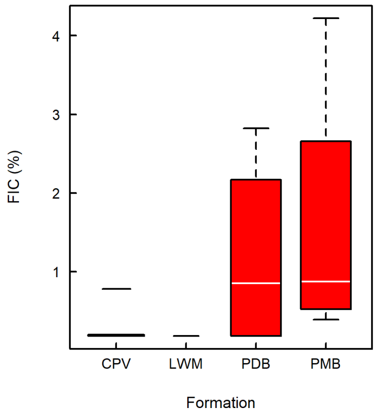




Peak Limestone Group (PKLM)

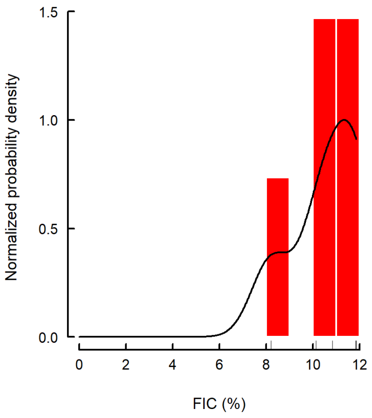
Carbon - fraction of inorganic (fIC)

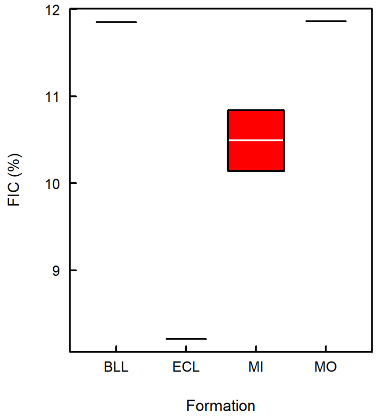
FIC (%)

Min = 8.21
Median = 10.8
Mean = 10.6
Max = 11.9
Std dev = 1.51
n = 5

BLL	Bee Low Limestone Formation (1)
ECL	Ecton Limestone Formation (1)
MI	Milldale Limestone Formation (2)
MO	Monsal Dale Limestone Formation (1)

Blue points are below the median
Red points are at or above the median





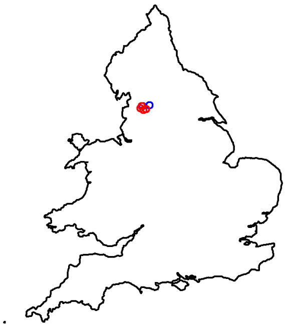
Bowland High Group (BOHI)

Carbon - fraction of inorganic (fIC)

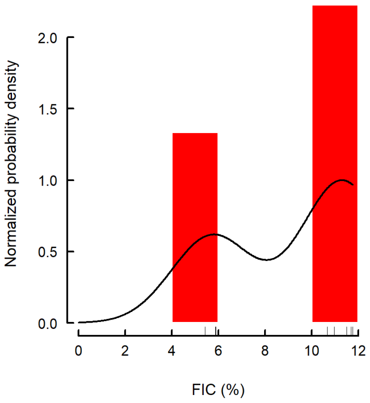
FIC (%)

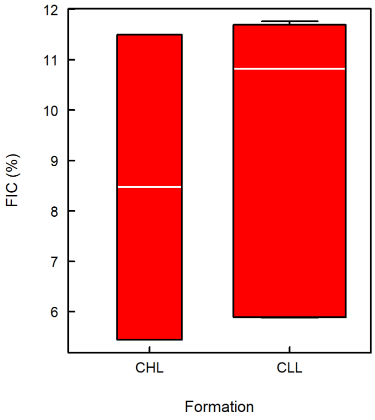
Min = 5.44
Median = 10.8
Mean = 9.22
Max = 11.8
Std dev = 2.91
n = 8

CHL	Chatburn Limestone Formation (2)
CLL	Clitheroe Limestone Formation (6)



Blue points are below the median
Red points are at or above the median





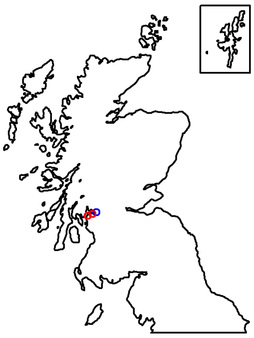
Inverclyde Group (INV)

Carbon - fraction of inorganic (fIC)

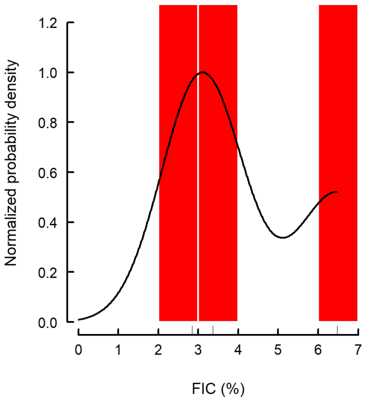
FIC (%)

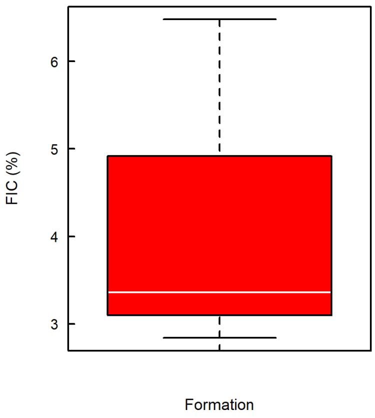
Min = 2.84
Median = 3.36
Mean = 4.23
Max = 6.48
Std dev = 1.97
n = 3

KNW	Kinnesswood Formation (3)



Blue points are below the median
Red points are at or above the median





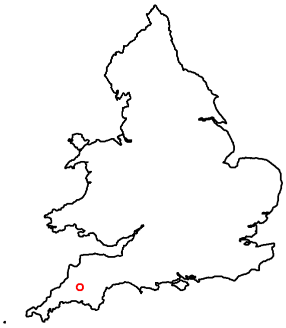
Transition Group (Devonian-Carboniferc

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 2.94
Median = 2.94
Mean = 2.94
Max = 2.94
Std dev = NA
n = 1

SBT South Brentor Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

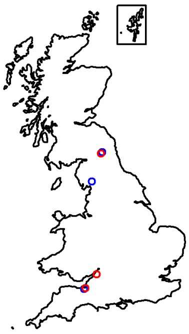
Other Carb. Limestone Supergroup (XC

Carbon - fraction of inorganic (fIC)

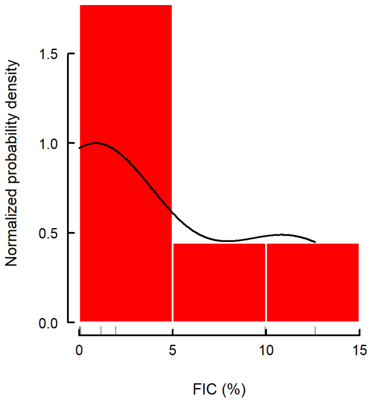
FIC (%)

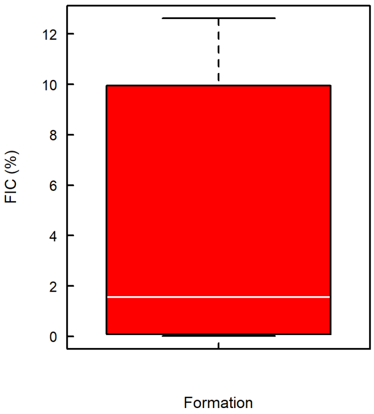
Min = 0.005
Median = 1.56
Mean = 4.29
Max = 12.6
Std dev = 5.53
n = 6

U Undifferentiated (6)



Blue points are below the median
Red points are at or above the median





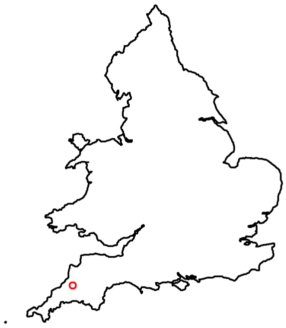
Other Culm Supergroup (XCU)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 1.25
Median = 1.25
Mean = 1.25
Max = 1.25
Std dev = NA
n = 1

U Undifferentiated (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

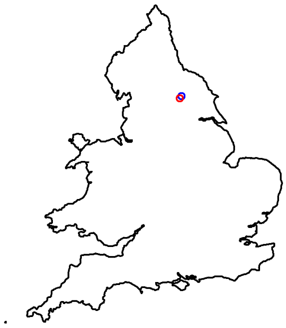
Other Carboniferous (XC)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 0.005
Median = 0.158
Mean = 0.158
Max = 0.31
Std dev = 0.216
n = 2

U Undifferentiated (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

6.5.7 Devonian

Exmoor Group (EXM)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 0.05
Median = 0.05
Mean = 0.05
Max = 0.05
Std dev = NA
n = 1

PLT Pilton Mudstone Formation (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Stratheden Group (SAG)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 0.09
Median = 0.09
Mean = 0.09
Max = 0.09
Std dev = NA
n = 1

SCK Stockiemuir Sandstone Formation (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

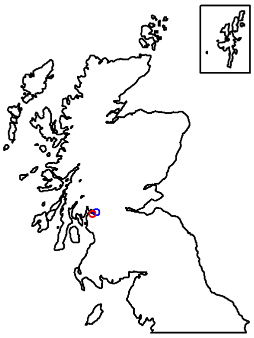
Fair Isle Group (FIL)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min	=	1.84
Median	=	1.96
Mean	=	1.96
Max	=	2.08
Std dev	=	0.17
n	=	2

BNG Bu Ness Sandstone Formation (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

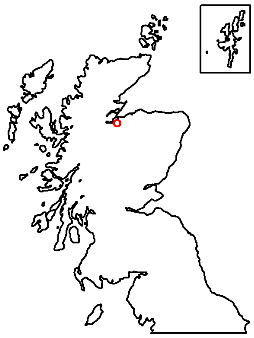
Inverness Sandstone Group (INS)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min	=	0.09
Median	=	0.09
Mean	=	0.09
Max	=	0.09
Std dev	=	0
n	=	2

DVC Daviot Conglomerate Formation (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Meadfoot Group (MDT)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 0.005
Median = 0.005
Mean = 0.005
Max = 0.005
Std dev = 0
n = 2

U	Undifferentiated (2)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

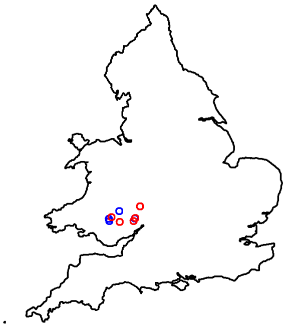
Lower Old Red Sandstone (LORS)

Carbon - fraction of inorganic (fIC)

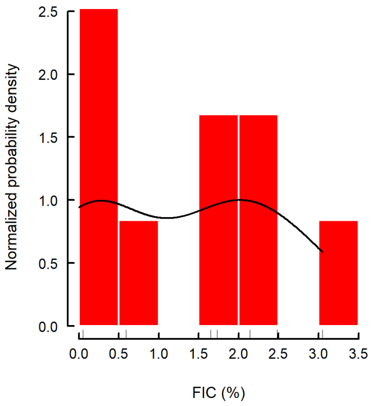
FIC (%)

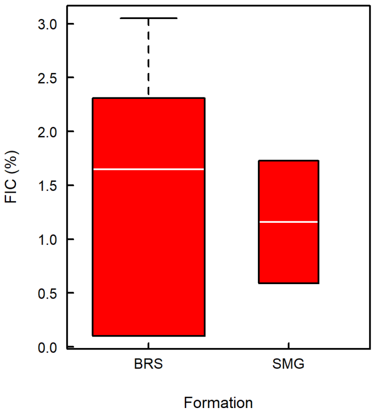
Min = 0.05
Median = 1.65
Mean = 1.31
Max = 3.05
Std dev = 1.15
n = 9

BRS	Brownstones Formation (7)
SMG	St Maughans Formation (2)



Blue points are below the median
Red points are at or above the median





Downton Group (DOW)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min	=	1.31
Median	=	1.31
Mean	=	1.31
Max	=	1.31
Std dev	=	NA
n	=	1

RG Raglan Mudstone Formation (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

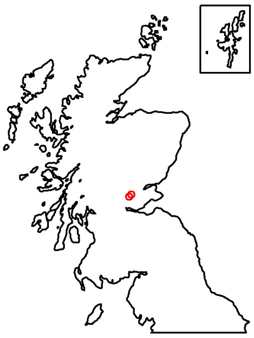
Arbuthnott-Garvock Group (ATGK)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min	=	0.09
Median	=	0.09
Mean	=	0.09
Max	=	0.09
Std dev	=	0
n	=	3

OVF Ochil Volcanic Formation (3)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

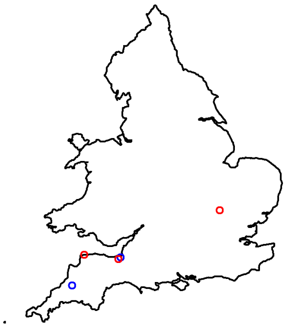
Other Devonian (XD)

Carbon - fraction of inorganic (fIC)

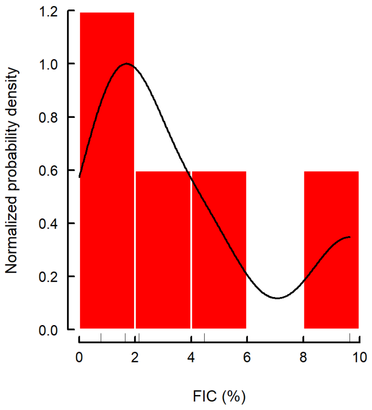
FIC (%)

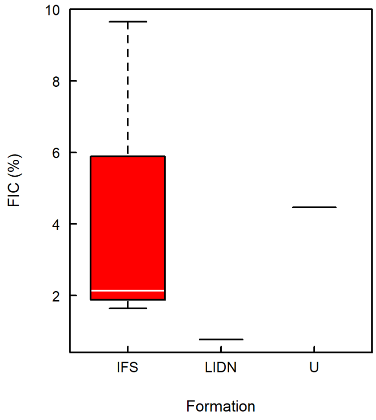
Min = 0.77
Median = 2.13
Mean = 3.73
Max = 9.65
Std dev = 3.58
n = 5

IFS	Ilfracombe Slates Formation (3)
LIDN	Liddaton Formation (1)
U	Undifferentiated (1)



Blue points are below the median
Red points are at or above the median





6.5.8 Pre-Devonian

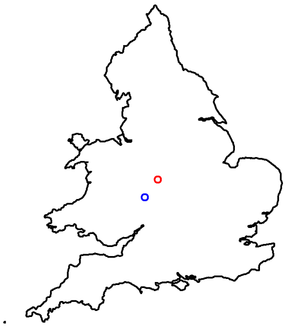
Lower Ludlow Shales Group (LLUS)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 1.26
Median = 1.93
Mean = 1.93
Max = 2.6
Std dev = 0.948
n = 2

U Undifferentiated (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Aberystwyth Grits Group (AGF)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 0.05
Median = 0.05
Mean = 0.05
Max = 0.05
Std dev = 0
n = 3

MYBA	Mynydd Bach Formation (3)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

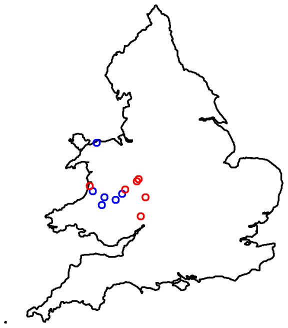
Other Silurian (XS)

Carbon - fraction of inorganic (fIC)

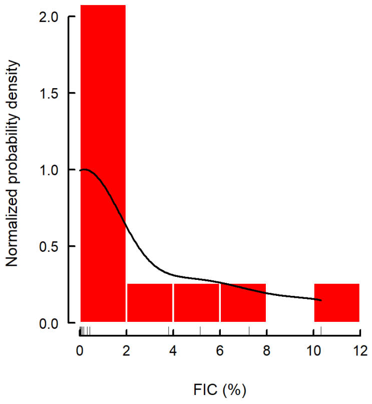
FIC (%)

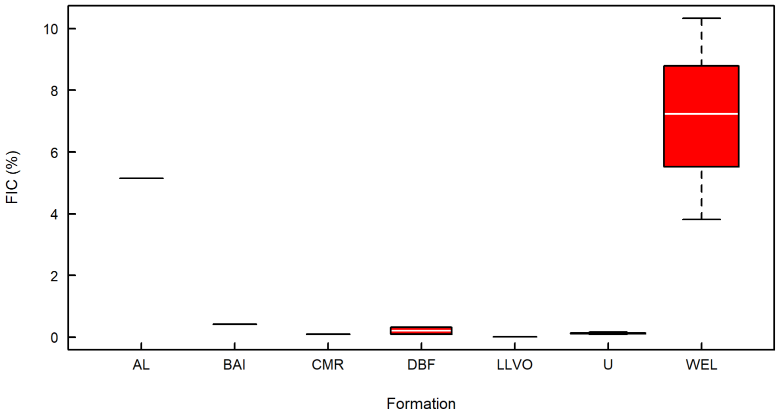
Min = 0.005
Median = 0.245
Mean = 2.31
Max = 10.3
Std dev = 3.52
n = 12

AL	Aymestry Limestone Formation (1)
BAI	Bailey Hill Formation (1)
CMR	Cwmere Formation (1)
DBF	Devil'S Bridge Formation (2)
LLVO	Llanwrtyd Volcanic Formation (1)
U	Undifferentiated (3)
WEL	Much Wenlock Limestone Formation (3)



Blue points are below the median
Red points are at or above the median





Builth Volcanic Group (BUVO)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min	=	0.005
Median	=	0.005
Mean	=	0.005
Max	=	0.005
Std dev	=	0
n	=	2

U	Undifferentiated (2)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

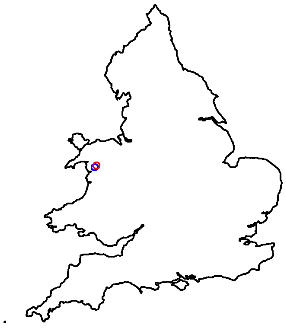
Mawddach Group (MWG)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min	=	0.05
Median	=	0.475
Mean	=	0.475
Max	=	0.9
Std dev	=	0.601
n	=	2

FF	Ffestiniog Flags Formation (1)
MW	Maentwrog Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

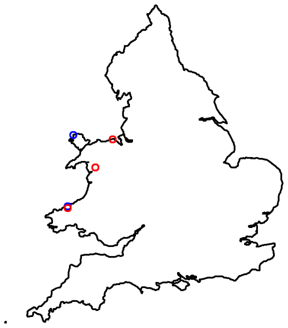
Other Ordovician (XO)

Carbon - fraction of inorganic (fIC)

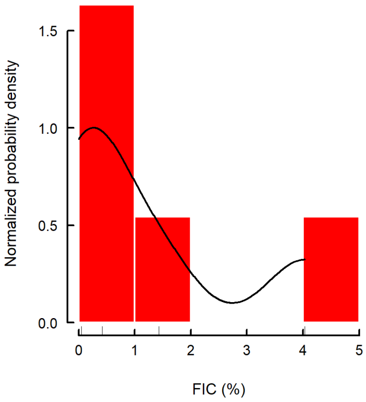
FIC (%)

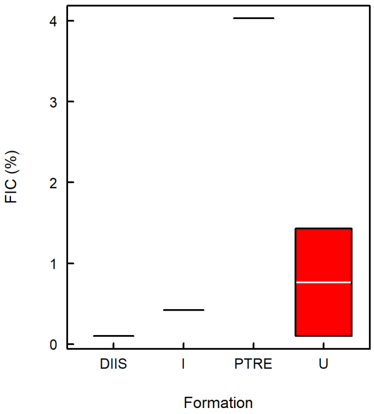
Min = 0.05
Median = 0.42
Mean = 1.2
Max = 4.03
Std dev = 1.68
n = 5

DIIS	Dinas Island Formation (1)
I	(1)
PTRE	Pentre Formation (1)
U	Undifferentiated (2)



Blue points are below the median
Red points are at or above the median





Mona Gneiss Suite (NMG)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 1.92
Median = 1.92
Mean = 1.92
Max = 1.92
Std dev = NA
n = 1

U	Undifferentiated (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

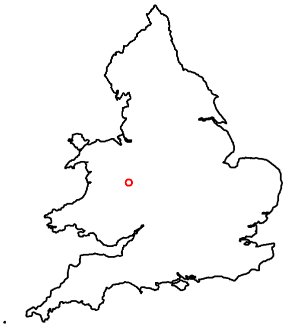
Stretton Group (YST)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 0.05
Median = 0.05
Mean = 0.05
Max = 0.05
Std dev = NA
n = 1

SYGP Synalds Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

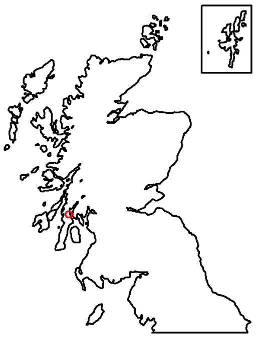
Argyll Group (ARGY)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 0.62
Median = 0.62
Mean = 0.62
Max = 0.62
Std dev = NA
n = 1

DBUE Upper Erins Quartzite Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

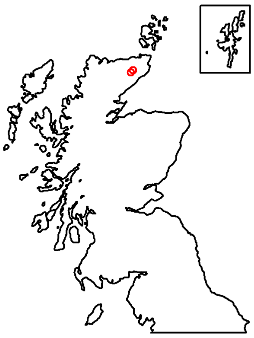
Loch Eil Group (LEIL)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 0.09
Median = 0.09
Mean = 0.09
Max = 0.09
Std dev = 0
n = 2

SUIS Suisgill Semipelite Formation (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Other Pre-Cambrian (XA)

Carbon - fraction of inorganic (fIC)

FIC (%)

Min = 0.05
Median = 0.05
Mean = 0.05
Max = 0.05
Std dev = NA
n = 1

U Undifferentiated (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

7 Extractable elements

7.1 USE AND INTERPRETATION OF EXTRACTABLE ELEMENT DATA

The use of experimental extraction measurements requires particular care in application. The different approaches and benefits of individual extraction approaches are discussed extensively in Section 7.2 below. As they are experimentally contrived measurements, rather than direct and absolute measurements of content there are inevitably limitations in how the data can be used. However, there is no doubt that the technique does provide a valuable tool for describing and comparing the geological formations, provided the data are used with the appropriate understanding of the limitations. The benefits for modelling of obtaining data for extractable Fe/Mn in particular were discussed further in Section 4.2. The analytical techniques used here also enable simultaneous determination of extractable SO_4 and these data are presented here also.

The 0.5 M acid-extraction used here is neither sufficiently strong to extract all elements from rocks (i.e. it will not dissolve most minerals) nor is it so weak that it reflects only soluble and readily-exchangeable elements. It should dissolve all the material that can be reasonably be expected to be labile under rather extreme environmental conditions such as acidic conditions and even to some extent reducing conditions. In particular, it provides an estimate of the readily soluble (and probably high-surface area) oxide materials notably of iron, manganese and aluminium, so-called ‘free’ material.

The concentration of extractable trace elements, many of which will often be associated with the above oxides, provides an indication of differences between different rock types. There is as yet no set of standards with which to relate the concentration of 0.5 M extractable trace elements to other properties but the opportunity for this will increase as the dataset increases.

Finally, it should be recognised that the concentration of extractable trace elements derived from these extraction experiments cannot be directly related to the likely concentrations found in water in contact with the mineral. A high concentration might indicate a particularly high ‘source’ term; equally, it might indicate a high ‘sink’ term. The acid extractant itself may actually enhance the uptake of some elements. For example, iron and aluminium oxides strongly bind phosphate, particularly at low pH. Therefore, addition of acid will dissolve and release phosphate associated from oxides that actually dissolve but will enhance the uptake of phosphate on the less soluble oxides that do not dissolve. The overall effect, as measured in the extract, will reflect the balance between these two processes.

7.2 MEASUREMENT OF EXTRACTABLE ELEMENTS

7.2.1 Analytical approaches

Two classes of methods have been developed for quantifying bioavailable Fe/Mn in geological materials. *Biotic* methods involve incubation of test material with iron-reducing bacteria. Fe/Mn consumption is then measured either directly or indirectly. *Abiotic* methods rely on chemical extractions that simulate bioreduction. They reductively dissolve a fraction of Fe/Mn that can be correlated with the bioavailable fraction.

Much of the attention in published literature on methods of analysis addressing bioavailability of sulphur has been concerned with biological or biochemical systems, such as uptake from food supplements or diet. in geological materials, with rather more concerned with sulphur in.

ABIOTIC METHOD FOR BIOAVAILABLE FE AND MN

Abiotic extraction methods which have been proposed are listed below, roughly in chronological order of their development.

0.5 M HCl. Several extraction times have been investigated, ranging from 1 hr (Heron et al., 1994b) through 24 hrs (Bekins et al., 2001; Cozzarelli et al., 2001; Tuccillo et al., 1999) to 3 days (Tuccillo et al., 1999). This extraction method leaves 95% of crystalline, less bioavailable Fe oxides (hematite, goethite, magnetite) undissolved (Broholm et al., 1998; Heron et al., 1994a).

5 M HCl. Using more concentrated acid at 90°C for 8 hours gives total extractable (non-structural) Fe and Mn (Chao and Zhou, 1983; Heron et al., 1994b). Fe mineral species that are less bioavailable, possibly magnetite (Fe_3O_4) or clay minerals with Fe in the structure, are extracted by 5 M HCl.

Ammonium oxalate. This method uses a 0.175 M ammonium oxalate – 0.1 M oxalic acid mixture (Tamm’s Reagent) in the dark (Chao and Zhou, 1983). Significant fractions of less-bioavailable magnetite or organic-complexed iron are dissolved. Therefore, this method is only specific to amorphous iron oxides in the absence of magnetite and organic matter complexes.

Hydroxylamine-hydrochloride. Extraction by 0.25 M hydroxylamine hydrochloride – 0.25 M HCl at 50°C for 30 minutes (1987). The authors considered this to be the best of five methods tested for extraction of amorphous iron(III) oxides on the basis of the short duration of the test, the minor dissolution of crystalline iron oxides (<1% of the total iron), specificity of the fraction extracted, and the close agreement with the benchmark Tamm’s reagent method, which is more difficult to perform. Less magnetite is extracted by this method than with the Tamm's reagent method. It is, therefore, considered more selective for amorphous Fe^{III} oxyhydroxide extraction compared with the latter method. However, this method extracts Fe^{II} as well as Fe^{III} and, therefore, overestimates the amount of amorphous Fe^{III} in reduced environments.

Hydroxylamine (acidic conditions). This is a development by Lovley and Phillips (Lovley and Phillips, 1986a) of the hydroxylamine hydrochloride method listed above. The modifications include reaction time and temperature, although a precise description of the method was not provided. It is reported as an improvement on the basis that, in contrast to acid extraction techniques, it does not extract high concentrations of Fe^{II} along with the Fe^{III}. Some good agreement was found between microbially reduced iron in a set of microcosm experiments and the fraction extracted by hydroxylamine (1991). However, the authors of both hydroxylamine methods reported inability of hydroxylamine to extract all of the amorphous/microbially reducible Fe^{III}. Therefore, the method does not give a quantitative value for microbially reducible Fe^{III}, but may be useful in identifying zones where Fe^{III} is available for microbial reduction. Lovley and Phillips conclude that the development of a technique which fully but selectively extracts all the amorphous Fe^{III} oxyhydroxides may not be possible.

Cr^{II} reagent. This method was proposed by Barcelona and Holm (1994a), but Heron et al (Ryan and Gschwend, 1991) considered the Cr^{II} reagent to be very unstable and reactive. Oxidation capacity determinations 15 to 20 times the expected values were obtained.

Ti^{III}-citrate. 0.05M Ti^{III} – 0.05M citrate – 0.05M EDTA with $NaHCO_3$ as pH buffer (Heron et al., 1994b; Tuccillo et al., 1999) reacted for 24 hrs (Tuccillo et al., 1999). The method is reported as extracting substantially larger fractions of hematite and goethite than the 0.5 M HCl method described above (Crouzet et al., 1998; Graf Pannatier, 1999; Heron et al., 1994a; Heron et al., 1994b).

Ti^{III}-EDTA. Extraction using a solution of 0.008 M Ti^{III} with 0.05 M EDTA (Heron et al., 1994a). This method is a further development of the Ti^{III}-citrate-EDTA method above using Ti^{III} as the reducing agent together with EDTA as a complexing agent. The citrate ligand and $NaHCO_3$ pH buffer were omitted to simplify the extraction and quantification reactions on the assumption that the buffering capacity of EDTA on its own was sufficient. The substantially reduced concentration of Ti^{III} still gives reasonable excess over the reducible fraction of most iron rich sediments, whilst the EDTA concentration was increased to just below its solubility limit. Excess of EDTA was intended to minimise competition for the Ti^{III} reductant from other cations that may be present.

This method has been found to reduce a well-described fraction of the total Fe/Mn minerals, namely ferrihydrite (98%), akageneite (100%), goethite and hematite (93%), magnetite (9%) and pyrolusite (99%), within an extraction period of 24 hrs (Broholm et al., 1998) although there is the possibility of interference from other reducible species e.g. sulphate and nitrate (Hacherl et al., 2001). The detection limit depends on accuracy of the redox titration and on the solid-solution ratio of the extraction: a detection limit of 4 μequiv g^{-1} was calculated for samples with a solid-solution ratio of approximately 1 g sediment to 10 mL of extractant.

Anthraquinone-2,6-disulfonate oxidation. This method is reported to provide a closer estimation of bioavailable iron oxides than other extraction methods (e.g. Lovley and Phillips, 1986a). Further study of the literature and possibly laboratory trials are required to verify the efficacy.

BIOTIC METHODS FOR BIOAVAILABLE FE AND MN

Laboratory microcosm assays can be either batch microcosms (e.g. Benner et al., 2002), or column experiments (Evans, 2000; Evans et al., 1999; Evans and Koenigsberg, 2001). These involve anaerobic incubation of aquifer material with amendments such as a carbon source (e.g. acetate), nutrients and iron reducing bacteria.

Bioavailable Ferric Iron Assay is a commercial product form of the microcosm assay (Roden and Urrutia, 2002). Reagent, including iron reducing bacteria, and nutrient is supplied in a dried state and incubated for a 30-day period in a test tube containing a sample of the sediment to be tested. Evolved iron(II) is measured using a colorimetric procedure (e.g. phenanthroline) or other method.

PREFERRED METHODS FOR BIOAVAILABLE FE AND MN

Conceptually, biotic tests employ the same type of microbiological, geochemical and physical processes as occur in the field to quantify reducible Fe/Mn. In contrast, abiotic methods use more aggressive physico-chemical processes to reduce a fraction of Fe/Mn that requires correlation with the microbiologically reducible fraction. Abiotic methods, therefore, attempt to simulate biotic processes and the latter provide a benchmark for the former.

A major disadvantage of biotic methods is the length of time it takes to conduct the assay. Even under conditions highly conducive to bioreduction, as in the case of the CDM assay, a 30-day incubation period is required. This disadvantage underscores the need to develop more rapid and tractable abiotic techniques, using biotic methods as the reference in one of two ways. The first approach employs ideal conditions for the bioreduction (e.g. ideal pH, electron donor concentration, nutrient availability) and quantifies the *potentially* bioavailable fraction. The second approach employs conditions as close as possible to ambient in an attempt to quantify the bioavailable fraction under *actual* aquifer conditions.

The definition of bioavailable Fe/Mn is clearly not straightforward. A range of factors – physical, geochemical, physiological, thermodynamic and mineralogical – controls bioavailability. Several of these controlling factors are environmental and hence vary from site to site. For example, the presence of humic acids or other natural ligands can influence the extent to which biogenic Fe^{II} is adsorbed onto Fe^{III} oxide and act as a barrier to further oxidation (Banfield and Hamers, 1997; Roden and Zachara, 1996). Hence, an advantage of biotic methods is that, unlike abiotic techniques, they are able to take into account the influence of some of these ambient conditions. The abiotic methods are perhaps better considered as providing only a 'potential' bioavailability. It seems reasonable, therefore, to calibrate abiotic methods against biotic methods in which the influence of ambient conditions has been eliminated. This allows standardisation of the biotic assay conditions, as with the CDM assay, and has the advantage of being simpler compared to reproducing ambient conditions in the incubation vessel. Caution must be exercised in the application of any laboratory measure of 'potential' bioavailable Fe/Mn to field conditions.

Sample disturbance and sample preparation must also be given careful consideration in the use of any of the methods. Particle size and available surface area have been found to influence bioavailability of iron oxyhydroxides (Lovley et al., 1993; Roden and Lovley, 1993) and are likely to be altered by compaction during transport or preparation methods such as disaggregation. Abiotic methods of determination will likewise be influenced by changes of particle size or surface area that impact availability of surface-active sites to reagents.

Nine abiotic methods of determining bioavailable Fe/Mn have been listed above. There is no clear line of distinction between bioavailable and biologically recalcitrant Fe/Mn oxides from the point of view of mineralogy. However, there is a consensus that less crystalline forms (e.g. amorphous iron oxyhydroxides) are more bioavailable than more crystalline forms (e.g. magnetite) (Heron et al., 1994a). Therefore, a possible, if relatively crude, criterion for selecting a suitable abiotic method of determination would be that it extracts a minimum of magnetite.

On the basis of this criterion, judgements can be made that:

- extraction using 5 M HCl and Tamm's reagent are not preferred, since they have been found to extract significant fractions of magnetite.
- Lovley's hydroxylamine method is claimed to be an advance on Chao's version so the latter need not be considered further, although Lovley found that his variation still failed to extract all of the amorphous Fe.
- the Cr^{II} reagent is reported to be unstable and too aggressive and is not preferred for this reason.
- extraction by Ti-Citrate-EDTA-$NaHCO_3$ is unsuitable since it is reported to extract substantially larger fractions of hematite and goethite compared with 0.5 M HCl.
- Heron's Ti-EDTA method is reported to extract a well-described and appropriate fraction of Fe/Mn minerals and has the added advantages of ease of quantification of the reducing agent and decreasing concentration of reducing agent to a level low enough for an appropriate quantification of reduction (McKeague, 1978).

Thus, assessment of the relative advantages and disadvantages of the various proposed abiotic methods results in a short-list of four extraction methods which merit further consideration: dilute HCl, hydroxylamine (acidic conditions), 0.008 M Ti^{III} – 0.05M EDTA and anthraquinone-2,6-disulfonate oxidation. The choice must be based on consideration of their practicability, reliability, cost and correlation with standardised biotic assays.

7.2.2 Preferred method of analysis

Extraction data recorded collected specifically for inclusion in this compilation were measured using the experimental procedures detailed below. It is clear from the review of previous published approaches that no single extraction method provides a universal solution, as different conditions and extractants will result in different yields. To characterise a rock fully, multiple extractions may be required, but the time and cost implications mitigate strongly against recommending multiple extractions as a routine approach for rapid and systematic characterisation of large number of samples. For the purposes of this compilation a single cold 0.5 M HCl extraction was chosen as being the best compromise. It has the benefits of ease and simplicity, being a moderately easy analytical matrix (although not as good in this respect as HNO_3), and of being sufficiently, but not overly, aggressive, removing the 'bioavailable' elements, without breaking down the more crystalline forms.

A portion of crushed and milled sample is placed into wide-necked, screw-top HDPE bottles and extracted into 0.5M HCl using a 1:20 solid/solution ratio. Usually 10 g in 200 mL is considered to be sufficient to provide a representative sample and avoid problems of small-scale heterogeneity. Where available sample weight is low then a smaller volume can be used, but the soil solution ratio is kept constant, e.g. 2.5 g of sample extracted into 50 mL HCl. The addition of acid has to be carried out carefully as many of the samples react energetically with the acid due to the presence of carbonate rocks. This poses a second problem for the extractions, as if the carbonate neutralises the acid significantly then the extractions will not all be under comparable conditions. To address this an additional aliquot of concentrated acid (6 M HCl) is added to each sample reaction vessel. The quantity of extra acid is calculated, from the result of the f_{IC} determination, to be sufficient to exactly neutralise the inorganic carbon content of the sample and leave approx. 0.5 M HCl as the extraction reagent.

After acidification the sample is shaken vigorously (up to 200 min^{-1}) for 24 hours, with the bottle caps firmly closed. Samples are then centrifuged at 8000 rpm (10 minutes) to achieve good phase separation, before being filtered (0.45 μm) and transferred to clean sample bottles pending analysis.

Analysis is carried out by Inductively-Coupled Plasma Optical-Emission Spectrometry (ICP-OES) or Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) depending on the element. Matrix matched standards may be used to improve analytical performance. The ICP techniques enable simultaneous determination of multiple elements; the concentration of (mainly metal) elements measured in the final filtered extraction solutions is converted back to give the extractable, and hence 'bioavailable' concentrations of the original solid samples (mg kg^1).

7.3 SUMMARY AND OVERVIEW OF EXTRACTION DATA

Available data for measurement of extractable Fe, Mn and S are presented in the following table for lithostratigraphical attributions at the Group level. For finer resolution showing data at Formation level please consult the figures in Sections 7.4, 7.4.1 and 7.5.1 respectively.

Table 7.1 Overall summary statistical values for extractable Fe data, tabulated by lithostratigraphical Group. Units of mg kg^{-1}.

LEX code	Group name	Min	P25	Median	Mean	P75	Max	n
	Quaternary							
GDU	Glacial Deposits	5080	8680	12300	12300	15900	19500	2
DUNW	Dunwich Group	542	542	542	542	542	542	1
	Palaeogene							
BA	Barton Group	379	379	379	379	379	379	1
BRB	Bracklesham Group	6210	6210	6210	6210	6210	6210	1
THAM	Thames Group	778	1560	3950	4340	4150	12400	6
LMBE	Lambeth Group	275	372	678	1330	1620	3710	5
XG	Other Palaeogene	959	1420	5740	13700	16300	44200	5
	Cretaceous							
CK	Chalk Group	4	224	285	392	532	1300	31
SELB	Selborne Group	1540	1820	2100	2720	2320	5840	5
W	Wealden Group	260	604	1360	6410	4180	28400	10
PB	Purbeck Group	9910	12700	15500	15500	18300	21200	2
XK	Other Cretaceous	16	2040	4650	18300	35300	76100	12
	Jurassic							
PL	Portland Group	92	127	254	944	1070	3180	4
AMG	Ancholme Group	3520	3930	4940	10400	10700	31900	11
CR	Corallian Group	333	2820	3710	7640	7780	36700	9
GOG	Great Oolite Group	4	736	3140	4030	5590	13500	30
INO	Inferior Oolite Group	4	739	2120	4500	3160	26400	9
RAG	Ravenscar Group	843	2320	3800	3800	5280	6750	2
LI	Lias Group	1020	2640	4910	8040	9640	24400	20
XJ	Other Jurassic	1680	1680	1680	1680	1680	1680	1
	Triassic							
PNG	Penarth Group	1380	1610	1840	1840	2060	2290	2
MMG	Mercia Mudstone Group	21	585	944	1390	1690	5450	29
SSG	Sherwood Sandstone Group	54	342	561	1060	885	6940	30
	Permian							
ZG	Zechstein Group	4	181	627	1090	1430	3780	7
EXE	Exeter Group	710	1780	2840	2840	3910	4980	2
WAWK	Warwickshire Group	278	278	278	278	278	278	1
XP	Other Permian	119	171	256	281	386	472	5

LEX code	Group name	Min	P25	Median	Mean	P75	Max	n
	Carboniferous							
PCM	Pennine Coal Measures Group	182	3350	6980	13100	16300	72600	24
HOWY	Holsworthy Group	2040	2500	2950	2950	3410	3870	2
MG	Millstone Grit Group	282	2110	3510	6350	8250	23800	15
YORE	Yoredale Group	870	870	870	870	870	870	1
CRAV	Craven Group	1650	1750	3440	6850	11300	16800	7
GSCL	Great Scar Limestone Group	4	55.2	106	106	158	209	2
PKLM	Peak Limestone Group	44	75	560	514	835	1060	5
BOHI	Bowland High Group	207	457	1360	1360	2120	2680	6
TRG	Transition Group (Devonian-Carboniferous)	19300	19300	19300	19300	19300	19300	1
XCL	Other Carb. Limestone Supergroup	4	148	1180	11600	2060	64800	6
XC	Other Carboniferous	304	2750	5200	5200	7660	10100	2
XCU	Other Culm Supergroup	61200	61200	61200	61200	61200	61200	1
	Devonian							
EXM	Exmoor Group	2620	2620	2620	2620	2620	2620	1
MDT	Meadfoot Group	143	385	626	626	868	1110	2
LORS	Lower Old Red Sandstone	185	421	568	739	585	1890	9
DOW	Downton Group	2230	2230	2230	2230	2230	2230	1
XD	Other Devonian	670	2100	3480	5480	6860	14300	4
	Pre-Devonian							
LLUS	Lower Ludlow Shales Group	3380	4800	6230	6230	7650	9070	2
AGF	Aberystwyth Grits Group	3240	3410	3580	3690	3920	4250	3
XS	Other Silurian	1380	2480	3340	5800	4500	26400	11
BUVO	Builth Volcanic Group	13300	13500	13700	13700	14000	14200	2
MWG	Mawddach Group	1690	1720	1750	1750	1780	1810	2
XO	Other Ordovician	1160	1600	2240	3390	4030	7920	4
XA	Other Pre-Cambrian	1750	1750	1750	1750	1750	1750	1
YST	Stretton Group	1040	1040	1040	1040	1040	1040	1

Table 7.2 Overall summary statistical values for extractable Mn data, tabulated by lithostratigraphical Group. Units of mg kg^{-1}.

LEX code	Group name	Min	P25	Median	Mean	P75	Max	n
	Quaternary							
GDU	Glacial Deposits	514	566	618	618	669	721	2
DUNW	Dunwich Group	80	80	80	80	80	80	1
	Palaeogene							
BA	Barton Group	13	13	13	13	13	13	1
BRB	Bracklesham Group	4	4	4	4	4	4	1
THAM	Thames Group	7	9.75	19	39.8	39.5	141	6
LMBE	Lambeth Group	2	3	4	12.6	26	28	5
XG	Other Palaeogene	4	19	22	205	485	494	5
	Cretaceous							
CK	Chalk Group	86	186	233	322	296	1140	31
SELB	Selborne Group	10	53	123	234	186	797	5
W	Wealden Group	9	26	65	231	127	949	10
PB	Purbeck Group	881	914	946	946	979	1010	2
XK	Other Cretaceous	2	12	128	355	548	1430	12
	Jurassic							
PL	Portland Group	27	45	72.5	81.2	109	153	4
AMG	Ancholme Group	43	86.5	111	140	183	334	11
CR	Corallian Group	58	108	229	299	416	622	9
GOG	Great Oolite Group	3	165	317	299	370	850	30
INO	Inferior Oolite Group	2	93	108	234	146	1310	9
RAG	Ravenscar Group	3	41.8	80.5	80.5	119	158	2
LI	Lias Group	43	165	256	468	353	2970	20
XJ	Other Jurassic	293	293	293	293	293	293	1
	Triassic							
PNG	Penarth Group	220	224	228	228	232	236	2
MMG	Mercia Mudstone Group	18	168	287	413	493	1810	29
SSG	Sherwood Sandstone Group	3	30.8	62	214	162	1920	30
	Permian							
ZG	Zechstein Group	82	110	111	147	184	244	7
EXE	Exeter Group	247	305	364	364	422	480	2
WAWK	Warwickshire Group	157	157	157	157	157	157	1
XP	Other Permian	9	16	18	21	24	38	5

LEX code	Group name	Min	P25	Median	Mean	P75	Max	n
	Carboniferous							
PCM	Pennine Coal Measures Group	2	74	284	682	838	3120	24
HOWY	Holsworthy Group	40	60.5	81	81	102	122	2
MG	Millstone Grit Group	17	25.5	88	326	160	2820	15
YORE	Yoredale Group	468	468	468	468	468	468	1
CRAV	Craven Group	88	162	260	383	582	847	7
GSCL	Great Scar Limestone Group	90	144	199	199	254	308	2
PKLM	Peak Limestone Group	129	271	326	506	728	1080	5
BOHI	Bowland High Group	130	152	379	505	791	1140	6
TRG	Transition Group (Devonian-Carboniferous)	2260	2260	2260	2260	2260	2260	1
XCL	Other Carb. Limestone Supergroup	10	29.2	94.5	495	339	2340	6
XC	Other Carboniferous	56	58.5	61	61	63.5	66	2
XCU	Other Culm Supergroup	9150	9150	9150	9150	9150	9150	1
	Devonian							
EXM	Exmoor Group	452	452	452	452	452	452	1
MDT	Meadfoot Group	3	57.2	112	112	166	220	2
LORS	Lower Old Red Sandstone	45	180	515	534	765	1100	9
DOW	Downton Group	392	392	392	392	392	392	1
XD	Other Devonian	562	782	1420	1380	2010	2110	4
	Pre-Devonian							
LLUS	Lower Ludlow Shales Group	312	420	529	529	638	746	2
AGF	Aberystwyth Grits Group	14	22	30	28.7	36	42	3
XS	Other Silurian	28	119	451	542	653	1760	11
BUVO	Builth Volcanic Group	170	336	502	502	667	833	2
MWG	Mawddach Group	29	203	377	377	551	725	2
XO	Other Ordovician	13	17.5	83.5	166	232	484	4
XA	Other Pre-Cambrian	90	90	90	90	90	90	1
YST	Stretton Group	57	57	57	57	57	57	1

Table 7.3 Overall summary statistical values for extractable S data, tabulated by lithostratigraphical Group. Measurements are expressed as SO_4, in units of mg kg^{-1}.

LEX code	Group name	Min	P25	Median	Mean	P75	Max	n
	Quaternary							
GDU	Glacial Deposits	30	52	74	74	96	118	2
DUNW	Dunwich Group	30	30	30	30	30	30	1
	Palaeogene							
BA	Barton Group	30	30	30	30	30	30	1
BRB	Bracklesham Group	15600	15600	15600	15600	15600	15600	1
THAM	Thames Group	30	653	2510	3860	3680	14000	6
LMBE	Lambeth Group	30	30	265	819	571	3200	5
XG	Other Palaeogene	806	1240	1960	4290	7580	9900	5
	Cretaceous							
CK	Chalk Group	30	30	30	68.3	30	326	31
SELB	Selborne Group	850	878	1060	1530	2160	2700	5
W	Wealden Group	30	30	30	260	248	1190	10
PB	Purbeck Group	1510	2000	2500	2500	2990	3490	2
XK	Other Cretaceous	30	54.8	2140	4290	6890	15800	12
	Jurassic							
PL	Portland Group	30	771	1240	1910	2380	5120	4
AMG	Ancholme Group	737	2300	5260	7930	11800	23200	11
CR	Corallian Group	30	939	3740	5240	7020	21500	9
GOG	Great Oolite Group	30	442	2390	7270	7990	61800	30
INO	Inferior Oolite Group	30	136	1520	4040	3200	14800	9
RAG	Ravenscar Group	30	2760	5480	5480	8200	10900	2
LI	Lias Group	30	1540	2220	5920	5490	44500	20
XJ	Other Jurassic	5920	5920	5920	5920	5920	5920	1
	Triassic							
PNG	Penarth Group	1540	1670	1800	1800	1930	2060	2
MMG	Mercia Mudstone Group	30	61	1740	22500	28800	128000	29
SSG	Sherwood Sandstone Group	30	30	30	680	30	16700	30
	Permian							
ZG	Zechstein Group	30	226	454	19300	979	132000	7
EXE	Exeter Group	30	30	30	30	30	30	2
WAWK	Warwickshire Group	30	30	30	30	30	30	1
XP	Other Permian	30	30	30	30	30	30	5

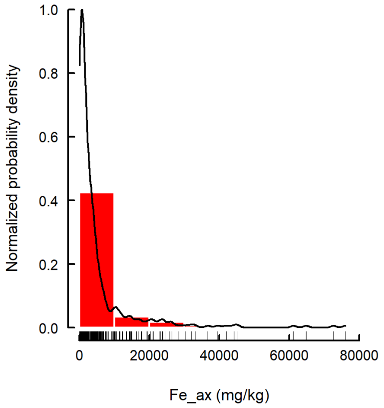
LEX code	Group name	Min	P25	Median	Mean	P75	Max	n
	Carboniferous							
PCM	Pennine Coal Measures Group	30	30	30	1180	254	12200	24
HOWY	Holsworthy Group	30	30	30	30	30	30	2
MG	Millstone Grit Group	30	138	458	3640	2760	20500	15
YORE	Yoredale Group	1730	1730	1730	1730	1730	1730	1
CRAV	Craven Group	30	116	562	10500	662	71600	7
GSCL	Great Scar Limestone Group	30	30	30	30	30	30	2
PKLM	Peak Limestone Group	30	30	30	177	120	675	5
BOHI	Bowland High Group	30	30	247	546	808	1800	6
TRG	Transition Group (Devonian-Carboniferous)	30	30	30	30	30	30	1
XCL	Other Carb. Limestone Supergroup	30	44	134	929	254	4970	6
XC	Other Carboniferous	206	1460	2710	2710	3960	5210	2
XCU	Other Culm Supergroup	131	131	131	131	131	131	1
	Devonian							
EXM	Exmoor Group	30	30	30	30	30	30	1
MDT	Meadfoot Group	30	30	30	30	30	30	2
LORS	Lower Old Red Sandstone	30	30	30	30	30	30	9
DOW	Downton Group	189	189	189	189	189	189	1
XD	Other Devonian	30	30	30	326	326	1210	4
	Pre-Devonian							
LLUS	Lower Ludlow Shales Group	30	30	30	30	30	30	2
AGF	Aberystwyth Grits Group	30	30	30	87.3	116	202	3
XS	Other Silurian	30	30	30	145	30	1290	11
BUVO	Builth Volcanic Group	30	166	301	301	436	572	2
MWG	Mawddach Group	30	60.8	91.5	91.5	122	153	2
XO	Other Ordovician	86	431	700	803	1070	1730	4
XA	Other Pre-Cambrian	30	30	30	30	30	30	1
YST	Stretton Group	30	30	30	30	30	30	1

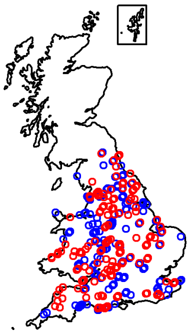
7.4 GEOLOGICAL ATLAS OF DATA FOR EXTRACTABLE FE

All Groups (All)

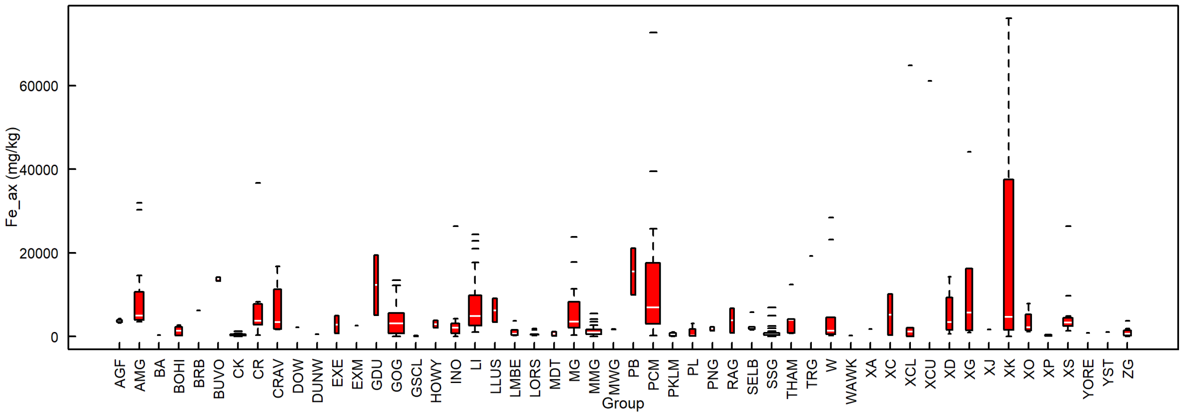
Extractable Fe

Fe_ax (mg/kg)





Blue points are below the median
Red points are at or above the median



7.4.1 Quaternary and Neogene

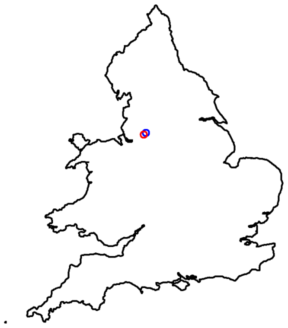
Glacial Deposits (GDU)

Extractable Fe

Fe_ax (mg/kg)

Min = 5080
Median = 12300
Mean = 12300
Max = 19500
Std dev = 10200
n = 2

U Undifferentiated (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Dunwich Group (DUNW)

Extractable Fe

Fe_ax (mg/kg)

Min = 542
Median = 542
Mean = 542
Max = 542
Std dev = NA
n = 1

KGCA Kesgrave Catchment Subgroup (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Palaeogene

Barton Group (BA)

Extractable Fe

Fe_ax (mg/kg)

Min = 379
Median = 379
Mean = 379
Max = 379
Std dev = NA
n = 1

BECH Becton Sand and Chama Sand Fms (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Bracklesham Group (BRB)

Extractable Fe

Fe_ax (mg/kg)

Min = 6210
Median = 6210
Mean = 6210
Max = 6210
Std dev = NA
n = 1

WTT	Wittering Formation (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

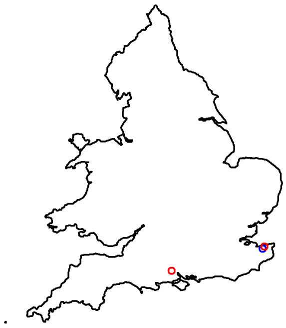
Thames Group (THAM)

Extractable Fe

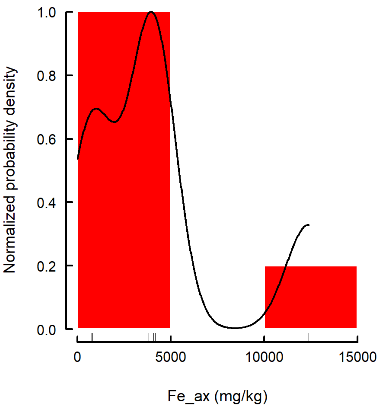
Fe_ax (mg/kg)

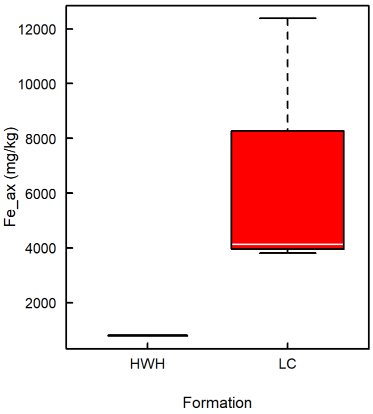
Min = 778
Median = 3950
Mean = 4340
Max = 12400
Std dev = 4250
n = 6

HWH	Harwich Formation (2)
LC	London Clay Formation (4)



Blue points are below the median
Red points are at or above the median





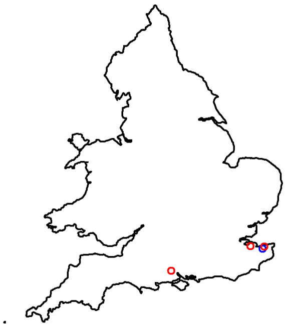
Lambeth Group (LMBE)

Extractable Fe

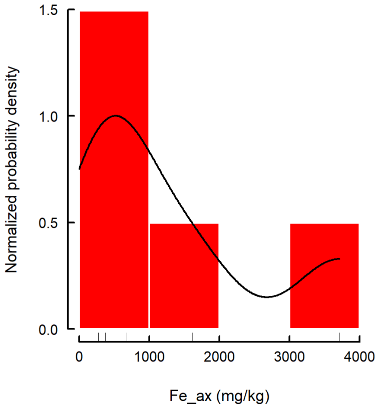
Fe_ax (mg/kg)

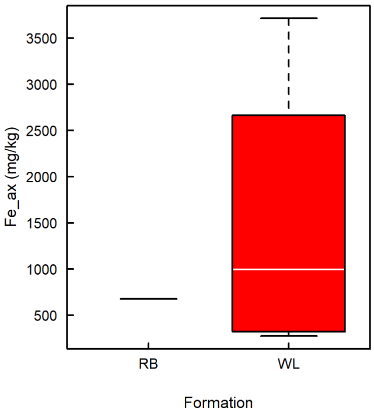
Min = 275
Median = 678
Mean = 1330
Max = 3710
Std dev = 1430
n = 5

RB	Reading Formation (1)
WL	Woolwich Formation (4)



Blue points are below the median
Red points are at or above the median





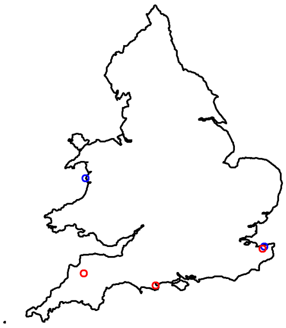
Other Palaeogene (XG)

Extractable Fe

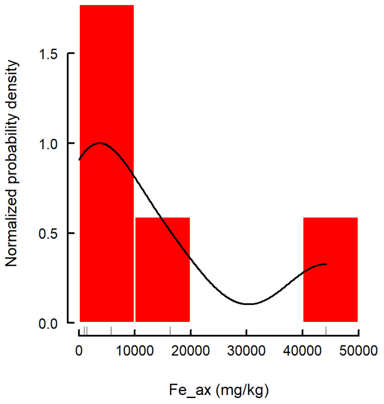
Fe_ax (mg/kg)

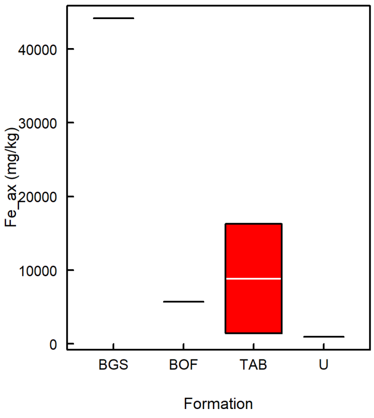
Min = 959
Median = 5740
Mean = 13700
Max = 44200
Std dev = 18100
n = 5

BGS	Bagshot Formation (1)
BOF	Bovey Formation (1)
TAB	Thanet Formation (2)
U	Undifferentiated (1)



Blue points are below the median
Red points are at or above the median





7.4.2 Cretaceous

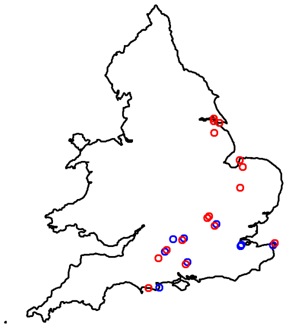
Chalk Group (CK)

Extractable Fe

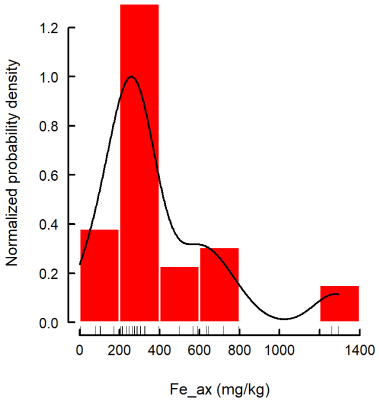
Fe_ax (mg/kg)

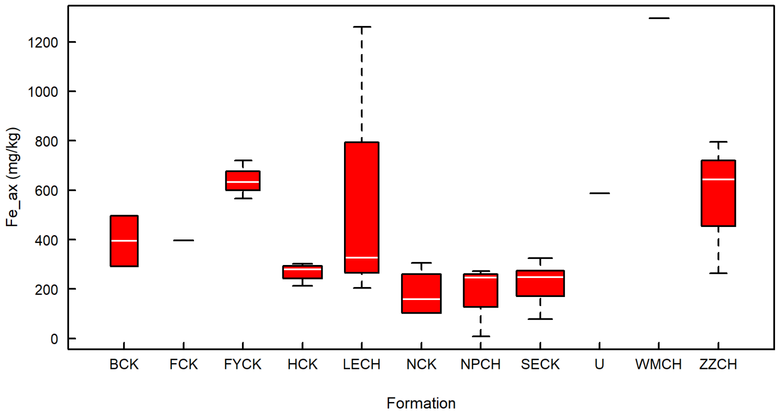
Min = 4
Median = 285
Mean = 392
Max = 1300
Std dev = 304
n = 31

BCK	Burnham Chalk Formation (2)
FCK	Flamborough Chalk Formation (1)
FYCK	Ferriby Chalk Formation (3)
HCK	Holywell Nodular Chalk Formation (4)
LECH	Lewes Nodular Chalk Formation (3)
NCK	Newhaven Chalk Formation (4)
NPCH	New Pit Chalk Formation (3)
SECK	Seaford Chalk Formation (6)
U	Undifferentiated (1)
WMCH	West Melbury Marly Chalk Formation (1)
ZZCH	Zig Zag Chalk Formation (3)



Blue points are below the median
Red points are at or above the median





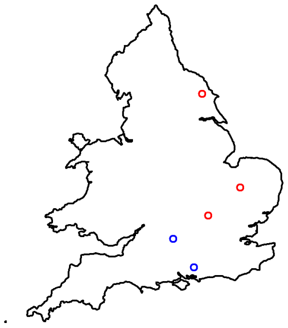
Selborne Group (SELB)

Extractable Fe

Fe_ax (mg/kg)

Min = 1540
Median = 2100
Mean = 2720
Max = 5840
Std dev = 1760
n = 5

GLT	Gault Formation (2)
UGS	Upper Greensand Formation (3)



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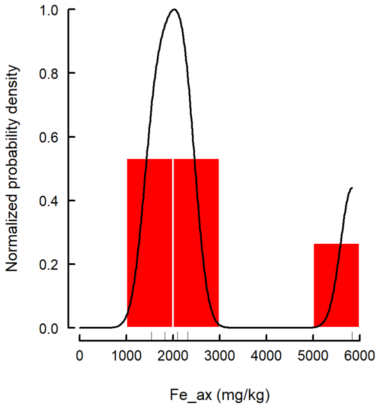
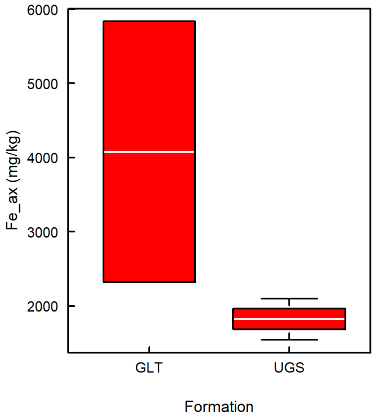




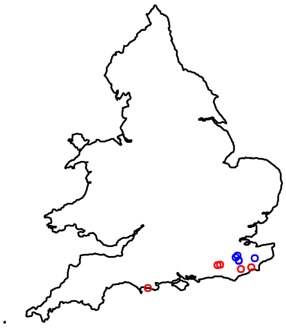
Wealden Group (W)

Extractable Fe

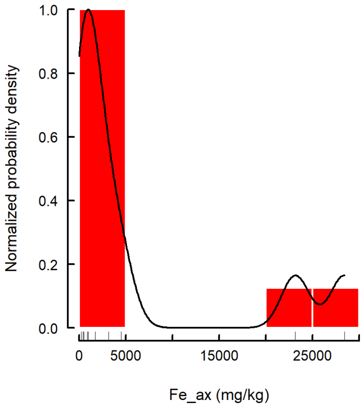
Fe_ax (mg/kg)

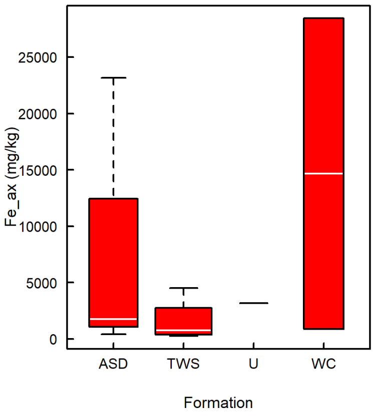
Min = 260
Median = 1360
Mean = 6410
Max = 28400
Std dev = 10400
n = 10

ASD	Ashdown Formation (3)
TWS	Tunbridge Wells Sand Formation (4)
U	Undifferentiated (1)
WC	Weald Clay Formation (2)



Blue points are below the median
Red points are at or above the median





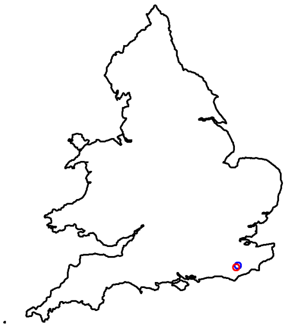
Purbeck Group (PB)

Extractable Fe

Fe_ax (mg/kg)

Min = 9910
Median = 15500
Mean = 15500
Max = 21100
Std dev = 7950
n = 2

DURN	Durlston Formation (1)
LULW	Lulworth Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

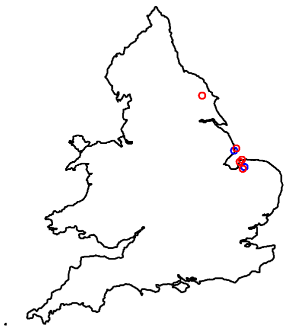
Other Cretaceous (XK)

Extractable Fe

Fe_ax (mg/kg)

Min = 16
Median = 4650
Mean = 18300
Max = 76100
Std dev = 24800
n = 12

CA	Carstone Formation (2)
DEB	Dersingham Formation (2)
HUCK	Hunstanton Formation (2)
ROH	Roach Formation (2)
SAS	Sandringham Sand Formation (3)
SPC	Speeton Clay Formation (1)



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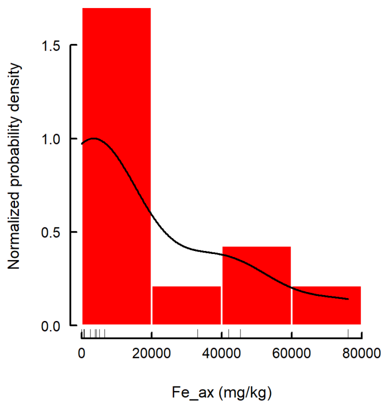
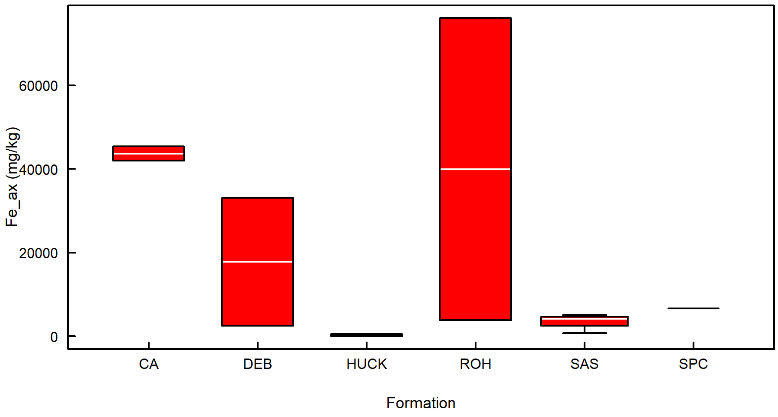
Red points are at or above the median





7.4.3 Jurassic

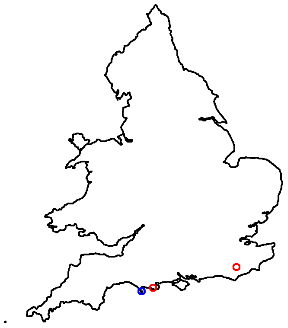
Portland Group (PL)

Extractable Fe

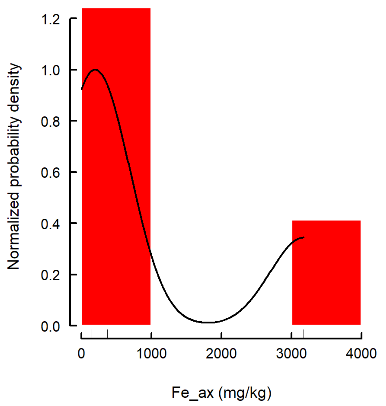
Fe_ax (mg/kg)

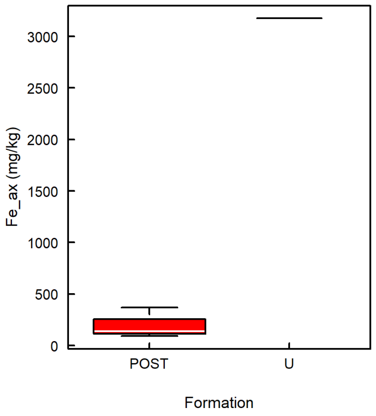
Min = 92
Median = 254
Mean = 944
Max = 3180
Std dev = 1490
n = 4

POST	Portland Stone Formation (3)
U	Undifferentiated (1)



Blue points are below the median
Red points are at or above the median





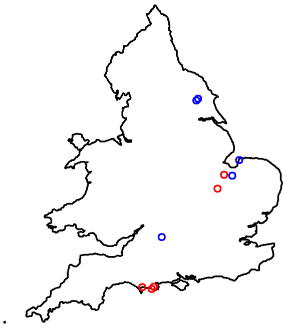
Ancholme Group (AMG)

Extractable Fe

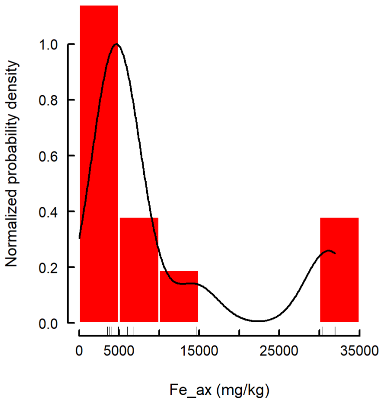
Fe_ax (mg/kg)

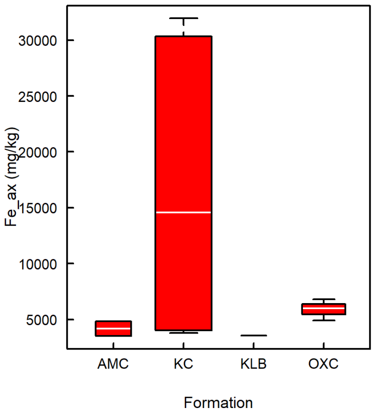
Min = 3520
Median = 4940
Mean = 10400
Max = 31900
Std dev = 10700
n = 11

AMC	Ampthill Clay Formation (2)
KC	Kimmeridge Clay Formation (5)
KLB	Kellaways Formation (1)
OXC	Oxford Clay Formation (3)



Blue points are below the median
Red points are at or above the median





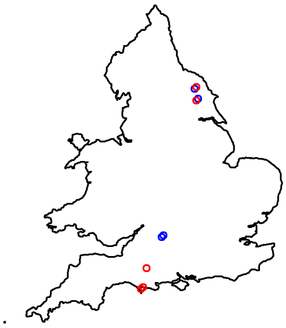
Corallian Group (CR)

Extractable Fe

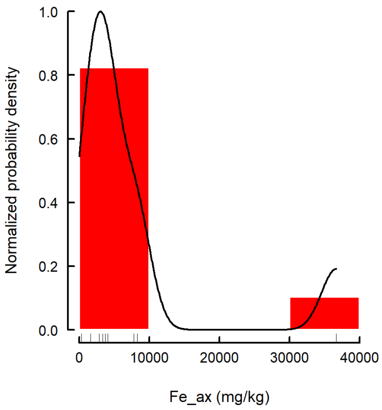
Fe_ax (mg/kg)

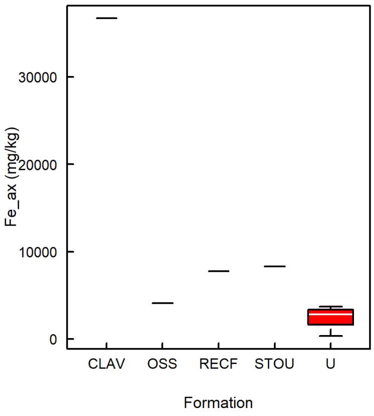
Min = 333
Median = 3710
Mean = 7640
Max = 36700
Std dev = 11200
n = 9

CLAV	Clavellata Formation (1)
OSS	Osmington Oolite Formation (1)
RECF	Redcliff Formation (1)
STOU	Stour Formation (1)
U	Undifferentiated (5)



Blue points are below the median
Red points are at or above the median





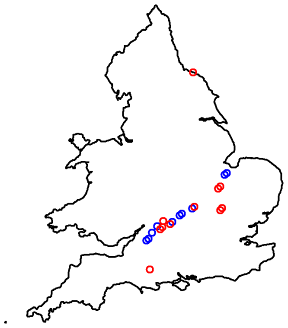
Great Oolite Group (GOG)

Extractable Fe

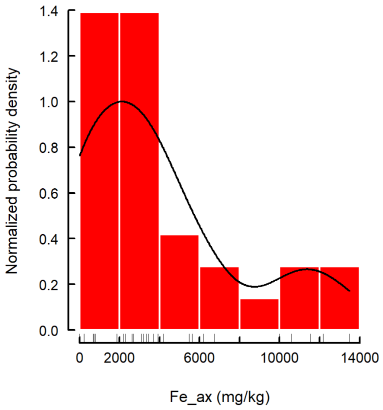
Fe_ax (mg/kg)

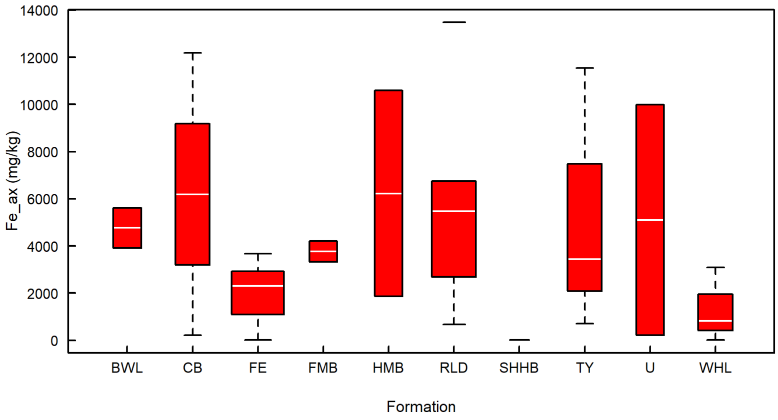
Min = 4
Median = 3140
Mean = 4030
Max = 13500
Std dev = 3950
n = 30

BWL	Blisworth Limestone Formation (2)
CB	Cornbrash Formation (3)
FE	Fuller'S Earth Formation (7)
FMB	Forest Marble Formation (2)
HMB	Hampen Formation (2)
RLD	Rutland Formation (5)
SHHB	Sharp'S Hill Formation (1)
TY	Taynton Limestone Formation (3)
U	Undifferentiated (2)
WHL	White Limestone Formation (3)



Blue points are below the median
Red points are at or above the median





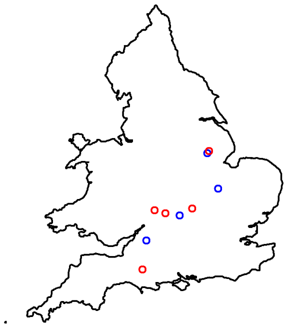
Inferior Oolite Group (INO)

Extractable Fe

Fe_ax (mg/kg)

Min = 4
Median = 2120
Mean = 4500
Max = 26400
Std dev = 8320
n = 9

BLPL	Birdlip Limestone Formation (2)
GRF	Grantham Formation (2)
LL	Lincolnshire Limestone Formation (2)
NS	Northampton Sand Formation (1)
U	Undifferentiated (2)



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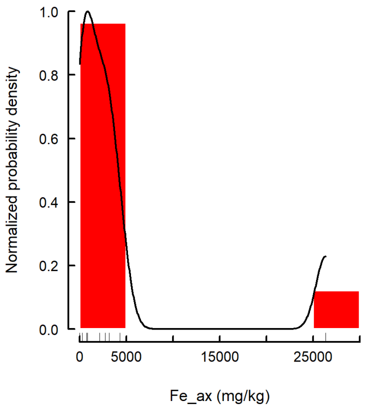
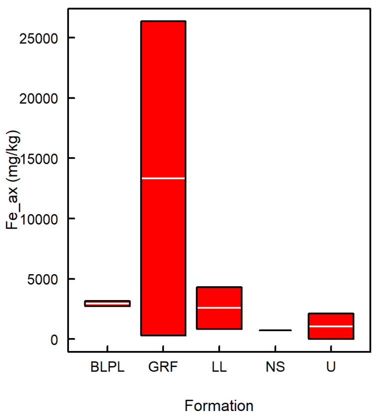
Red points are at or above the median





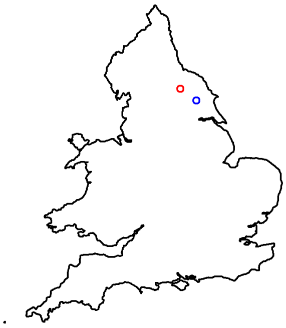
Ravenscar Group (RAG)

Extractable Fe

Fe_ax (mg/kg)

Min = 843
Median = 3800
Mean = 3800
Max = 6750
Std dev = 4180
n = 2

SCY	Scalby Formation (1)
U	Undifferentiated (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

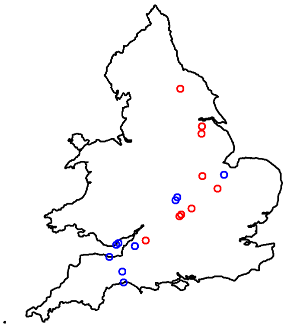
Lias Group (LI)

Extractable Fe

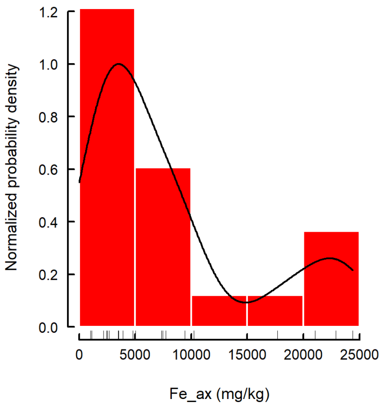
Fe_ax (mg/kg)

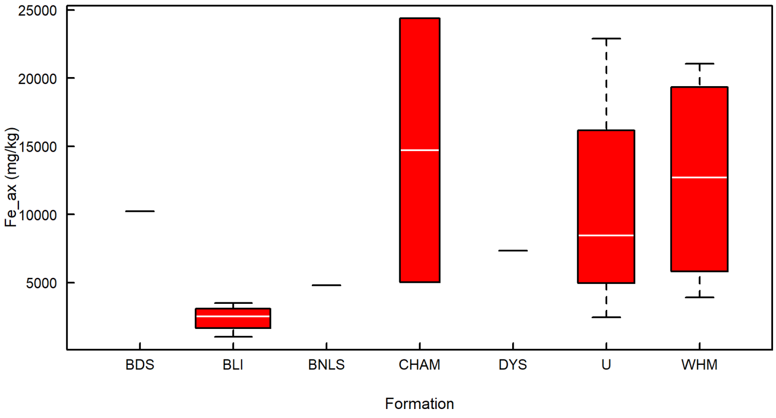
Min = 1020
Median = 4910
Mean = 8040
Max = 24400
Std dev = 7460
n = 20

BDS	Bridport Sand Formation (1)
BLI	Blue Lias Formation (7)
BNLS	Beacon Limestone Formation (1)
CHAM	Charmouth Mudstone Formation (2)
DYS	Dyrham Formation (1)
U	Undifferentiated (4)
WHM	Whitby Mudstone Formation (4)



Blue points are below the median
Red points are at or above the median





Other Jurassic (XJ)

Extractable Fe

Fe_ax (mg/kg)

Min = 1680
Median = 1680
Mean = 1680
Max = 1680
Std dev = NA
n = 1

SAS Sandringham Sand Formation (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

7.4.4 Triassic

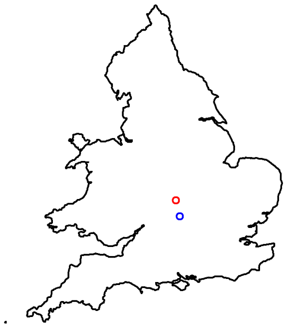
Penarth Group (PNG)

Extractable Fe

Fe_ax (mg/kg)

Min = 1380
Median = 1840
Mean = 1840
Max = 2290
Std dev = 639
n = 2

U Undifferentiated (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

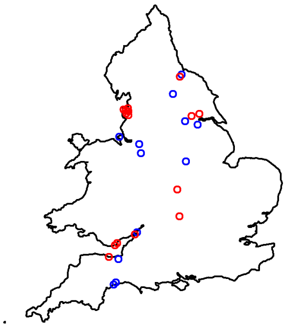
Mercia Mudstone Group (MMG)

Extractable Fe

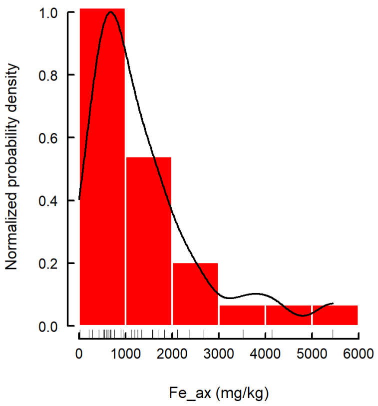
Fe_ax (mg/kg)

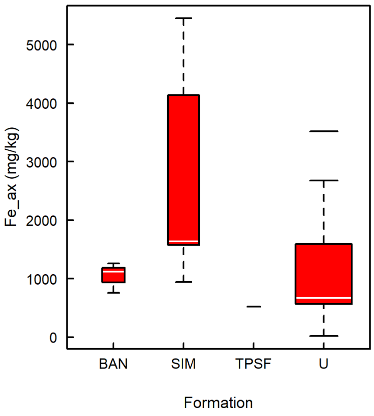
Min = 21
Median = 944
Mean = 1390
Max = 5450
Std dev = 1240
n = 29

BAN	Blue Anchor Formation (3)
SIM	Sidmouth Mudstone Formation (6)
TPSF	Tarporley Siltstone Formation (1)
U	Undifferentiated (19)



Blue points are below the median
Red points are at or above the median





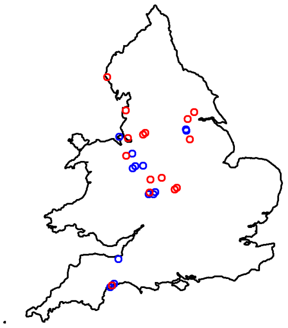
Sherwood Sandstone Group (SSG)

Extractable Fe

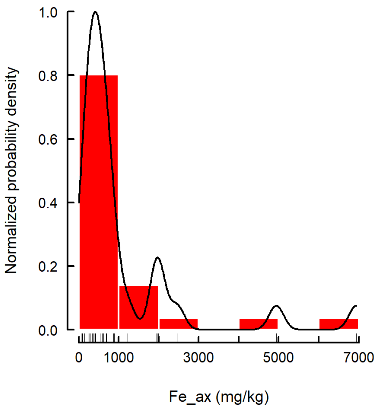
Fe_ax (mg/kg)

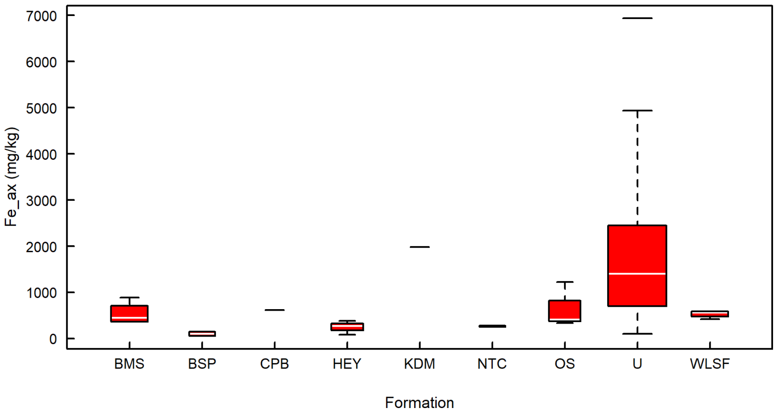
Min = 54
Median = 561
Mean = 1060
Max = 6940
Std dev = 1490
n = 30

BMS	Bromsgrove Sandstone Formation (4)
BSP	Budleigh Salterton Pebble Beds Formation (2
CPB	Chester Pebble Beds Formation (1)
HEY	Helsby Sandstone Formation (3)
KDM	Kidderminster Formation (1)
NTC	Nottingham Castle Sandstone Formation (2)
OS	Otter Sandstone Formation (3)
U	Undifferentiated (10)
WLSF	Wilmslow Sandstone Formation (4)



Blue points are below the median
Red points are at or above the median





7.4.5 Permian

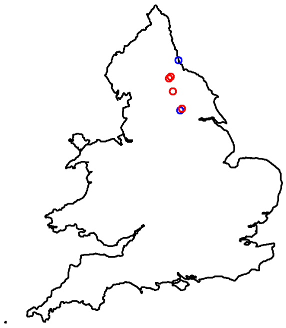
Zechstein Group (ZG)

Extractable Fe

Fe_ax (mg/kg)

Min = 4
Median = 627
Mean = 1090
Max = 3780
Std dev = 1350
n = 7

BTH	Brotherton Formation (1)
CDF	Cadeby Formation (1)
EDT	Edlington Formation (1)
RML	Raisby Formation (1)
ROX	Roxby Formation (1)
U	Undifferentiated (2)



Blue points are below the median
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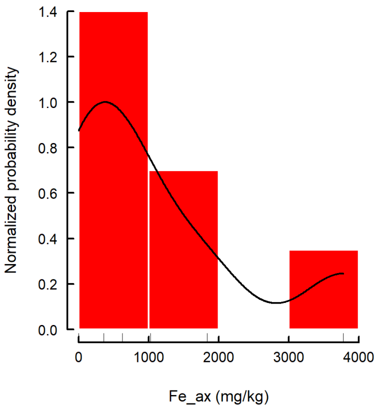
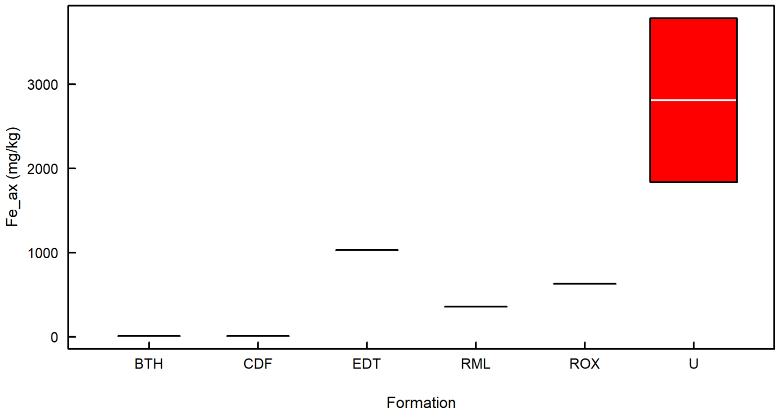




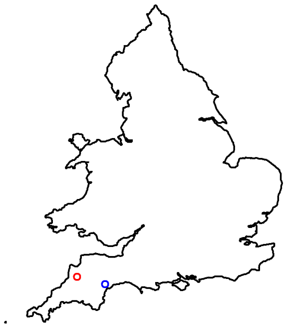
Exeter Group (EXE)

Extractable Fe

Fe_ax (mg/kg)

Min = 710
Median = 2840
Mean = 2840
Max = 4980
Std dev = 3020
n = 2

BOB	Bow Breccia Formation (1)
HVBR	Heavitree Breccia Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Warwickshire Group (WAWK)

Extractable Fe

Fe_ax (mg/kg)

Min = 278
Median = 278
Mean = 278
Max = 278
Std dev = NA
n = 1

SAL Salop Formation (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Other Permian (XP)

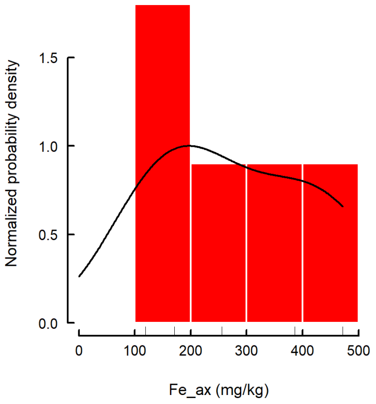
Extractable Fe

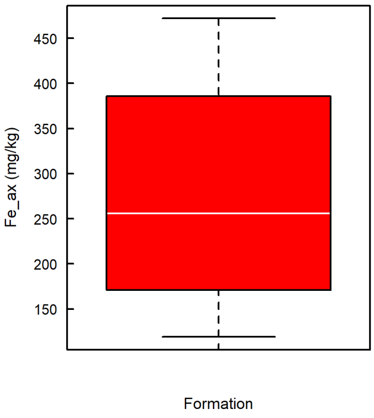
Fe_ax (mg/kg)

Min = 119
Median = 256
Mean = 281
Max = 472
Std dev = 147
n = 5

BRI Bridgnorth Sandstone Formation (5)

Blue points are below the median
Red points are at or above the median





7.4.6 Carboniferous

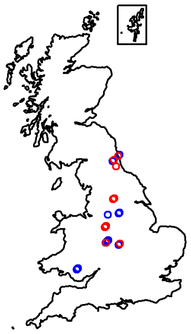
Pennine Coal Measures Group (PCM)

Extractable Fe

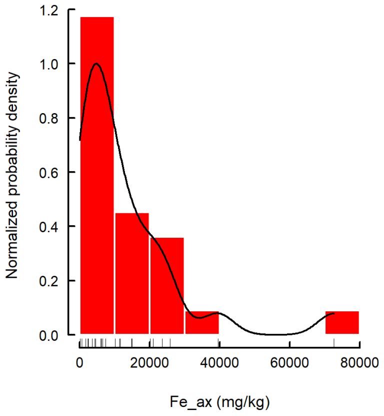
Fe_ax (mg/kg)

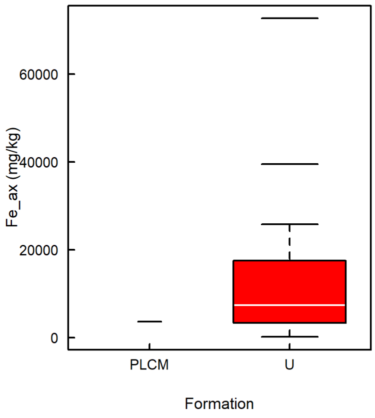
Min = 182
Median = 6980
Mean = 13100
Max = 72600
Std dev = 16000
n = 24

PLCM Pennine Lower Coal Measures Formation (1)
U Undifferentiated (23)



Blue points are below the median
Red points are at or above the median





Holsworthy Group (HOWY)

Extractable Fe

Fe_ax (mg/kg)

Min = 2040
Median = 2950
Mean = 2950
Max = 3870
Std dev = 1290
n = 2

BF Bude Formation (2)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

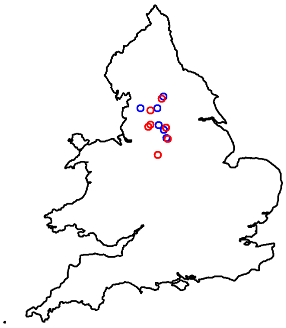
Millstone Grit Group (MG)

Extractable Fe

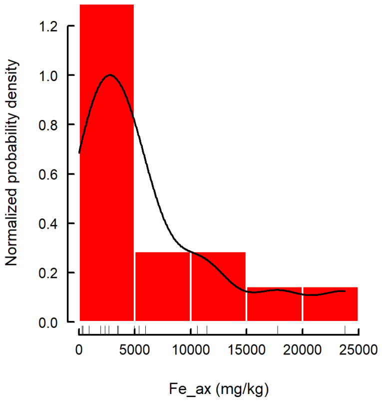
Fe_ax (mg/kg)

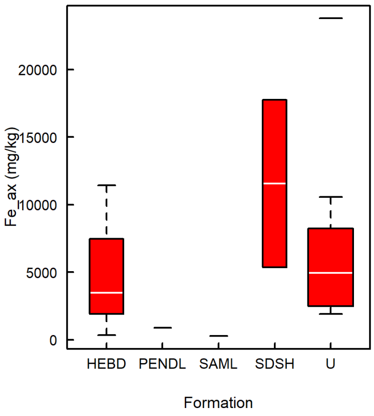
Min = 282
Median = 3510
Mean = 6350
Max = 23800
Std dev = 6810
n = 15

HEBD	Hebden Formation (4)
PENDL	Pendleton Formation (1)
SAML	Samlesbury Formation (1)
SDSH	Sabden Shales (2)
U	Undifferentiated (7)



Blue points are below the median
Red points are at or above the median





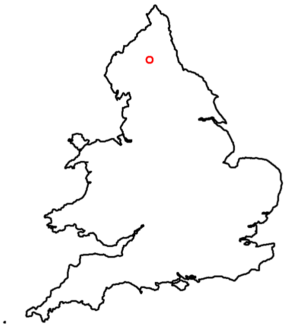
Yoredale Group (YORE)

Extractable Fe

Fe_ax (mg/kg)

Min = 870
Median = 870
Mean = 870
Max = 870
Std dev = NA
n = 1

SMGP	Stainmore Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

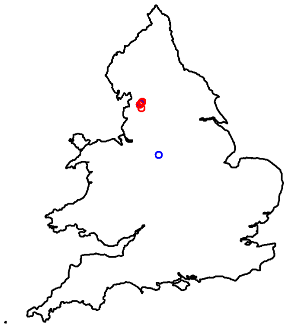
Craven Group (CRAV)

Extractable Fe

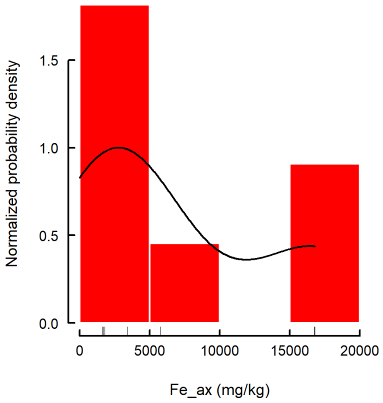
Fe_ax (mg/kg)

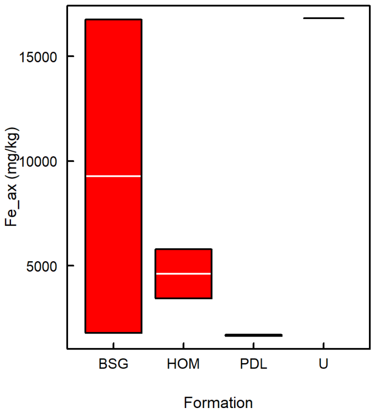
Min = 1650
Median = 3440
Mean = 6850
Max = 16800
Std dev = 6940
n = 7

BSG	Bowland Shale Formation (2)
HOM	Hodder Mudstone Formation (2)
PDL	Pendleside Limestone Formation (2)
U	Undifferentiated (1)



Blue points are below the median
Red points are at or above the median





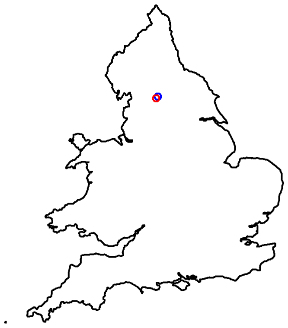
Great Scar Limestone Group (GSCL)

Extractable Fe

Fe_ax (mg/kg)

Min = 4
Median = 106
Mean = 106
Max = 209
Std dev = 145
n = 2

KLSL	Kilnsey Formation (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Peak Limestone Group (PKLM)

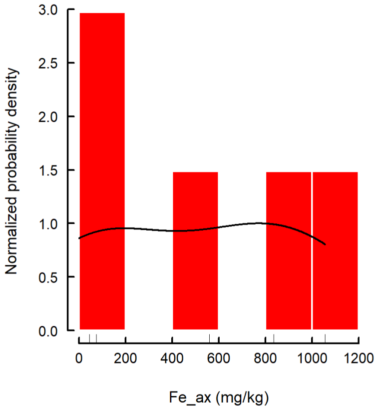
Extractable Fe

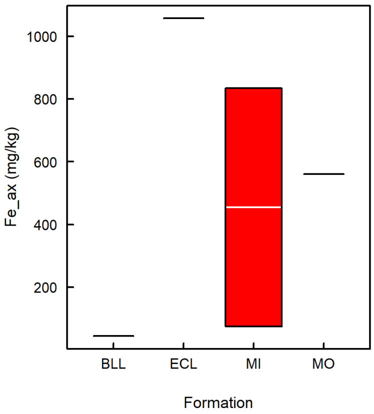
Fe_ax (mg/kg)

Min = 44
Median = 560
Mean = 514
Max = 1060
Std dev = 451
n = 5

BLL	Bee Low Limestone Formation (1)
ECL	Ecton Limestone Formation (1)
MI	Milldale Limestone Formation (2)
MO	Monsal Dale Limestone Formation (1)

Blue points are below the median
Red points are at or above the median





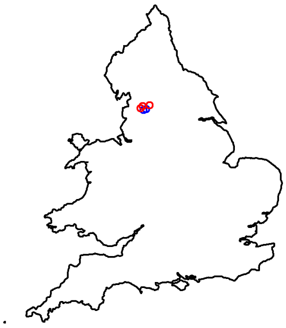
Bowland High Group (BOHI)

Extractable Fe

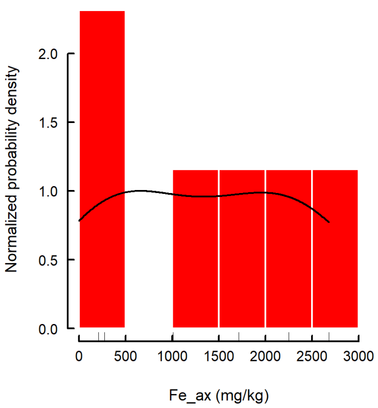
Fe_ax (mg/kg)

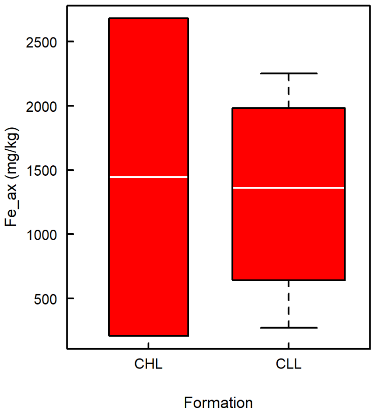
Min = 207
Median = 1360
Mean = 1360
Max = 2680
Std dev = 1030
n = 6

CHL	Chatburn Limestone Formation (2)
CLL	Clitheroe Limestone Formation (4)



Blue points are below the median
Red points are at or above the median





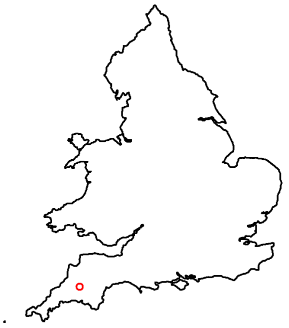
Transition Group (Devonian-Carboniferc

Extractable Fe

Fe_ax (mg/kg)

Min = 19300
Median = 19300
Mean = 19300
Max = 19300
Std dev = NA
n = 1

SBT South Brentor Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

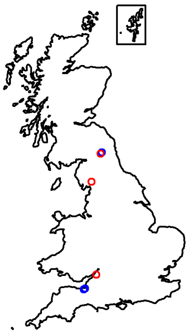
Other Carb. Limestone Supergroup (XC

Extractable Fe

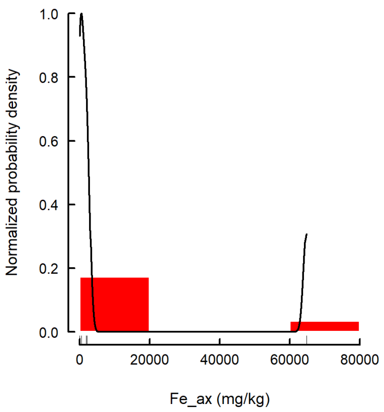
Fe_ax (mg/kg)

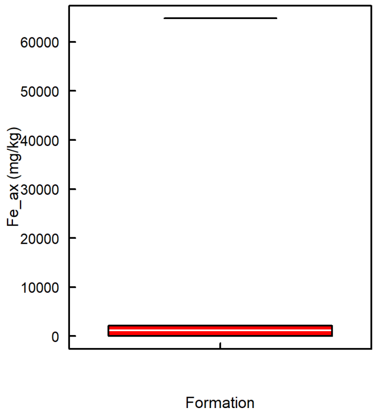
Min = 4
Median = 1180
Mean = 11600
Max = 64800
Std dev = 26100
n = 6

U Undifferentiated (6)



Blue points are below the median
Red points are at or above the median





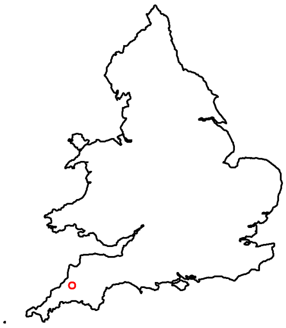
Other Culm Supergroup (XCU)

Extractable Fe

Fe_ax (mg/kg)

Min = 61200
Median = 61200
Mean = 61200
Max = 61200
Std dev = NA
n = 1

U Undifferentiated (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

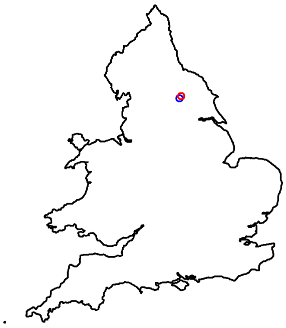
Other Carboniferous (XC)

Extractable Fe

Fe_ax (mg/kg)

Min = 304
Median = 5200
Mean = 5200
Max = 10100
Std dev = 6930
n = 2

U Undifferentiated (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

7.4.7 Devonian

Exmoor Group (EXM)

Extractable Fe

Fe_ax (mg/kg)

Min = 2620
Median = 2620
Mean = 2620
Max = 2620
Std dev = NA
n = 1

PLT Pilton Mudstone Formation (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

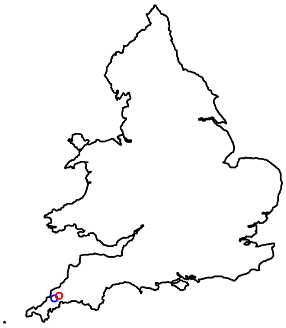
Meadfoot Group (MDT)

Extractable Fe

Fe_ax (mg/kg)

Min = 143
Median = 626
Mean = 626
Max = 1110
Std dev = 684
n = 2

U Undifferentiated (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

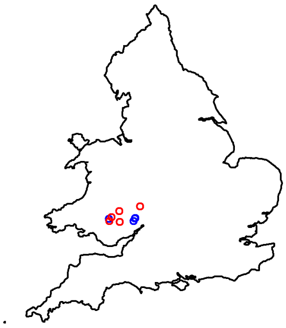
Lower Old Red Sandstone (LORS)

Extractable Fe

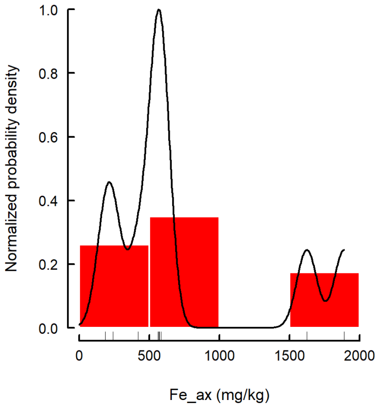
Fe_ax (mg/kg)

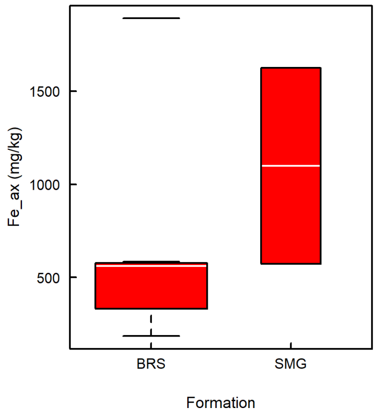
Min = 185
Median = 568
Mean = 739
Max = 1890
Std dev = 600
n = 9

BRS Brownstones Formation (7)
SMG St Maughans Formation (2)



Blue points are below the median
Red points are at or above the median





Downton Group (DOW)

Extractable Fe

Fe_ax (mg/kg)

Min = 2230
Median = 2230
Mean = 2230
Max = 2230
Std dev = NA
n = 1

RG Raglan Mudstone Formation (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

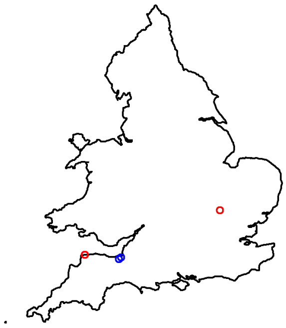
Other Devonian (XD)

Extractable Fe

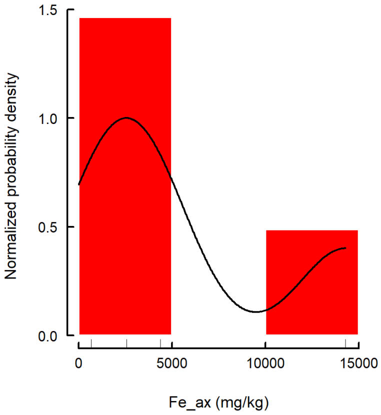
Fe_ax (mg/kg)

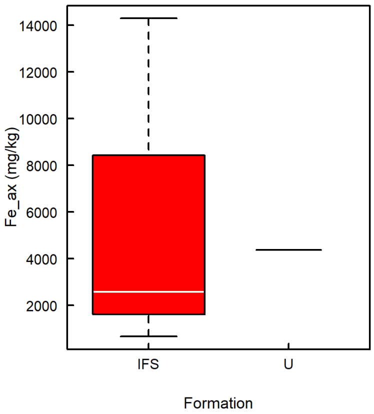
Min = 670
Median = 3480
Mean = 5480
Max = 14300
Std dev = 6070
n = 4

IFS Ilfracombe Slates Formation (3)
U Undifferentiated (1)



Blue points are below the median
Red points are at or above the median





7.4.8 Pre-Devonian

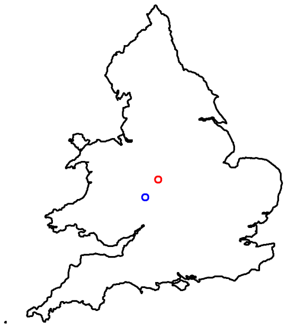
Lower Ludlow Shales Group (LLUS)

Extractable Fe

Fe_ax (mg/kg)

Min = 3380
Median = 6230
Mean = 6230
Max = 9070
Std dev = 4020
n = 2

U Undifferentiated (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

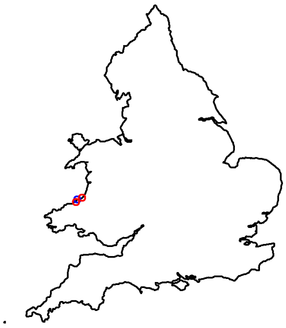
Aberystwyth Grits Group (AGF)

Extractable Fe

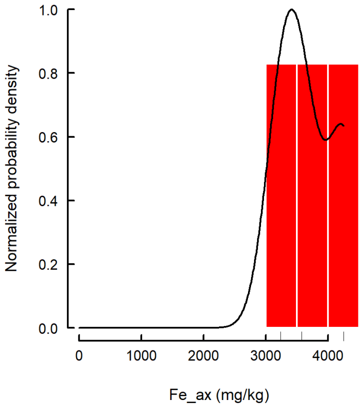
Fe_ax (mg/kg)

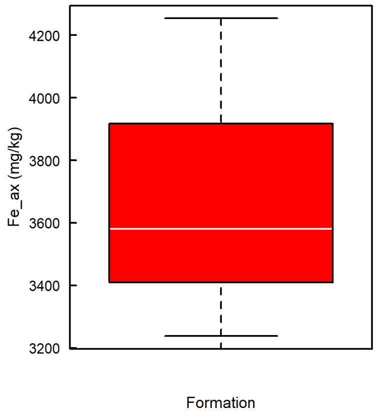
Min = 3240
Median = 3580
Mean = 3690
Max = 4250
Std dev = 517
n = 3

MYBA	Mynydd Bach Formation (3)



Blue points are below the median
Red points are at or above the median





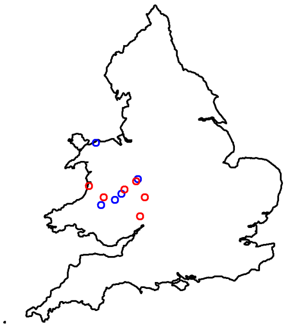
Other Silurian (XS)

Extractable Fe

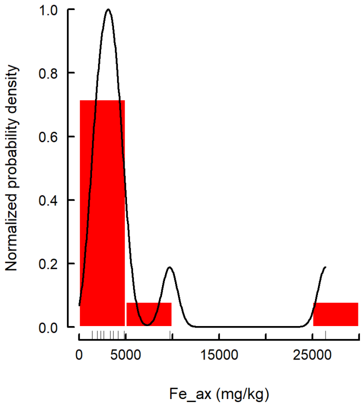
Fe_ax (mg/kg)

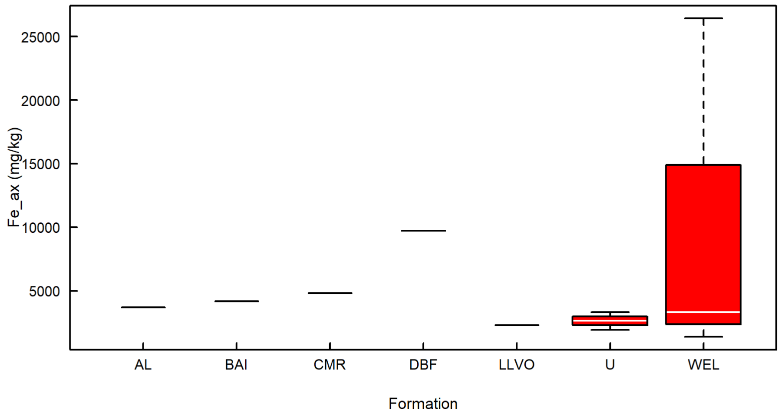
Min = 1380
Median = 3340
Mean = 5800
Max = 26400
Std dev = 7190
n = 11

AL	Aymestry Limestone Formation (1)
BAI	Bailey Hill Formation (1)
CMR	Cwmere Formation (1)
DBF	Devil'S Bridge Formation (1)
LLVO	Llanwrtyd Volcanic Formation (1)
U	Undifferentiated (3)
WEL	Much Wenlock Limestone Formation (3)



Blue points are below the median
Red points are at or above the median





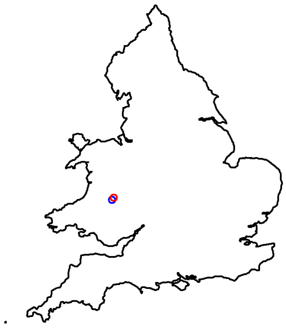
Builth Volcanic Group (BUVO)

Extractable Fe

Fe_ax (mg/kg)

Min = 13300
Median = 13700
Mean = 13700
Max = 14200
Std dev = 642
n = 2

U Undifferentiated (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

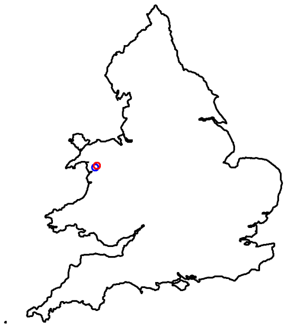
Mawddach Group (MWG)

Extractable Fe

Fe_ax (mg/kg)

Min = 1690
Median = 1750
Mean = 1750
Max = 1810
Std dev = 86.3
n = 2

FF Ffestiniog Flags Formation (1)
MW Maentwrog Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

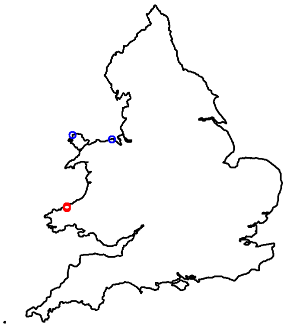
Other Ordovician (XO)

Extractable Fe

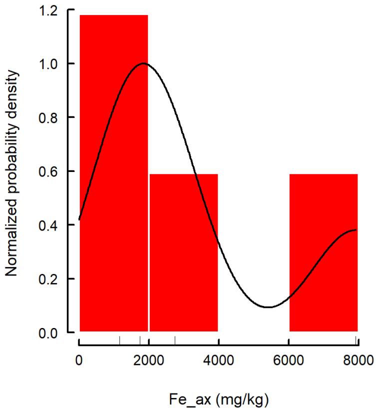
Fe_ax (mg/kg)

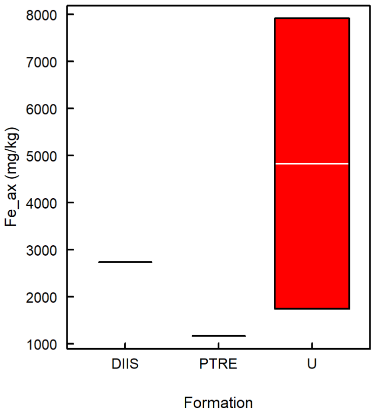
Min = 1160
Median = 2240
Mean = 3390
Max = 7920
Std dev = 3090
n = 4

DIIS	Dinas Island Formation (1)
PTRE	Pentre Formation (1)
U	Undifferentiated (2)



Blue points are below the median
Red points are at or above the median





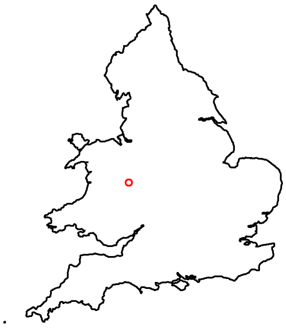
Stretton Group (YST)

Extractable Fe

Fe_ax (mg/kg)

Min = 1040
Median = 1040
Mean = 1040
Max = 1040
Std dev = NA
n = 1

SYGP	Synalds Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Other Pre-Cambrian (XA)

Extractable Fe

Fe_ax (mg/kg)

Min = 1750
Median = 1750
Mean = 1750
Max = 1750
Std dev = NA
n = 1

U Undifferentiated (1)

Blue points are below the median
Red points are at or above the median

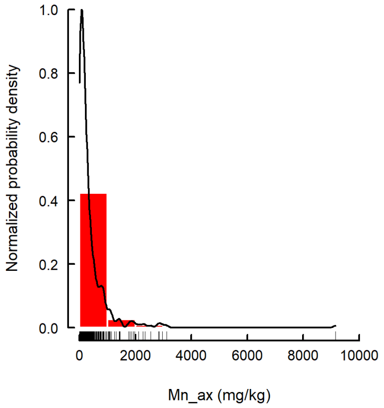
Not enough data for plotting

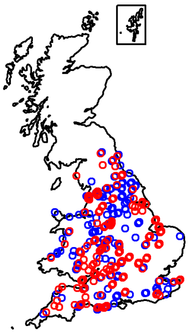
7.5 GEOLOGICAL ATLAS OF DATA FOR EXTRACTABLE MN

All Groups (All)

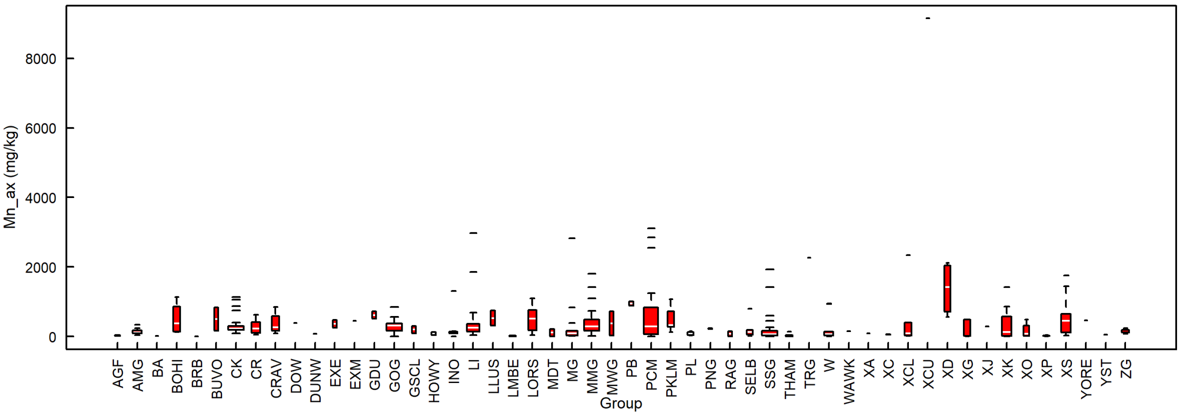
Extractable Mn

Mn_ax (mg/kg)





Blue points are below the median
Red points are at or above the median



7.5.1 Quaternary and Neogene

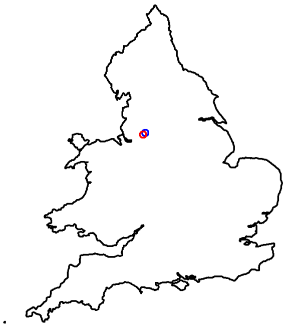
Glacial Deposits (GDU)

Extractable Mn

Mn_ax (mg/kg)

Min = 514
Median = 618
Mean = 618
Max = 721
Std dev = 146
n = 2

U Undifferentiated (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Dunwich Group (DUNW)

Extractable Mn

Mn_ax (mg/kg)

Min = 80
Median = 80
Mean = 80
Max = 80
Std dev = NA
n = 1

KGCA Kesgrave Catchment Subgroup (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Palaeogene

Barton Group (BA)

Extractable Mn

Mn_ax (mg/kg)

Min = 13
Median = 13
Mean = 13
Max = 13
Std dev = NA
n = 1

BECH Becton Sand and Chama Sand Fms (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Bracklesham Group (BRB)

Extractable Mn

Mn_ax (mg/kg)

Min = 4
Median = 4
Mean = 4
Max = 4
Std dev = NA
n = 1

WTT Wittering Formation (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

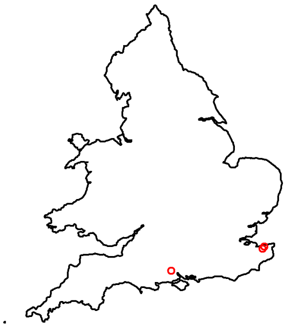
Thames Group (THAM)

Extractable Mn

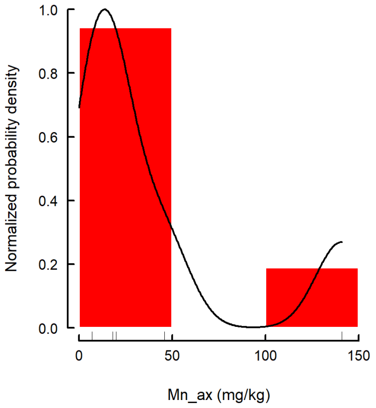
Mn_ax (mg/kg)

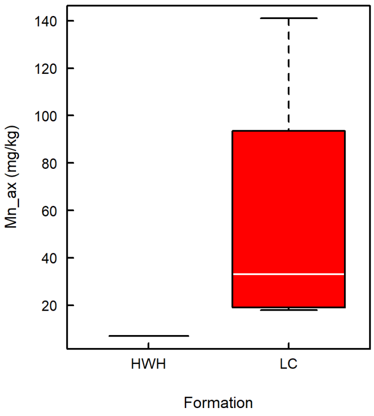
Min = 7
Median = 19
Mean = 39.8
Max = 141
Std dev = 51.6
n = 6

HWH	Harwich Formation (2)
LC	London Clay Formation (4)



Blue points are below the median
Red points are at or above the median





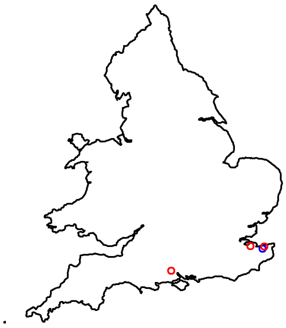
Lambeth Group (LMBE)

Extractable Mn

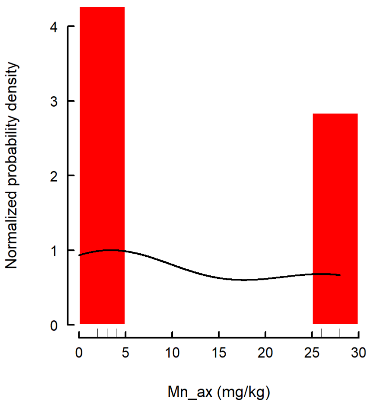
Mn_ax (mg/kg)

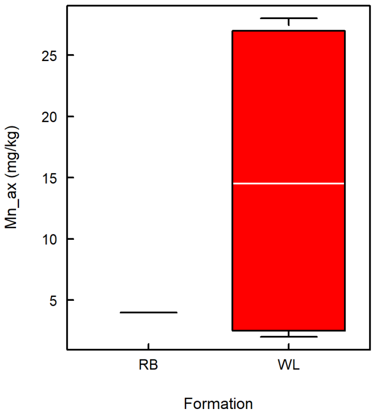
Min = 2
Median = 4
Mean = 12.6
Max = 28
Std dev = 13.2
n = 5

RB	Reading Formation (1)
WL	Woolwich Formation (4)



Blue points are below the median
Red points are at or above the median





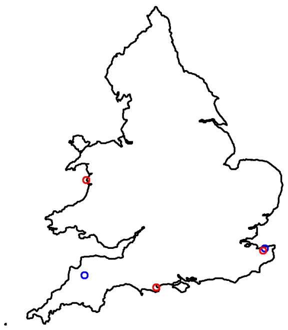
Other Palaeogene (XG)

Extractable Mn

Mn_ax (mg/kg)

Min = 4
Median = 22
Mean = 205
Max = 494
Std dev = 260
n = 5

BGS	Bagshot Formation (1)
BOF	Bovey Formation (1)
TAB	Thanet Formation (2)
U	Undifferentiated (1)



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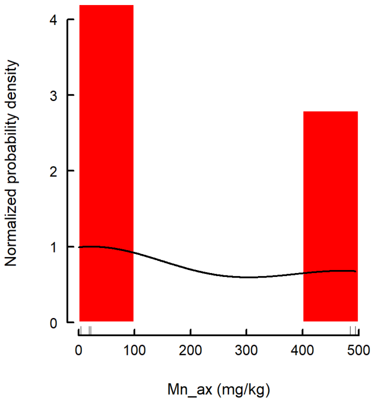
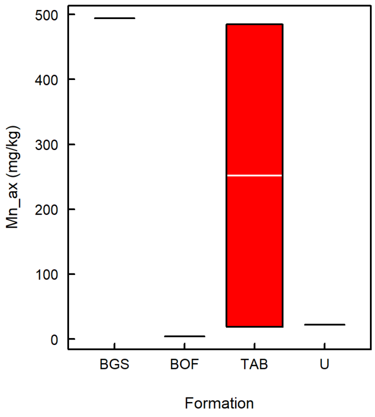




7.5.2 Cretaceous

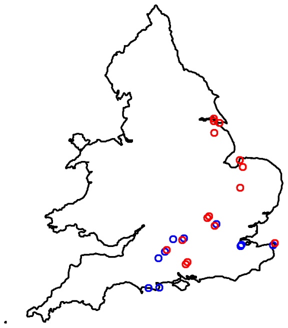
Chalk Group (CK)

Extractable Mn

Mn_ax (mg/kg)

Min = 86
Median = 233
Mean = 322
Max = 1140
Std dev = 264
n = 31

BCK	Burnham Chalk Formation (2)
FCK	Flamborough Chalk Formation (1)
FYCK	Ferriby Chalk Formation (3)
HCK	Holywell Nodular Chalk Formation (4)
LECH	Lewes Nodular Chalk Formation (3)
NCK	Newhaven Chalk Formation (4)
NPCH	New Pit Chalk Formation (3)
SECK	Seaford Chalk Formation (6)
U	Undifferentiated (1)
WMCH	West Melbury Marly Chalk Formation (1)
ZZCH	Zig Zag Chalk Formation (3)



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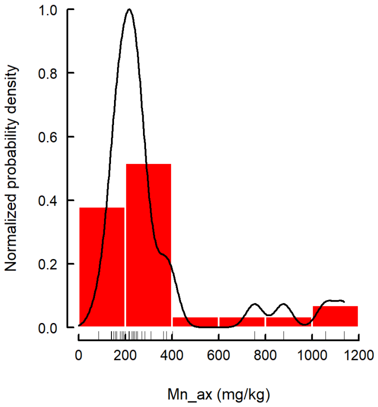
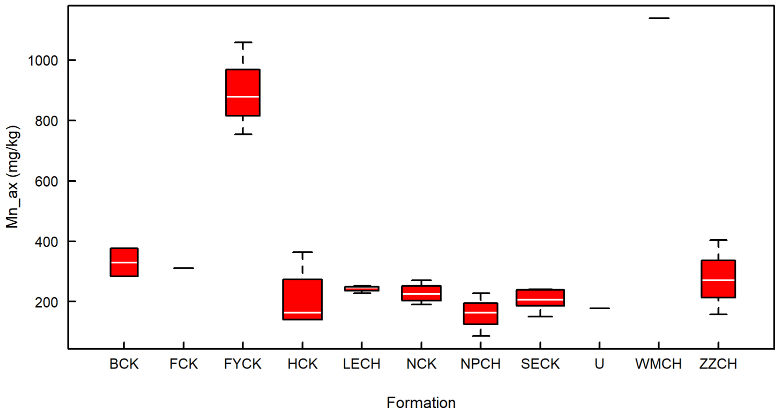
Red points are at or above the median





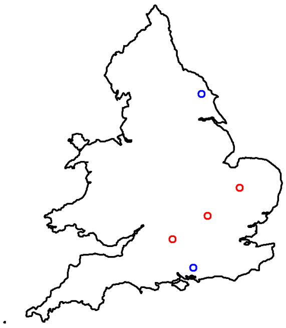
Selborne Group (SELB)

Extractable Mn

Mn_ax (mg/kg)

Min = 10
Median = 123
Mean = 234
Max = 797
Std dev = 322
n = 5

GLT	Gault Formation (2)
UGS	Upper Greensand Formation (3)



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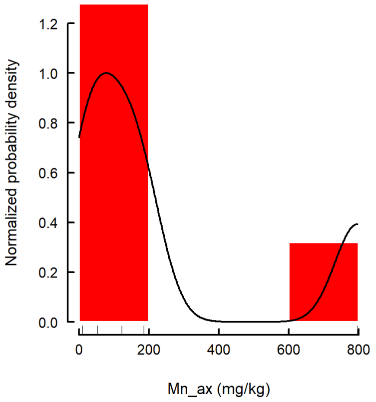
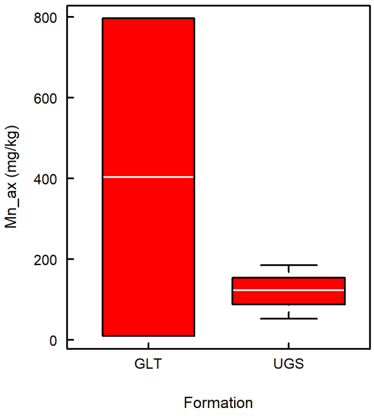




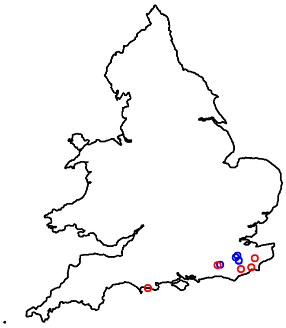
Wealden Group (W)

Extractable Mn

Mn_ax (mg/kg)

Min = 9
Median = 65
Mean = 231
Max = 949
Std dev = 376
n = 10

ASD	Ashdown Formation (3)
TWS	Tunbridge Wells Sand Formation (4)
U	Undifferentiated (1)
WC	Weald Clay Formation (2)



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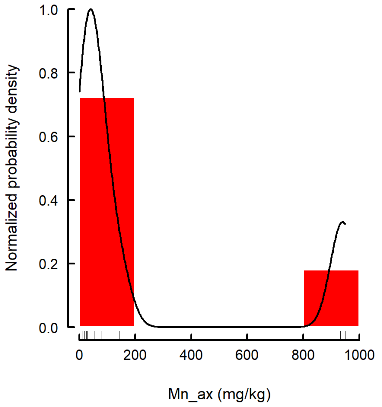
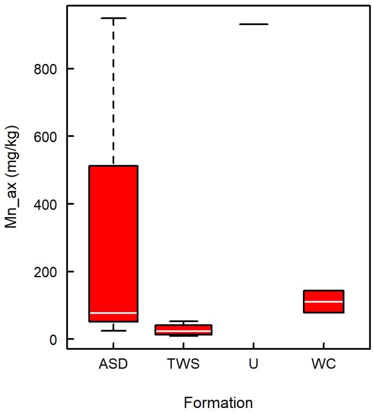
Red points are at or above the median





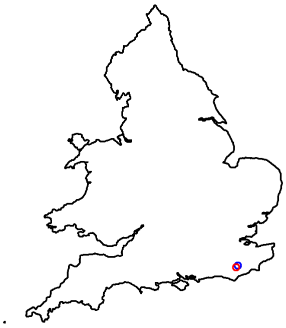
Purbeck Group (PB)

Extractable Mn

Mn_ax (mg/kg)

Min = 881
Median = 946
Mean = 946
Max = 1010
Std dev = 92.6
n = 2

DURN	Durlston Formation (1)
LULW	Lulworth Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

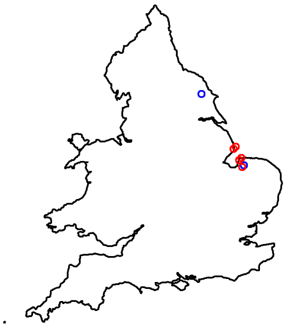
Other Cretaceous (XK)

Extractable Mn

Mn_ax (mg/kg)

Min = 2
Median = 128
Mean = 355
Max = 1430
Std dev = 450
n = 12

CA	Carstone Formation (2)
DEB	Dersingham Formation (2)
HUCK	Hunstanton Formation (2)
ROH	Roach Formation (2)
SAS	Sandringham Sand Formation (3)
SPC	Speeton Clay Formation (1)



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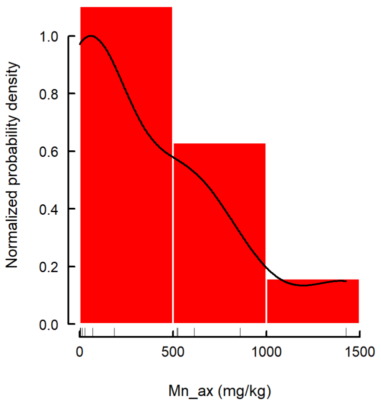
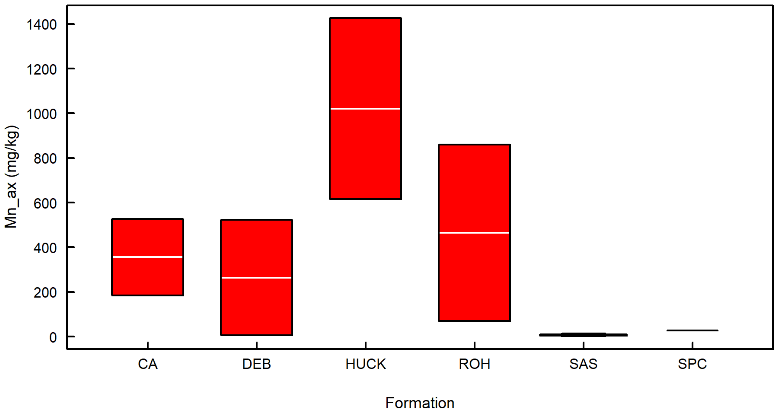
Red points are at or above the median





7.5.3 Jurassic

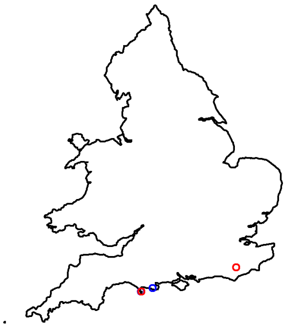
Portland Group (PL)

Extractable Mn

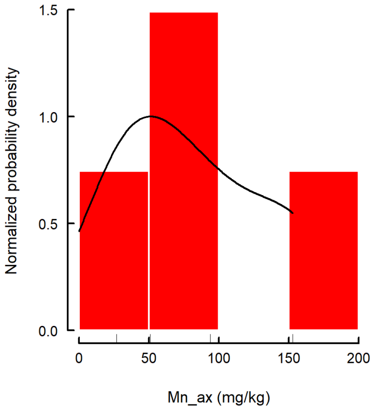
Mn_ax (mg/kg)

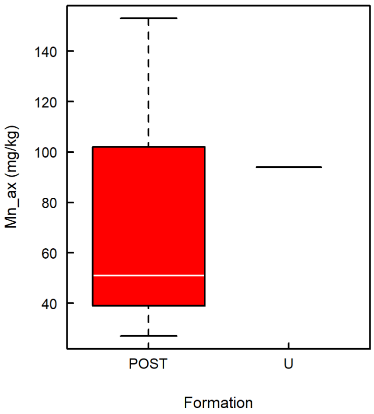
Min = 27
Median = 72.5
Mean = 81.2
Max = 153
Std dev = 55.3
n = 4

POST	Portland Stone Formation (3)
U	Undifferentiated (1)



Blue points are below the median
Red points are at or above the median





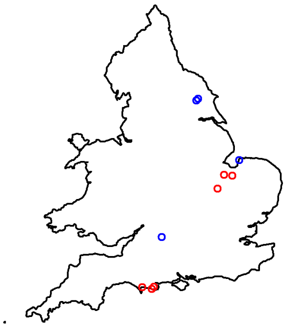
Ancholme Group (AMG)

Extractable Mn

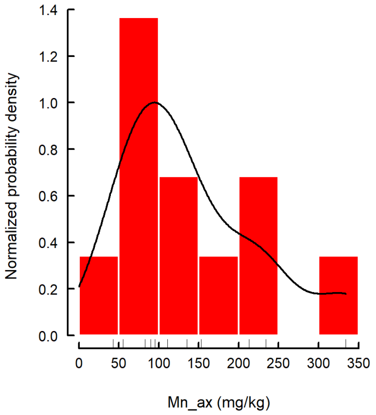
Mn_ax (mg/kg)

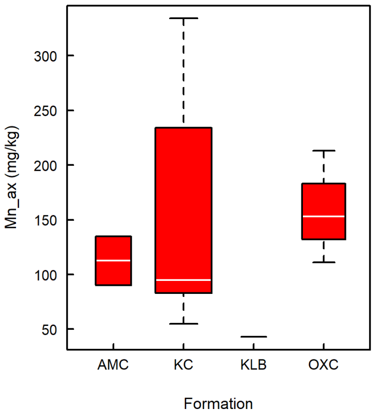
Min = 43
Median = 111
Mean = 141
Max = 334
Std dev = 87.9
n = 11

AMC	Ampthill Clay Formation (2)
KC	Kimmeridge Clay Formation (5)
KLB	Kellaways Formation (1)
OXC	Oxford Clay Formation (3)



Blue points are below the median
Red points are at or above the median





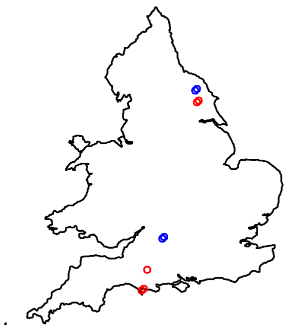
Corallian Group (CR)

Extractable Mn

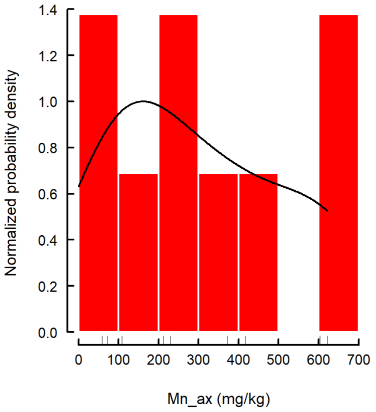
Mn_ax (mg/kg)

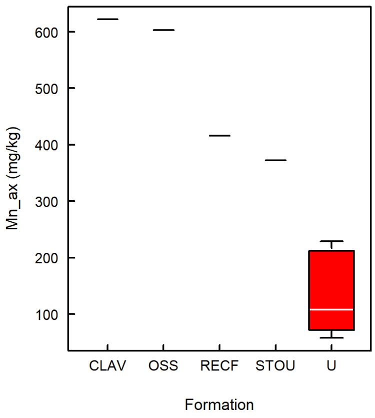
Min = 58
Median = 229
Mean = 299
Max = 622
Std dev = 216
n = 9

CLAV	Clavellata Formation (1)
OSS	Osmington Oolite Formation (1)
RECF	Redcliff Formation (1)
STOU	Stour Formation (1)
U	Undifferentiated (5)



Blue points are below the median
Red points are at or above the median





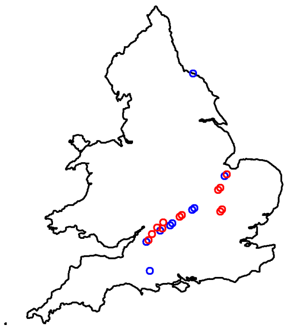
Great Oolite Group (GOG)

Extractable Mn

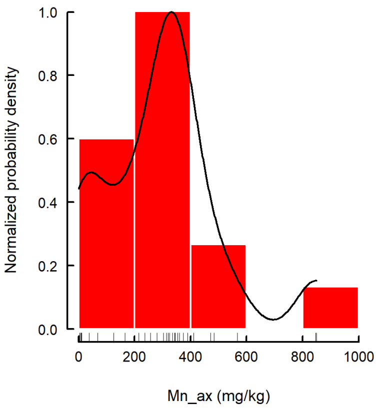
Mn_ax (mg/kg)

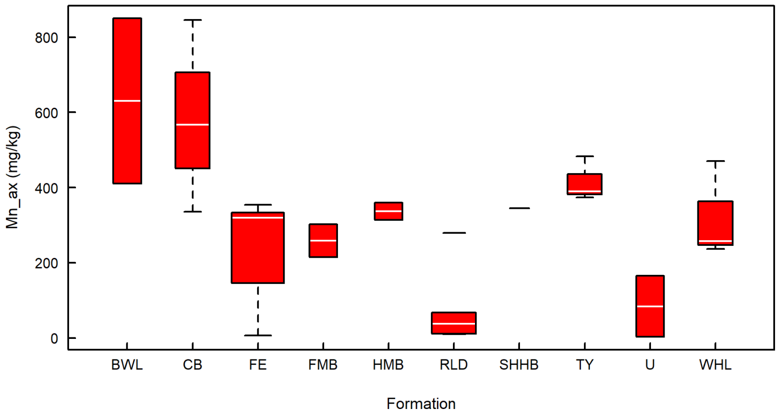
Min = 3
Median = 317
Mean = 299
Max = 850
Std dev = 213
n = 30

BWL	Blisworth Limestone Formation (2)
CB	Cornbrash Formation (3)
FE	Fuller'S Earth Formation (7)
FMB	Forest Marble Formation (2)
HMB	Hampen Formation (2)
RLD	Rutland Formation (5)
SHHB	Sharp'S Hill Formation (1)
TY	Taynton Limestone Formation (3)
U	Undifferentiated (2)
WHL	White Limestone Formation (3)



Blue points are below the median
Red points are at or above the median





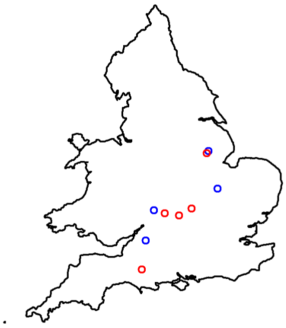
Inferior Oolite Group (INO)

Extractable Mn

Mn_ax (mg/kg)

Min = 2
Median = 108
Mean = 234
Max = 1310
Std dev = 405
n = 9

BLPL	Birdlip Limestone Formation (2)
GRF	Grantham Formation (2)
LL	Lincolnshire Limestone Formation (2)
NS	Northampton Sand Formation (1)
U	Undifferentiated (2)



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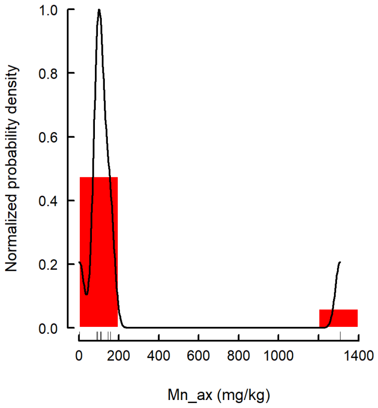
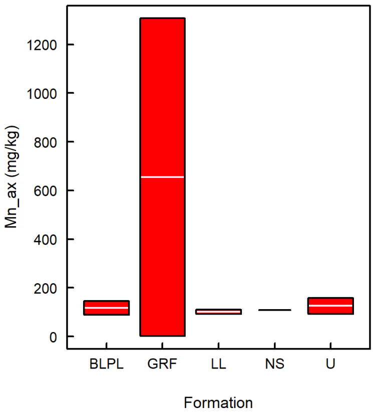




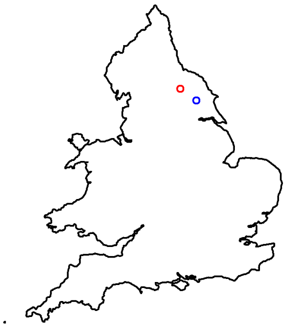
Ravenscar Group (RAG)

Extractable Mn

Mn_ax (mg/kg)

Min = 3
Median = 80.5
Mean = 80.5
Max = 158
Std dev = 110
n = 2

SCY	Scalby Formation (1)
U	Undifferentiated (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

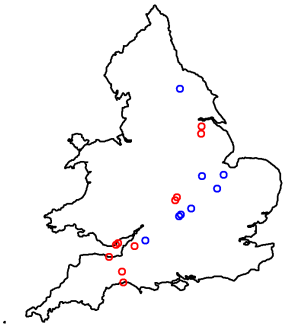
Lias Group (LI)

Extractable Mn

Mn_ax (mg/kg)

Min = 43
Median = 256
Mean = 468
Max = 2970
Std dev = 709
n = 20

BDS	Bridport Sand Formation (1)
BLI	Blue Lias Formation (7)
BNLS	Beacon Limestone Formation (1)
CHAM	Charmouth Mudstone Formation (2)
DYS	Dyrham Formation (1)
U	Undifferentiated (4)
WHM	Whitby Mudstone Formation (4)



Blue points are below the median
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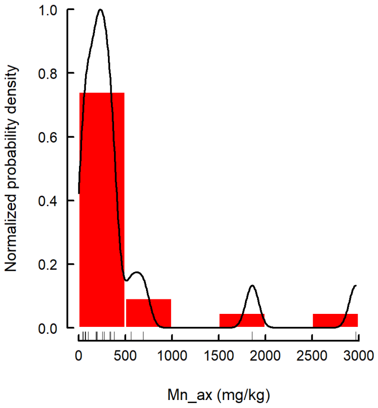
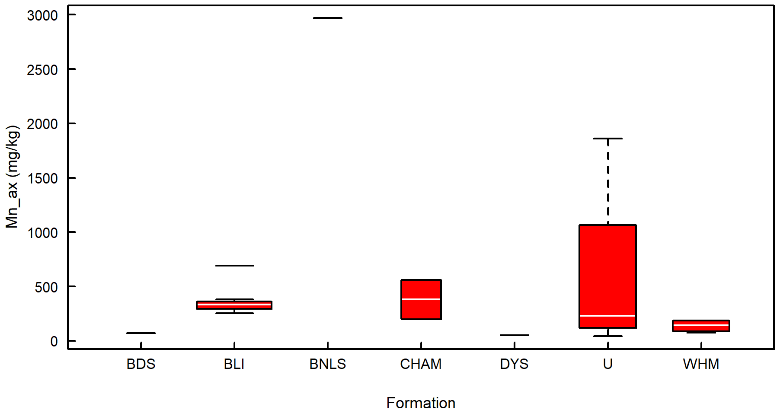




Other Jurassic (XJ)

Extractable Mn

Mn_ax (mg/kg)

Min = 293
Median = 293
Mean = 293
Max = 293
Std dev = NA
n = 1

SAS Sandringham Sand Formation (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

7.5.4 Triassic

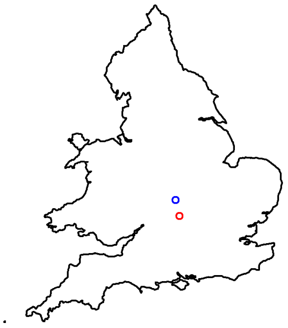
Penarth Group (PNG)

Extractable Mn

Mn_ax (mg/kg)

Min = 220
Median = 228
Mean = 228
Max = 236
Std dev = 11.3
n = 2

U	Undifferentiated (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

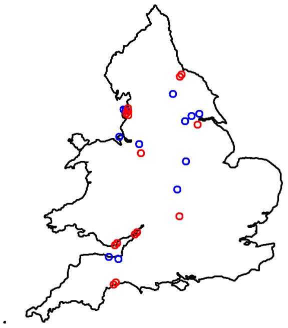
Mercia Mudstone Group (MMG)

Extractable Mn

Mn_ax (mg/kg)

Min = 18
Median = 287
Mean = 413
Max = 1810
Std dev = 415
n = 29

BAN	Blue Anchor Formation (3)
SIM	Sidmouth Mudstone Formation (6)
TPSF	Tarporley Siltstone Formation (1)
U	Undifferentiated (19)



Blue points are below the median
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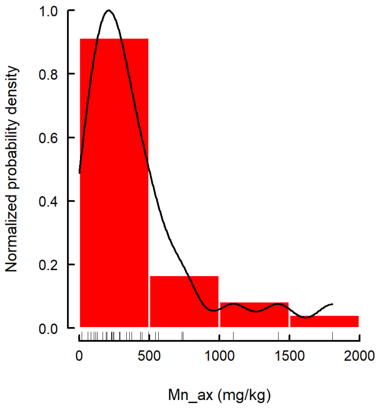
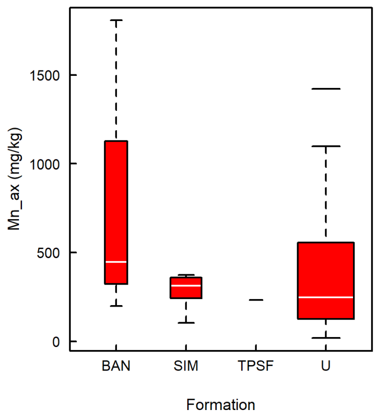




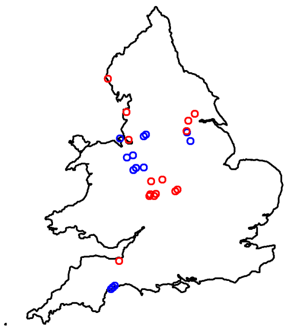
Sherwood Sandstone Group (SSG)

Extractable Mn

Mn_ax (mg/kg)

Min = 3
Median = 62
Mean = 214
Max = 1920
Std dev = 424
n = 30

BMS	Bromsgrove Sandstone Formation (4)
BSP	Budleigh Salterton Pebble Beds Formation (2
CPB	Chester Pebble Beds Formation (1)
HEY	Helsby Sandstone Formation (3)
KDM	Kidderminster Formation (1)
NTC	Nottingham Castle Sandstone Formation (2)
OS	Otter Sandstone Formation (3)
U	Undifferentiated (10)
WLSF	Wilmslow Sandstone Formation (4)



Blue points are below the median
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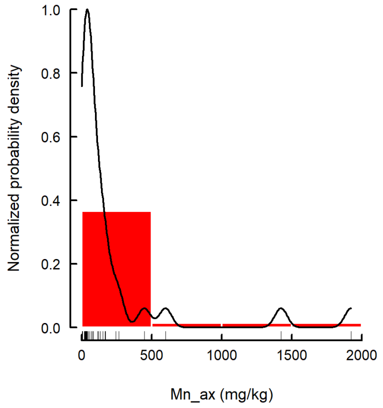
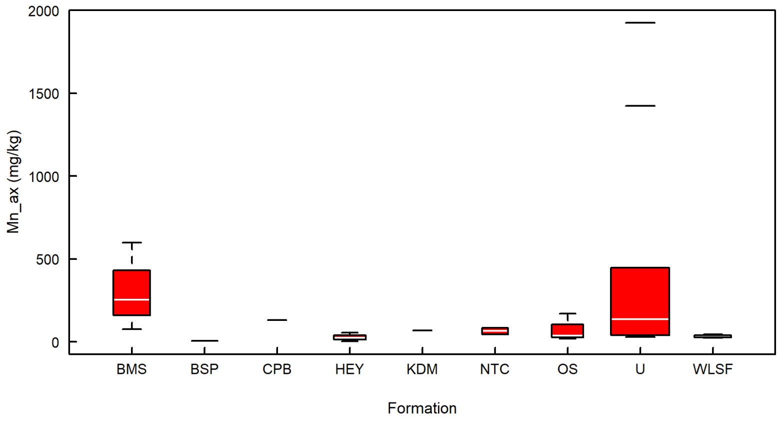




7.5.5 Permian

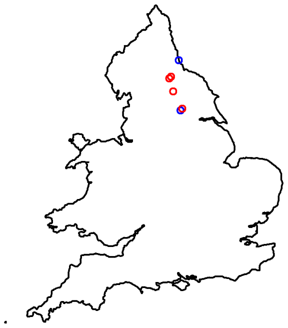
Zechstein Group (ZG)

Extractable Mn

Mn_ax (mg/kg)

Min = 82
Median = 111
Mean = 147
Max = 244
Std dev = 58.4
n = 7

BTH	Brotherton Formation (1)
CDF	Cadeby Formation (1)
EDT	Edlington Formation (1)
RML	Raisby Formation (1)
ROX	Roxby Formation (1)
U	Undifferentiated (2)



Blue points are below the median
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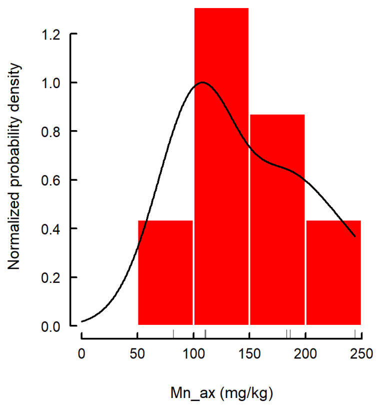
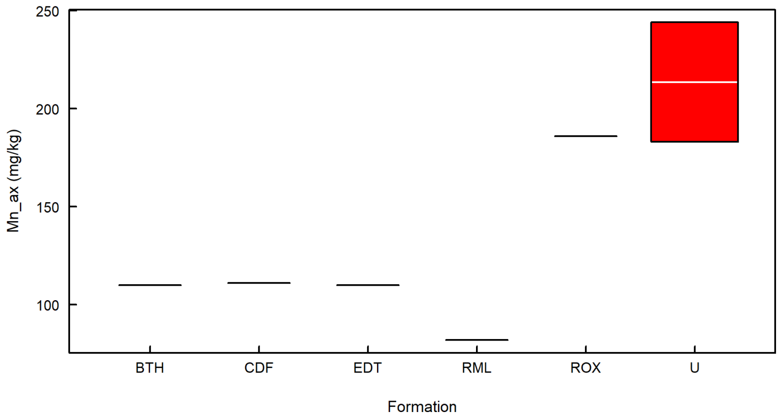




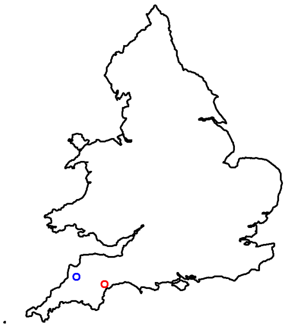
Exeter Group (EXE)

Extractable Mn

Mn_ax (mg/kg)

Min	=	247
Median	=	364
Mean	=	364
Max	=	480
Std dev	=	165
n	=	2

BOB	Bow Breccia Formation (1)
HVBR	Heavitree Breccia Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Warwickshire Group (WAWK)

Extractable Mn

Mn_ax (mg/kg)

Min	=	157
Median	=	157
Mean	=	157
Max	=	157
Std dev	=	NA
n	=	1

SAL	Salop Formation (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Other Permian (XP)

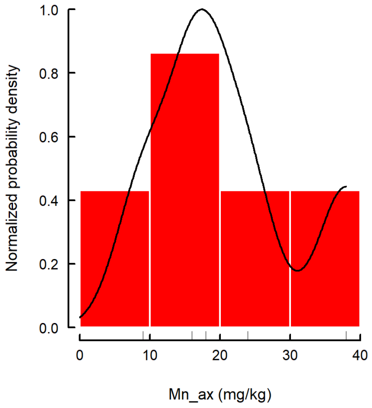
Extractable Mn

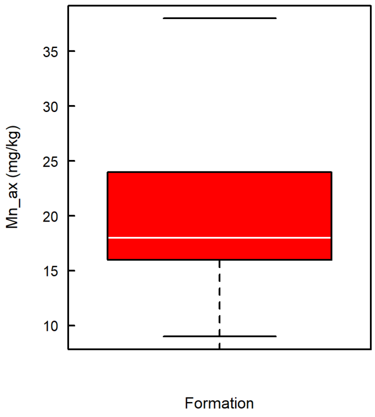
Mn_ax (mg/kg)

Min = 9
Median = 18
Mean = 21
Max = 38
Std dev = 10.9
n = 5

BRI Bridgnorth Sandstone Formation (5)

Blue points are below the median
Red points are at or above the median





7.5.6 Carboniferous

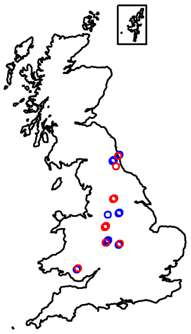
Pennine Coal Measures Group (PCM)

Extractable Mn

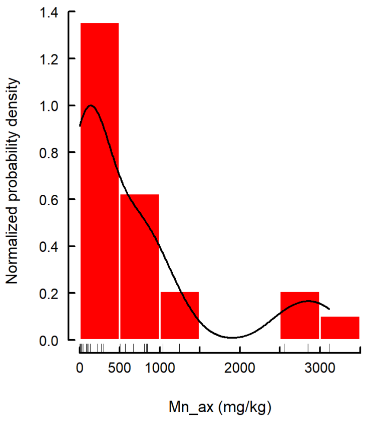
Mn_ax (mg/kg)

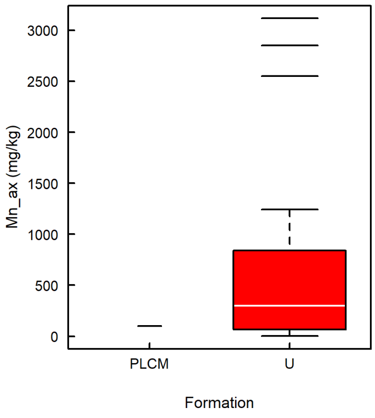
Min = 2
Median = 284
Mean = 682
Max = 3120
Std dev = 912
n = 24

PLCM Pennine Lower Coal Measures Formation (1)
U Undifferentiated (23)



Blue points are below the median
Red points are at or above the median





Holsworthy Group (HOWY)

Extractable Mn

Mn_ax (mg/kg)

Min = 40
Median = 81
Mean = 81
Max = 122
Std dev = 58
n = 2

BF	Bude Formation (2)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

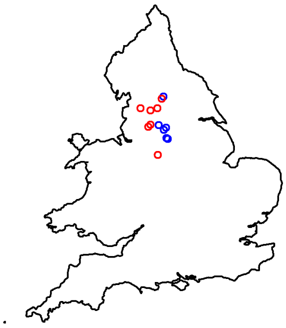
Millstone Grit Group (MG)

Extractable Mn

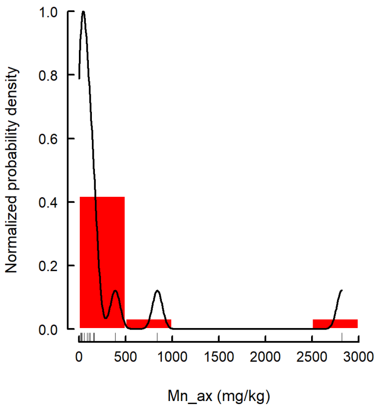
Mn_ax (mg/kg)

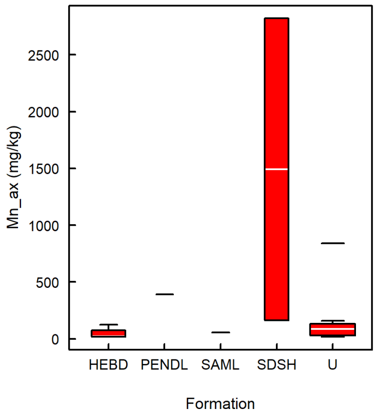
Min = 17
Median = 88
Mean = 326
Max = 2820
Std dev = 723
n = 15

HEBD	Hebden Formation (4)
PENDL	Pendleton Formation (1)
SAML	Samlesbury Formation (1)
SDSH	Sabden Shales (2)
U	Undifferentiated (7)



Blue points are below the median
Red points are at or above the median





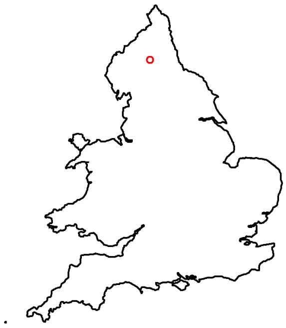
Yoredale Group (YORE)

Extractable Mn

Mn_ax (mg/kg)

Min = 468
Median = 468
Mean = 468
Max = 468
Std dev = NA
n = 1

SMGP	Stainmore Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

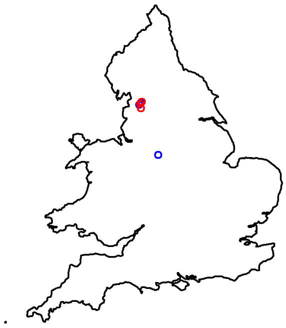
Craven Group (CRAV)

Extractable Mn

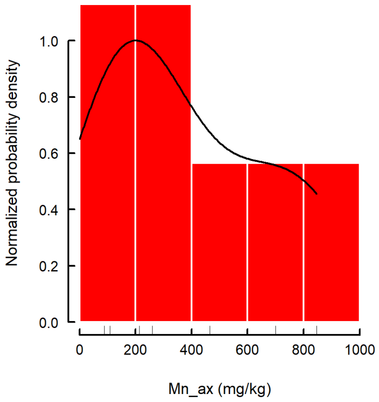
Mn_ax (mg/kg)

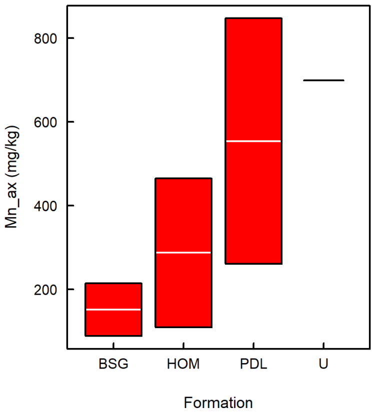
Min = 88
Median = 260
Mean = 383
Max = 847
Std dev = 297
n = 7

BSG	Bowland Shale Formation (2)
HOM	Hodder Mudstone Formation (2)
PDL	Pendleside Limestone Formation (2)
U	Undifferentiated (1)



Blue points are below the median
Red points are at or above the median





Great Scar Limestone Group (GSCL)

Extractable Mn

Mn_ax (mg/kg)

Min = 90
Median = 199
Mean = 199
Max = 308
Std dev = 154
n = 2

KLSL	Kilnsey Formation (2)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

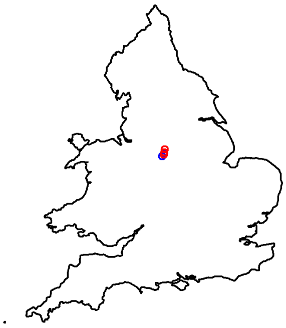
Peak Limestone Group (PKLM)

Extractable Mn

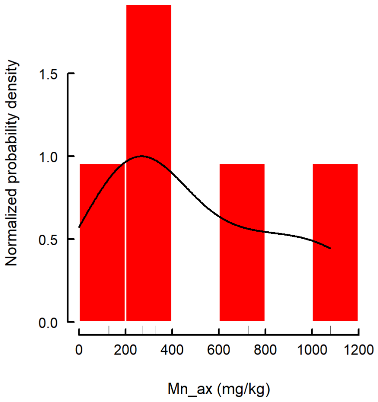
Mn_ax (mg/kg)

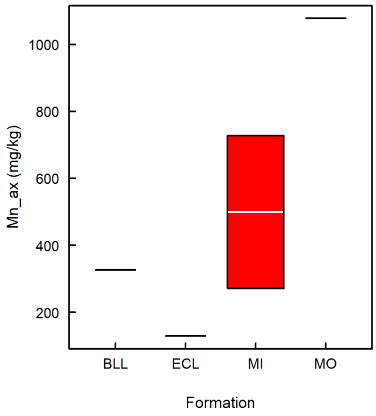
Min = 129
Median = 326
Mean = 506
Max = 1080
Std dev = 389
n = 5

BLL	Bee Low Limestone Formation (1)
ECL	Ecton Limestone Formation (1)
MI	Milldale Limestone Formation (2)
MO	Monsal Dale Limestone Formation (1)



Blue points are below the median
Red points are at or above the median





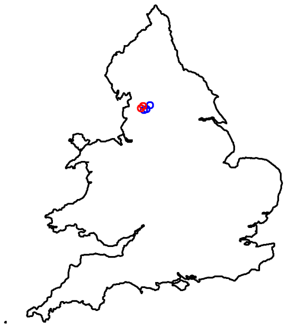
Bowland High Group (BOHI)

Extractable Mn

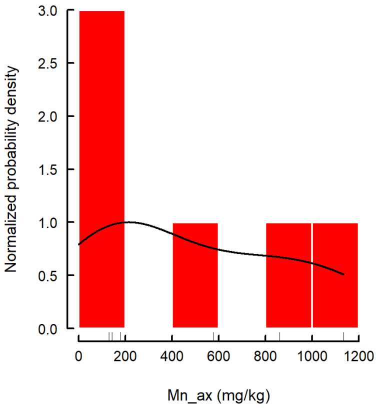
Mn_ax (mg/kg)

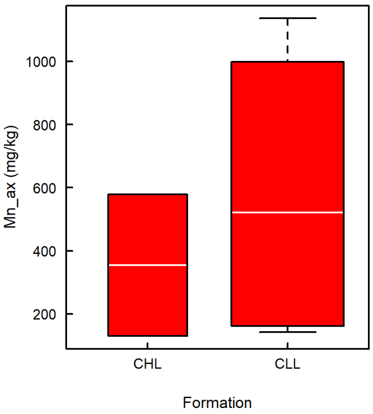
Min = 130
Median = 379
Mean = 505
Max = 1140
Std dev = 426
n = 6

CHL	Chatburn Limestone Formation (2)
CLL	Clitheroe Limestone Formation (4)



Blue points are below the median
Red points are at or above the median





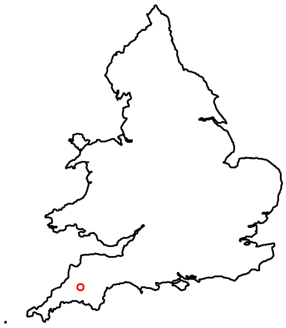
Transition Group (Devonian-Carboniferc

Extractable Mn

Mn_ax (mg/kg)

Min = 2260
Median = 2260
Mean = 2260
Max = 2260
Std dev = NA
n = 1

SBT	South Brentor Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

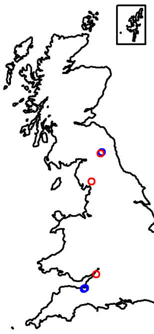
Other Carb. Limestone Supergroup (XC

Extractable Mn

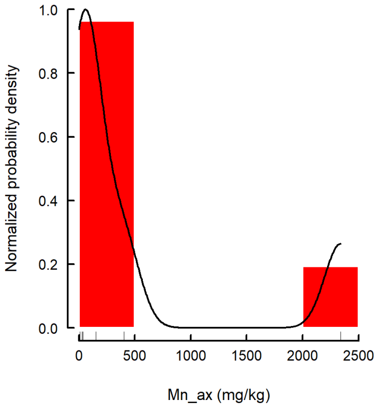
Mn_ax (mg/kg)

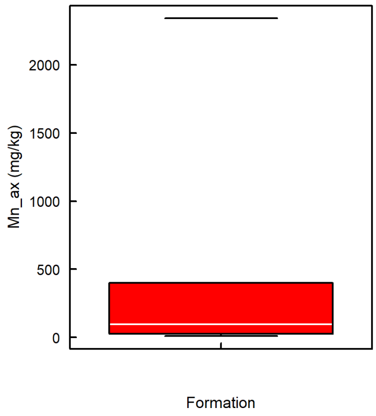
Min = 10
Median = 94.5
Mean = 495
Max = 2340
Std dev = 916
n = 6

U Undifferentiated (6)



Blue points are below the median
Red points are at or above the median





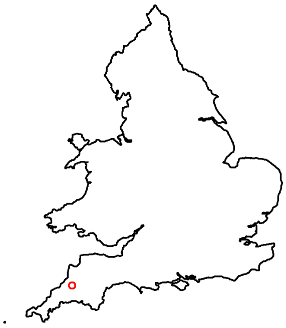
Other Culm Supergroup (XCU)

Extractable Mn

Mn_ax (mg/kg)

Min = 9150
Median = 9150
Mean = 9150
Max = 9150
Std dev = NA
n = 1

U Undifferentiated (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

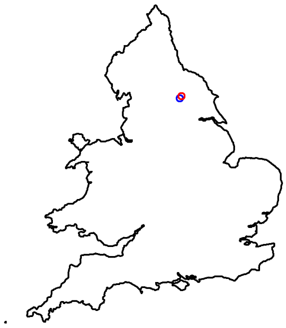
Other Carboniferous (XC)

Extractable Mn

Mn_ax (mg/kg)

Min = 56
Median = 61
Mean = 61
Max = 66
Std dev = 7.07
n = 2

U Undifferentiated (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

7.5.7 Devonian

Exmoor Group (EXM)

Extractable Mn

Mn_ax (mg/kg)

Min = 452
Median = 452
Mean = 452
Max = 452
Std dev = NA
n = 1

PLT Pilton Mudstone Formation (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

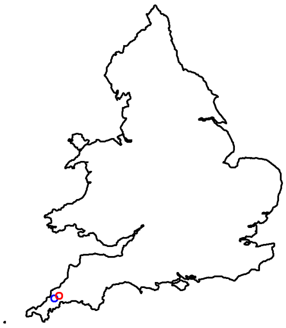
Meadfoot Group (MDT)

Extractable Mn

Mn_ax (mg/kg)

Min = 3
Median = 112
Mean = 112
Max = 220
Std dev = 153
n = 2

U Undifferentiated (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

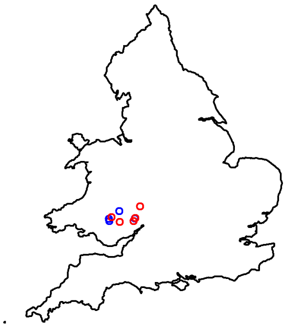
Lower Old Red Sandstone (LORS)

Extractable Mn

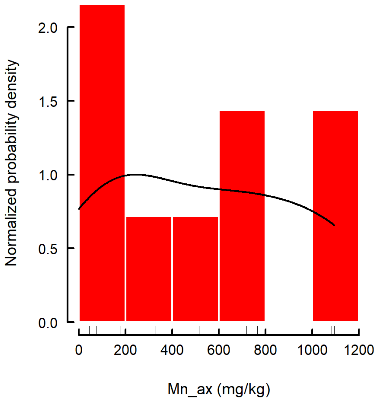
Mn_ax (mg/kg)

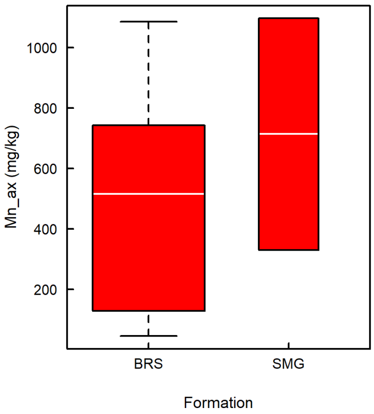
Min = 45
Median = 515
Mean = 534
Max = 1100
Std dev = 407
n = 9

BRS Brownstones Formation (7)
SMG St Maughans Formation (2)



Blue points are below the median
Red points are at or above the median





Downton Group (DOW)

Extractable Mn

Mn_ax (mg/kg)

Min = 392
Median = 392
Mean = 392
Max = 392
Std dev = NA
n = 1

RG Raglan Mudstone Formation (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

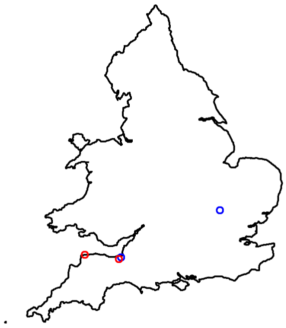
Other Devonian (XD)

Extractable Mn

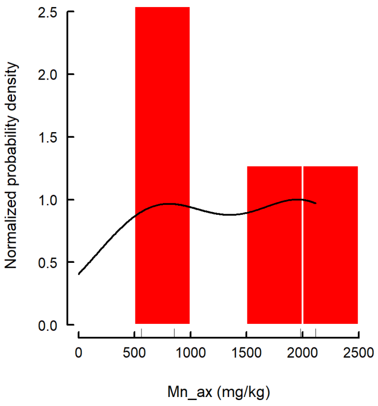
Mn_ax (mg/kg)

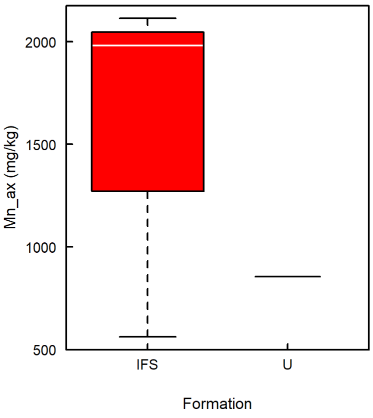
Min = 562
Median = 1420
Mean = 1380
Max = 2110
Std dev = 784
n = 4

IFS Ilfracombe Slates Formation (3)
U Undifferentiated (1)



Blue points are below the median
Red points are at or above the median





7.5.8 Pre-Devonian

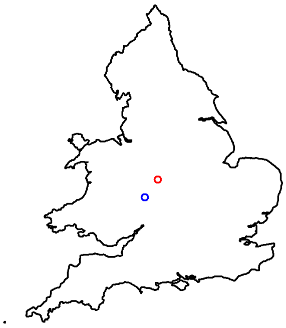
Lower Ludlow Shales Group (LLUS)

Extractable Mn

Mn_ax (mg/kg)

Min = 312
Median = 529
Mean = 529
Max = 746
Std dev = 307
n = 2

U Undifferentiated (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

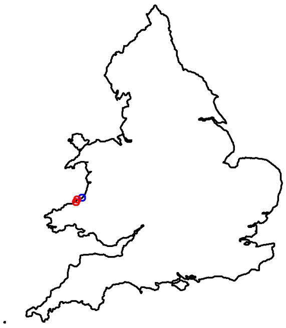
Aberystwyth Grits Group (AGF)

Extractable Mn

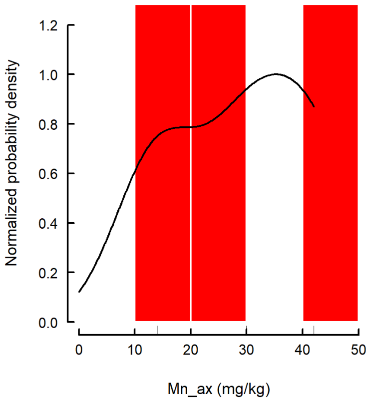
Mn_ax (mg/kg)

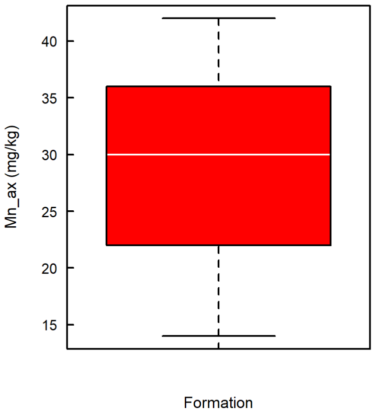
Min = 14
Median = 30
Mean = 28.7
Max = 42
Std dev = 14
n = 3

MYBA Mynydd Bach Formation (3)



Blue points are below the median
Red points are at or above the median





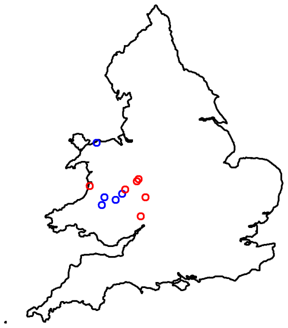
Other Silurian (XS)

Extractable Mn

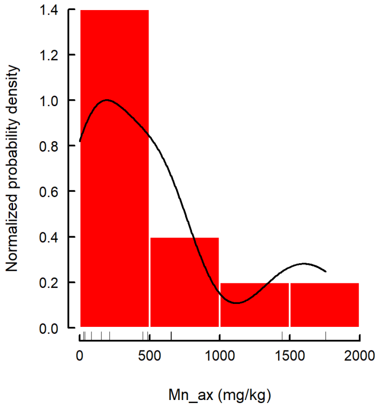
Mn_ax (mg/kg)

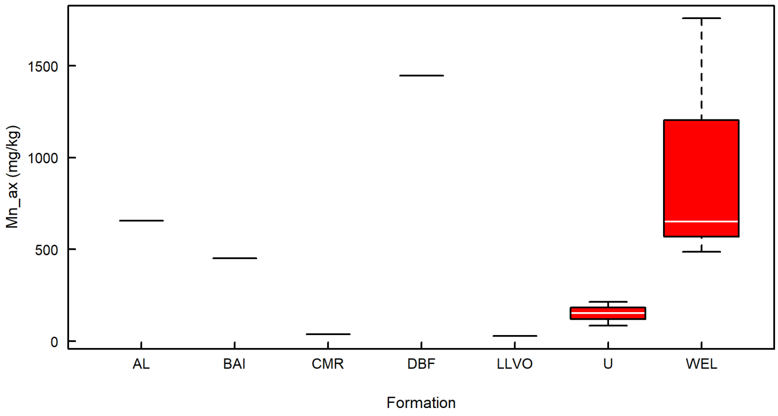
Min = 28
Median = 451
Mean = 542
Max = 1760
Std dev = 576
n = 11

AL	Aymestry Limestone Formation (1)
BAI	Bailey Hill Formation (1)
CMR	Cwmere Formation (1)
DBF	Devil'S Bridge Formation (1)
LLVO	Llanwrtyd Volcanic Formation (1)
U	Undifferentiated (3)
WEL	Much Wenlock Limestone Formation (3)



Blue points are below the median
Red points are at or above the median





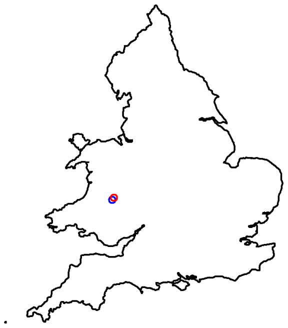
Builth Volcanic Group (BUVO)

Extractable Mn

Mn_ax (mg/kg)

Min = 170
Median = 502
Mean = 502
Max = 833
Std dev = 469
n = 2

U Undifferentiated (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

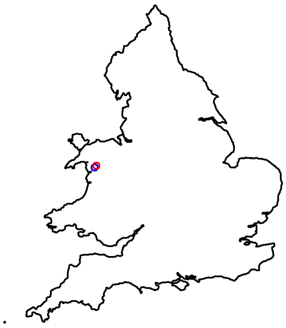
Mawddach Group (MWG)

Extractable Mn

Mn_ax (mg/kg)

Min	=	29
Median	=	377
Mean	=	377
Max	=	725
Std dev	=	492
n	=	2

FF	Ffestiniog Flags Formation (1)
MW	Maentwrog Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

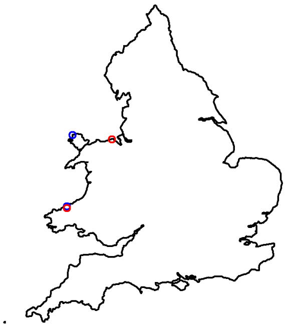
Other Ordovician (XO)

Extractable Mn

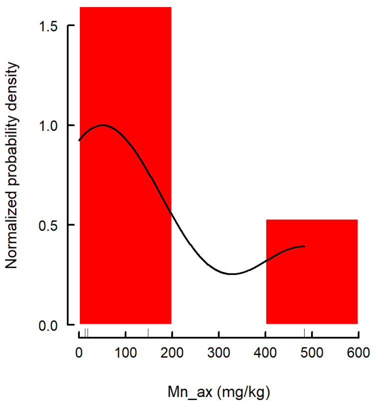
Mn_ax (mg/kg)

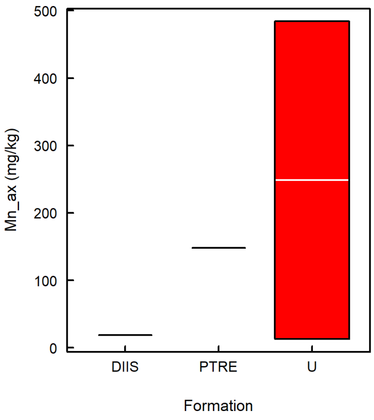
Min	=	13
Median	=	83.5
Mean	=	166
Max	=	484
Std dev	=	221
n	=	4

DIIS	Dinas Island Formation (1)
PTRE	Pentre Formation (1)
U	Undifferentiated (2)



Blue points are below the median
Red points are at or above the median





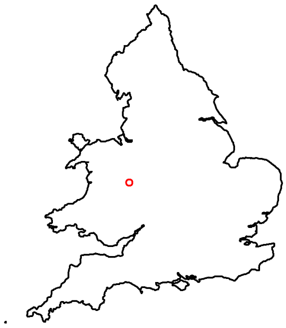
Stretton Group (YST)

Extractable Mn

Mn_ax (mg/kg)

Min = 57
Median = 57
Mean = 57
Max = 57
Std dev = NA
n = 1

SYGP Synalds Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Other Pre-Cambrian (XA)

Extractable Mn

Mn_ax (mg/kg)

Min = 90
Median = 90
Mean = 90
Max = 90
Std dev = NA
n = 1

U Undifferentiated (1)

Blue points are below the median
Red points are at or above the median

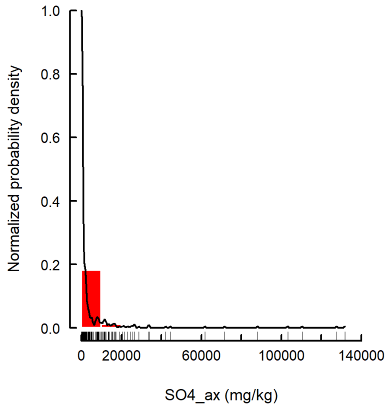
Not enough data for plotting

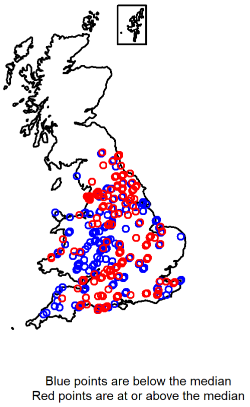
7.6 GEOLOGICAL ATLAS OF DATA FOR EXTRACTABLE S

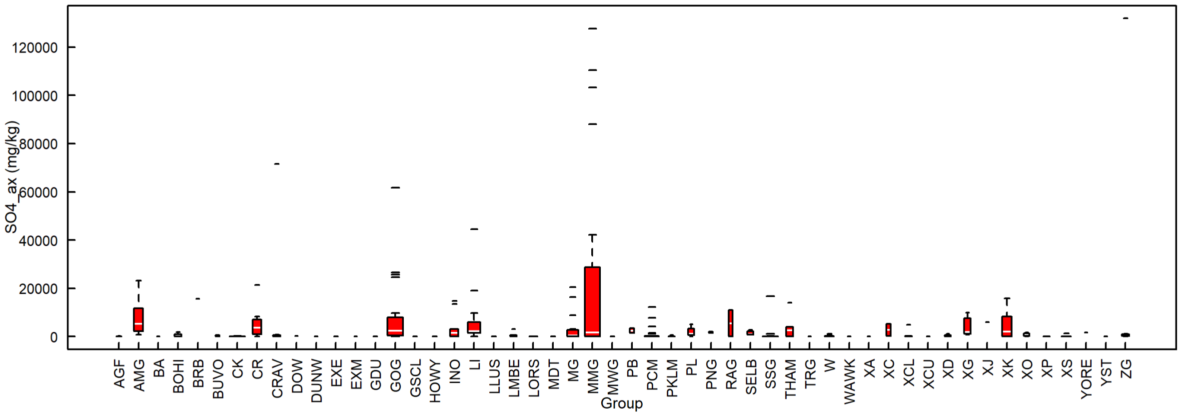
All Groups (All)

Extractable SO4

SO4_ax (mg/kg)







7.6.1 Quaternary and Neogene

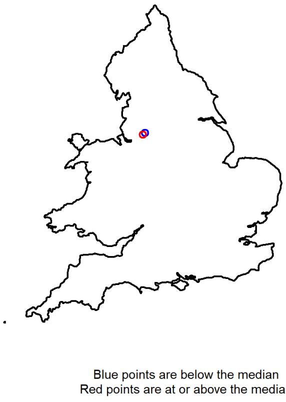
Glacial Deposits (GDU)

Extractable SO4

SO4_ax (mg/kg)

Min = 30
Median = 74
Mean = 74
Max = 118
Std dev = 62.2
n = 2

U Undifferentiated (2)



Not enough data for plotting

Dunwich Group (DUNW)

Extractable SO4

SO4_ax (mg/kg)

Min = 30
Median = 30
Mean = 30
Max = 30
Std dev = NA
n = 1

KGCA Kesgrave Catchment Subgroup (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Palaeogene

Barton Group (BA)

Extractable SO4

SO4_ax (mg/kg)

Min = 30
Median = 30
Mean = 30
Max = 30
Std dev = NA
n = 1

BECH Becton Sand and Chama Sand Fms (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Bracklesham Group (BRB)

Extractable SO4

SO4_ax (mg/kg)

Min = 15600
Median = 15600
Mean = 15600
Max = 15600
Std dev = NA
n = 1

WTT	Wittering Formation (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

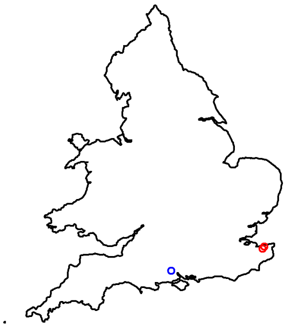
Thames Group (THAM)

Extractable SO4

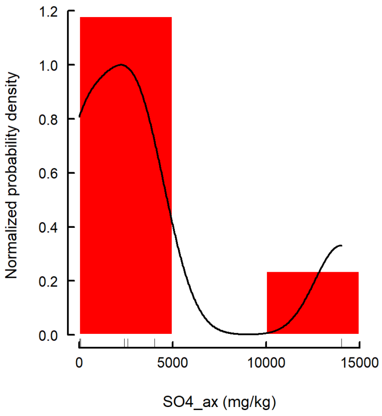
SO4_ax (mg/kg)

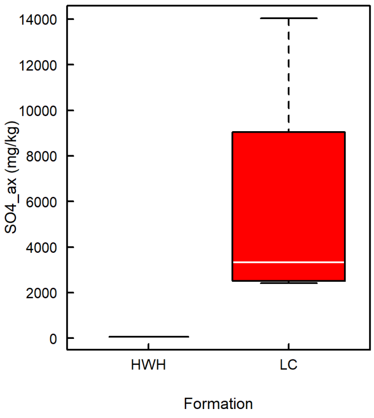
Min = 30
Median = 2510
Mean = 3860
Max = 14000
Std dev = 5220
n = 6

HWH	Harwich Formation (2)
LC	London Clay Formation (4)



Blue points are below the median
Red points are at or above the median





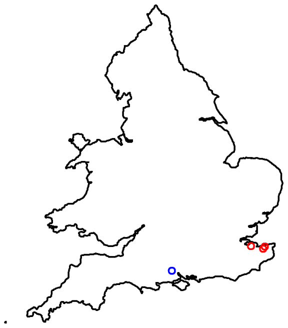
Lambeth Group (LMBE)

Extractable SO4

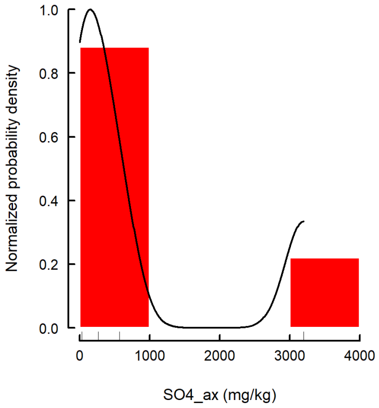
SO4_ax (mg/kg)

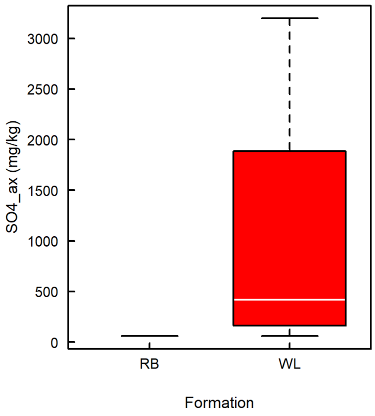
Min = 30
Median = 265
Mean = 819
Max = 3200
Std dev = 1350
n = 5

RB Reading Formation (1)
WL Woolwich Formation (4)



Blue points are below the median
Red points are at or above the median





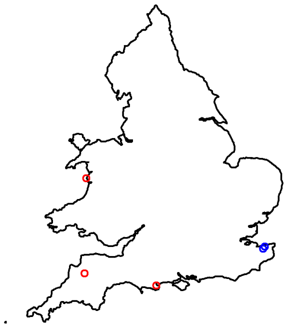
Other Palaeogene (XG)

Extractable SO4

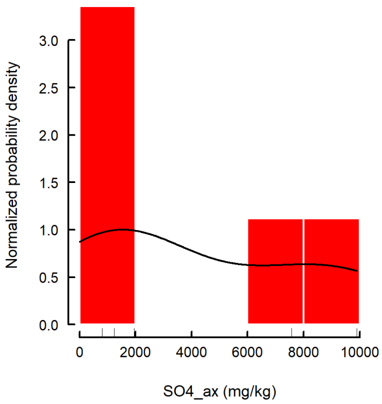
SO4_ax (mg/kg)

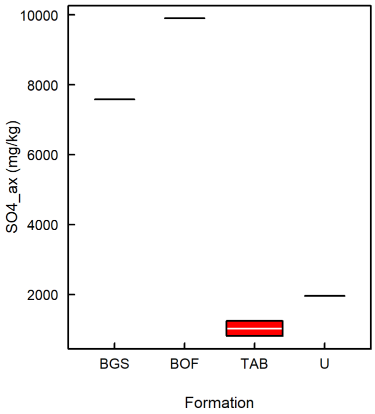
Min = 806
Median = 1960
Mean = 4290
Max = 9900
Std dev = 4160
n = 5

BGS Bagshot Formation (1)
BOF Bovey Formation (1)
TAB Thanet Formation (2)
U Undifferentiated (1)



Blue points are below the median
Red points are at or above the median





7.6.2 Cretaceous

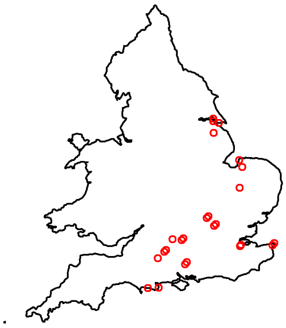
Chalk Group (CK)

Extractable SO4

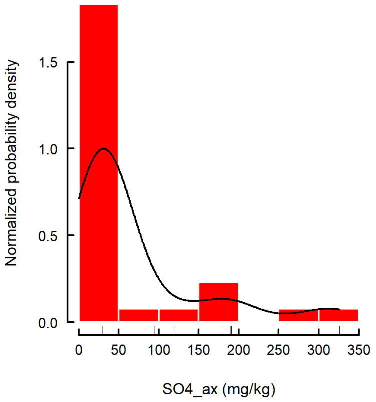
SO4_ax (mg/kg)

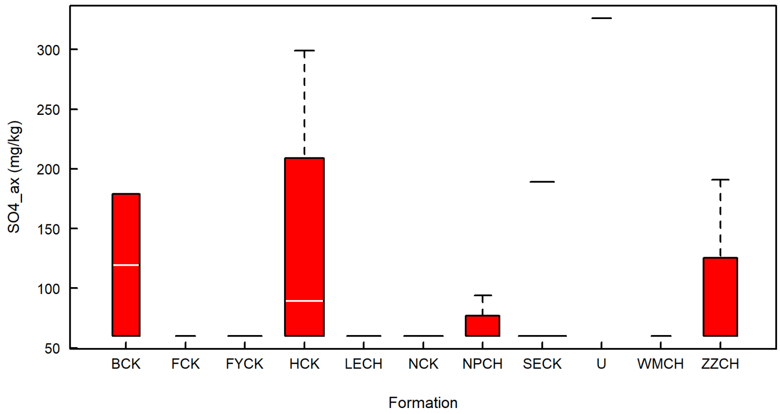
Min = 30
Median = 30
Mean = 68.3
Max = 326
Std dev = 81.6
n = 31

BCK	Burnham Chalk Formation (2)
FCK	Flamborough Chalk Formation (1)
FYCK	Ferriby Chalk Formation (3)
HCK	Holywell Nodular Chalk Formation (4)
LECH	Lewes Nodular Chalk Formation (3)
NCK	Newhaven Chalk Formation (4)
NPCH	New Pit Chalk Formation (3)
SECK	Seaford Chalk Formation (6)
U	Undifferentiated (1)
WMCH	West Melbury Marly Chalk Formation (1)
ZZCH	Zig Zag Chalk Formation (3)



Blue points are below the median
Red points are at or above the median





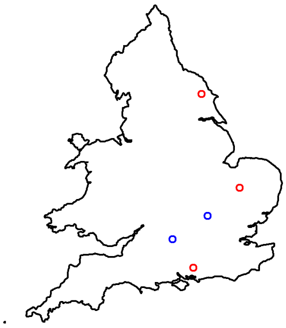
Selborne Group (SELB)

Extractable SO4

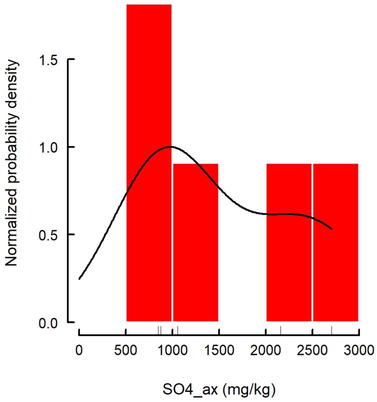
SO4_ax (mg/kg)

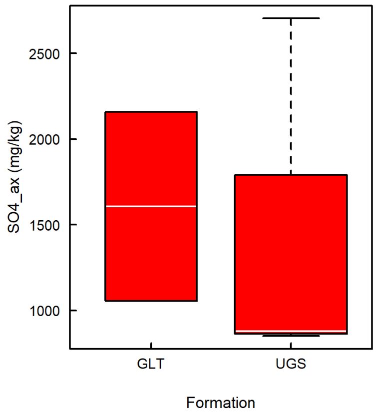
Min = 850
Median = 1060
Mean = 1530
Max = 2700
Std dev = 849
n = 5

GLT	Gault Formation (2)
UGS	Upper Greensand Formation (3)



Blue points are below the median
Red points are at or above the median





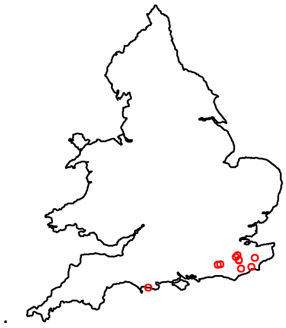
Wealden Group (W)

Extractable SO4

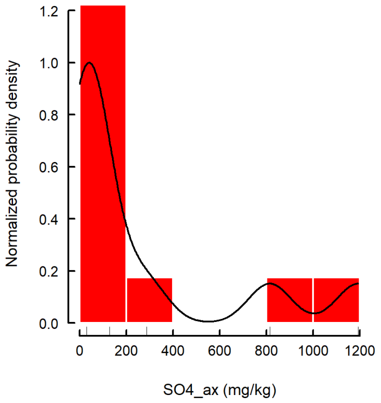
SO4_ax (mg/kg)

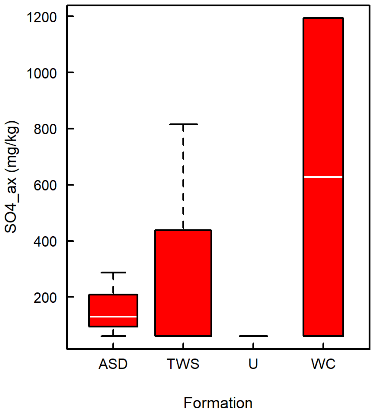
Min = 30
Median = 30
Mean = 260
Max = 1190
Std dev = 410
n = 10

ASD	Ashdown Formation (3)
TWS	Tunbridge Wells Sand Formation (4)
U	Undifferentiated (1)
WC	Weald Clay Formation (2)



Blue points are below the median
Red points are at or above the median





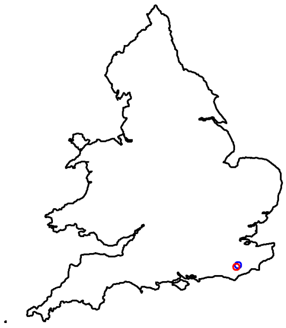
Purbeck Group (PB)

Extractable SO4

SO4_ax (mg/kg)

Min = 1510
Median = 2500
Mean = 2500
Max = 3490
Std dev = 1400
n = 2

DURN	Durlston Formation (1)
LULW	Lulworth Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

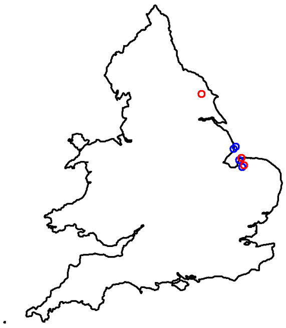
Other Cretaceous (XK)

Extractable SO4

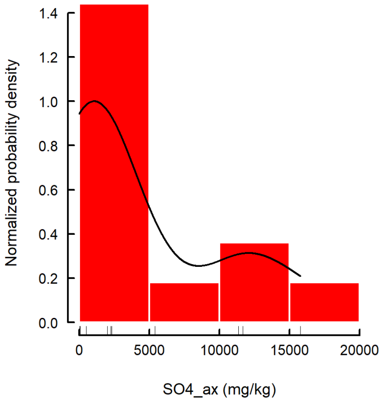
SO4_ax (mg/kg)

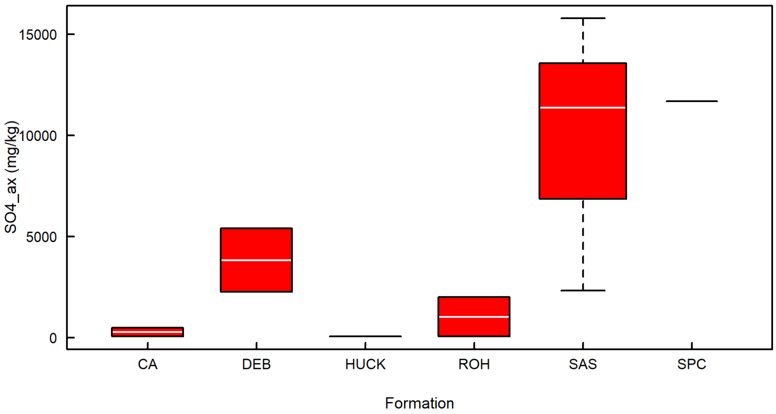
Min = 30
Median = 2140
Mean = 4290
Max = 15800
Std dev = 5540
n = 12

CA	Carstone Formation (2)
DEB	Dersingham Formation (2)
HUCK	Hunstanton Formation (2)
ROH	Roach Formation (2)
SAS	Sandringham Sand Formation (3)
SPC	Speeton Clay Formation (1)



Blue points are below the median
Red points are at or above the median





7.6.3 Jurassic

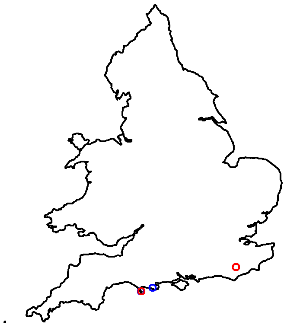
Portland Group (PL)

Extractable SO4

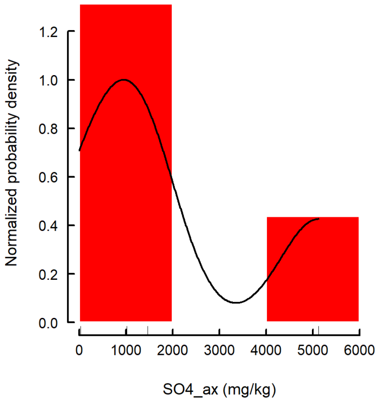
SO4_ax (mg/kg)

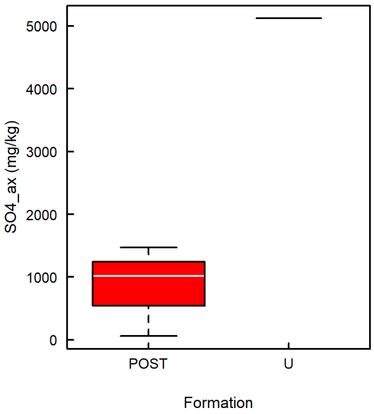
Min = 30
Median = 1240
Mean = 1910
Max = 5120
Std dev = 2220
n = 4

POST	Portland Stone Formation (3)
U	Undifferentiated (1)



Blue points are below the median
Red points are at or above the median





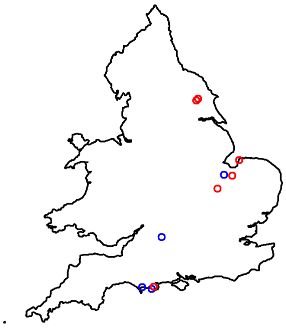
Ancholme Group (AMG)

Extractable SO4

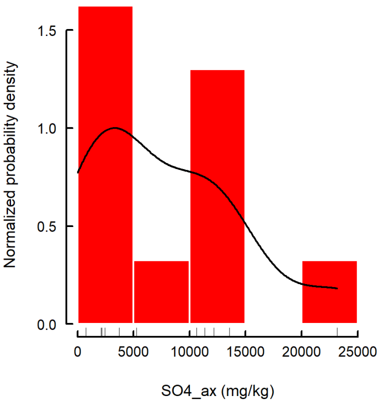
SO4_ax (mg/kg)

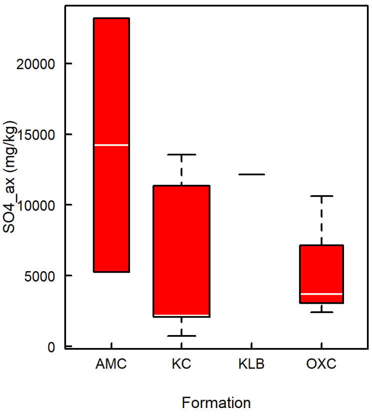
Min = 737
Median = 5260
Mean = 7930
Max = 23200
Std dev = 6900
n = 11

AMC	Ampthill Clay Formation (2)
KC	Kimmeridge Clay Formation (5)
KLB	Kellaways Formation (1)
OXC	Oxford Clay Formation (3)



Blue points are below the median
Red points are at or above the median





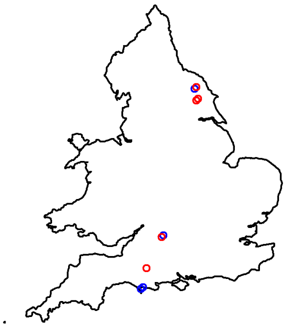
Corallian Group (CR)

Extractable SO4

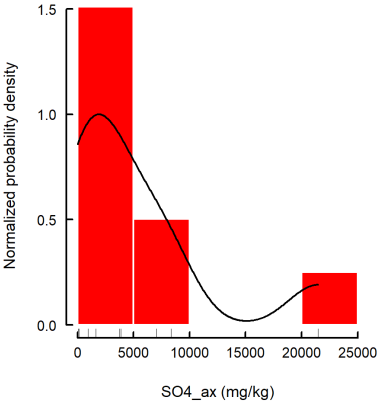
SO4_ax (mg/kg)

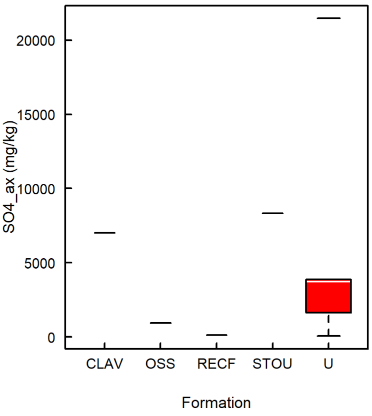
Min = 30
Median = 3740
Mean = 5240
Max = 21500
Std dev = 6750
n = 9

CLAV	Clavellata Formation (1)
OSS	Osmington Oolite Formation (1)
RECF	Redcliff Formation (1)
STOU	Stour Formation (1)
U	Undifferentiated (5)



Blue points are below the median
Red points are at or above the median





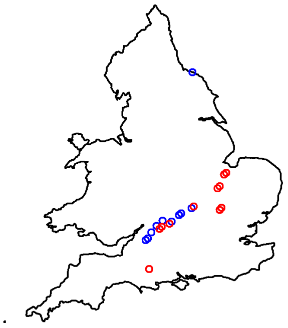
Great Oolite Group (GOG)

Extractable SO4

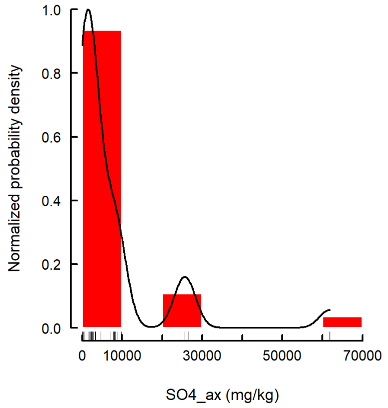
SO4_ax (mg/kg)

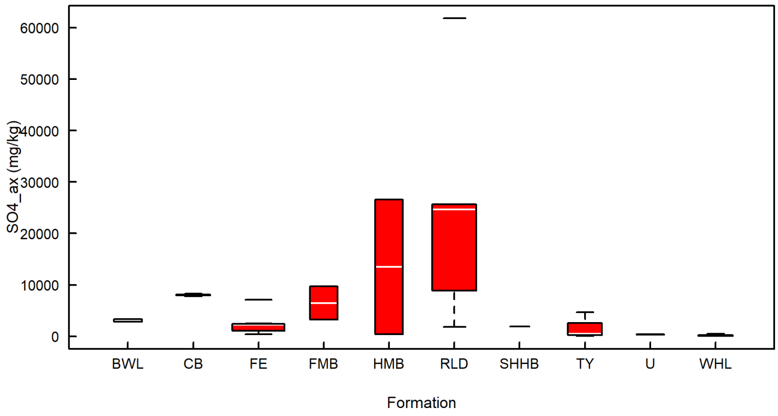
Min = 30
Median = 2390
Mean = 7270
Max = 61800
Std dev = 12700
n = 30

BWL	Blisworth Limestone Formation (2)
CB	Cornbrash Formation (3)
FE	Fuller'S Earth Formation (7)
FMB	Forest Marble Formation (2)
HMB	Hampen Formation (2)
RLD	Rutland Formation (5)
SHHB	Sharp'S Hill Formation (1)
TY	Taynton Limestone Formation (3)
U	Undifferentiated (2)
WHL	White Limestone Formation (3)



Blue points are below the median
Red points are at or above the median





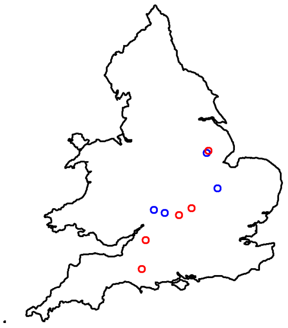
Inferior Oolite Group (INO)

Extractable SO4

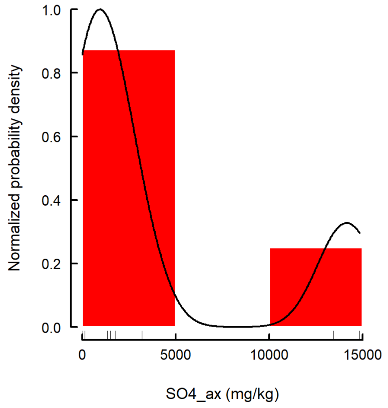
SO4_ax (mg/kg)

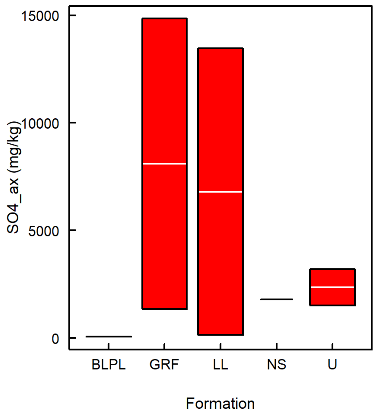
Min = 30
Median = 1520
Mean = 4040
Max = 14800
Std dev = 5840
n = 9

BLPL	Birdlip Limestone Formation (2)
GRF	Grantham Formation (2)
LL	Lincolnshire Limestone Formation (2)
NS	Northampton Sand Formation (1)
U	Undifferentiated (2)



Blue points are below the median
Red points are at or above the median





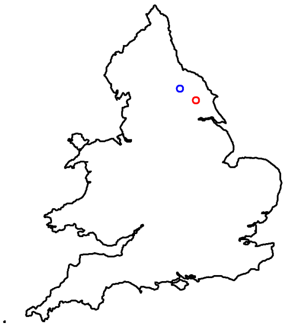
Ravenscar Group (RAG)

Extractable SO4

SO4_ax (mg/kg)

Min = 30
Median = 5480
Mean = 5480
Max = 10900
Std dev = 7710
n = 2

SCY	Scalby Formation (1)
U	Undifferentiated (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

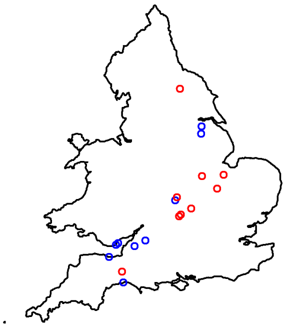
Lias Group (LI)

Extractable SO4

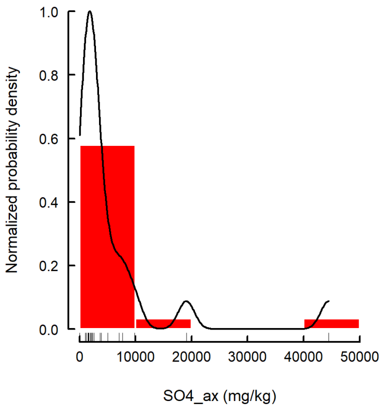
SO4_ax (mg/kg)

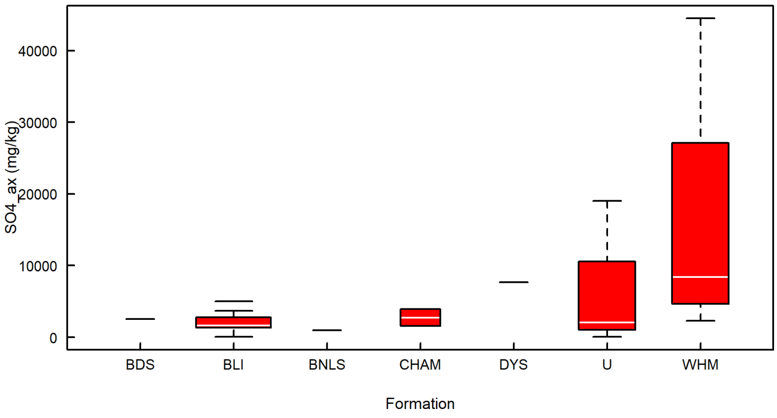
Min = 30
Median = 2220
Mean = 5920
Max = 44500
Std dev = 10100
n = 20

BDS	Bridport Sand Formation (1)
BLI	Blue Lias Formation (7)
BNLS	Beacon Limestone Formation (1)
CHAM	Charmouth Mudstone Formation (2)
DYS	Dyrham Formation (1)
U	Undifferentiated (4)
WHM	Whitby Mudstone Formation (4)



Blue points are below the median
Red points are at or above the median





Other Jurassic (XJ)

Extractable SO4

SO4_ax (mg/kg)

Min = 5920
Median = 5920
Mean = 5920
Max = 5920
Std dev = NA
n = 1

SAS Sandringham Sand Formation (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

7.6.4 Triassic

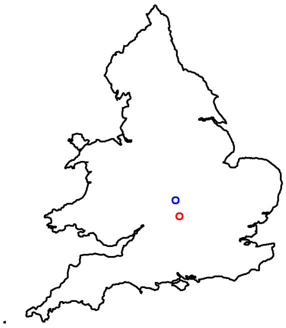
Penarth Group (PNG)

Extractable SO4

SO4_ax (mg/kg)

Min = 1540
Median = 1800
Mean = 1800
Max = 2060
Std dev = 364
n = 2

U Undifferentiated (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

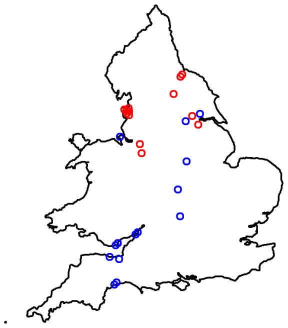
Mercia Mudstone Group (MMG)

Extractable SO4

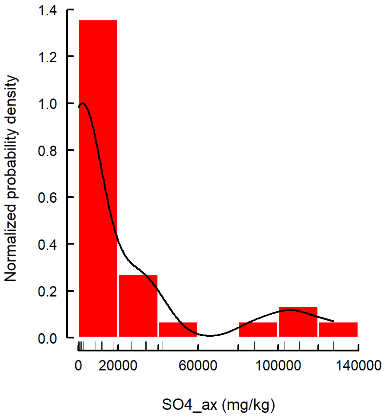
SO4_ax (mg/kg)

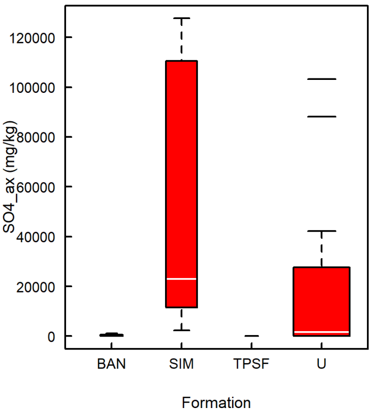
Min = 30
Median = 1740
Mean = 22500
Max = 128000
Std dev = 37100
n = 29

BAN	Blue Anchor Formation (3)
SIM	Sidmouth Mudstone Formation (6)
TPSF	Tarporley Siltstone Formation (1)
U	Undifferentiated (19)



Blue points are below the median
Red points are at or above the median





Sherwood Sandstone Group (SSG)

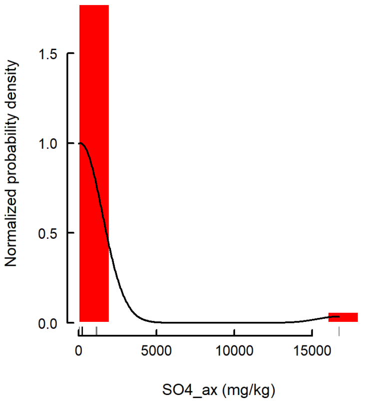
Extractable SO4

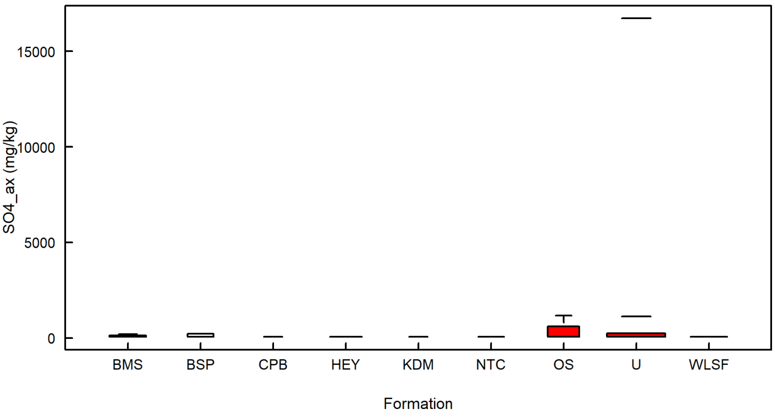
SO4_ax (mg/kg)

Min = 30
Median = 30
Mean = 680
Max = 16700
Std dev = 3040
n = 30

BMS	Bromsgrove Sandstone Formation (4)
BSP	Budleigh Salterton Pebble Beds Formation (2
CPB	Chester Pebble Beds Formation (1)
HEY	Helsby Sandstone Formation (3)
KDM	Kidderminster Formation (1)
NTC	Nottingham Castle Sandstone Formation (2)
OS	Otter Sandstone Formation (3)
U	Undifferentiated (10)
WLSF	Wilmslow Sandstone Formation (4)

Blue points are below the median
Red points are at or above the median





7.6.5 Permian

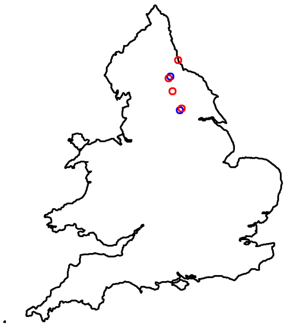
Zechstein Group (ZG)

Extractable SO4

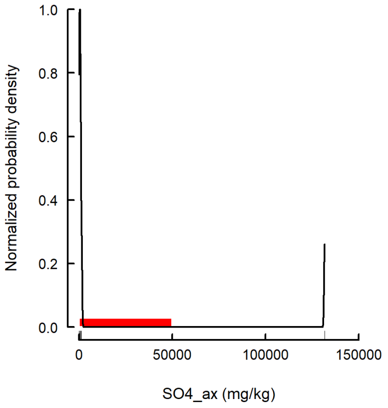
SO4_ax (mg/kg)

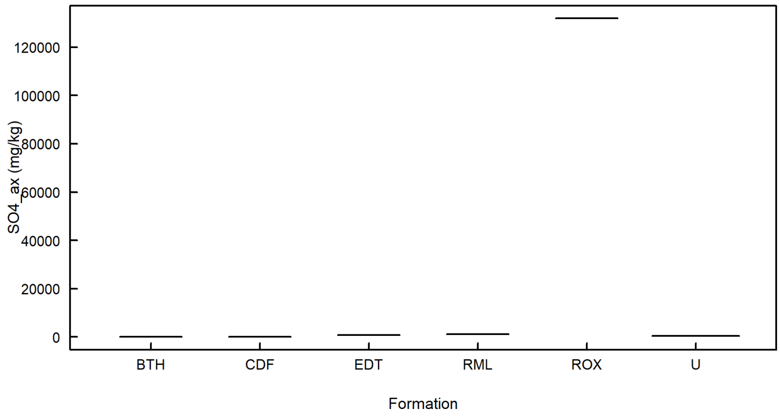
Min = 30
Median = 454
Mean = 19300
Max = 132000
Std dev = 49700
n = 7

BTH	Brotherton Formation (1)
CDF	Cadeby Formation (1)
EDT	Edlington Formation (1)
RML	Raisby Formation (1)
ROX	Roxby Formation (1)
U	Undifferentiated (2)



Blue points are below the median
Red points are at or above the median





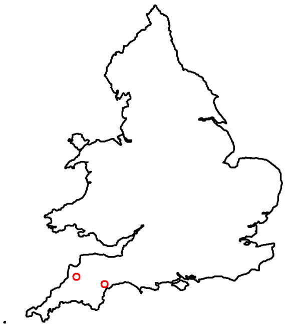
Exeter Group (EXE)

Extractable SO4

SO4_ax (mg/kg)

Min = 30
Median = 30
Mean = 30
Max = 30
Std dev = 0
n = 2

BOB	Bow Breccia Formation (1)
HVBR	Heavitree Breccia Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Warwickshire Group (WAWK)

Extractable SO4

SO4_ax (mg/kg)

Min = 30
Median = 30
Mean = 30
Max = 30
Std dev = NA
n = 1

SAL Salop Formation (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Other Permian (XP)

Extractable SO4

SO4_ax (mg/kg)

Min = 30
Median = 30
Mean = 30
Max = 30
Std dev = 0
n = 5

BRI Bridgnorth Sandstone Formation (5)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

7.6.6 Carboniferous

Pennine Coal Measures Group (PCM)

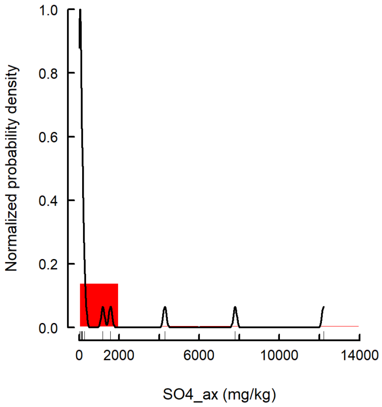
Extractable SO4

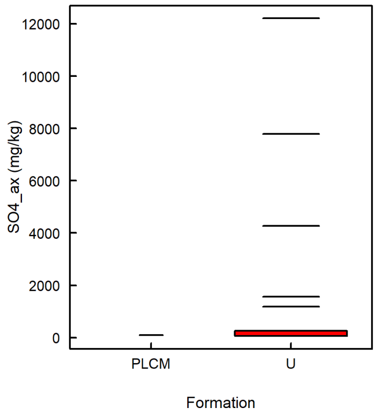
SO4_ax (mg/kg)

Min = 30
Median = 30
Mean = 1180
Max = 12200
Std dev = 2940
n = 24

PLCM	Pennine Lower Coal Measures Formation (1)
U	Undifferentiated (23)

Blue points are below the median
Red points are at or above the median





Holsworthy Group (HOWY)

Extractable SO4

SO4_ax (mg/kg)

Min = 30
Median = 30
Mean = 30
Max = 30
Std dev = 0
n = 2

BF	Bude Formation (2)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

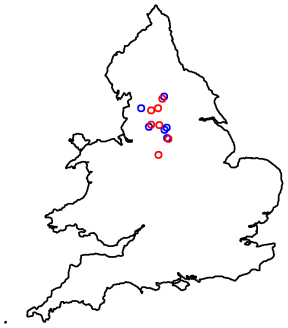
Millstone Grit Group (MG)

Extractable SO4

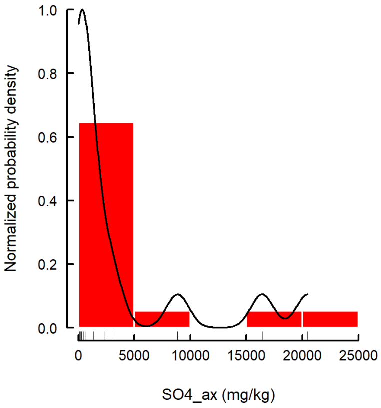
SO4_ax (mg/kg)

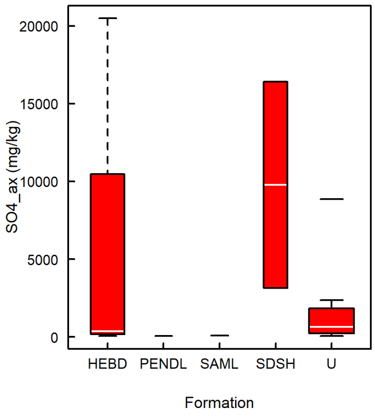
Min = 30
Median = 458
Mean = 3640
Max = 20500
Std dev = 6470
n = 15

HEBD	Hebden Formation (4)
PENDL	Pendleton Formation (1)
SAML	Samlesbury Formation (1)
SDSH	Sabden Shales (2)
U	Undifferentiated (7)



Blue points are below the median
Red points are at or above the median





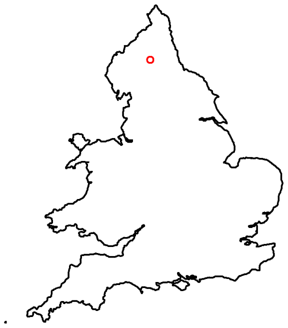
Yoredale Group (YORE)

Extractable SO4

SO4_ax (mg/kg)

Min = 1730
Median = 1730
Mean = 1730
Max = 1730
Std dev = NA
n = 1

SMGP	Stainmore Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

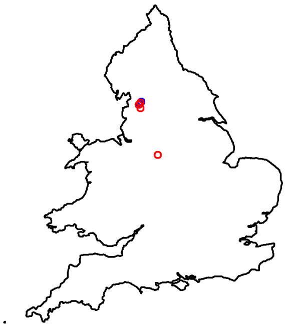
Craven Group (CRAV)

Extractable SO4

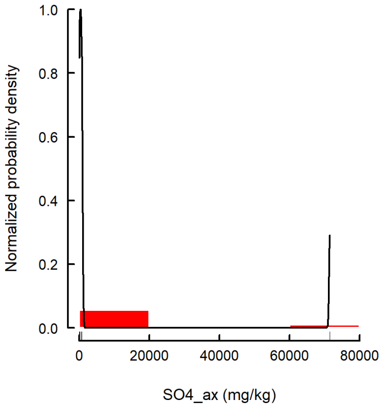
SO4_ax (mg/kg)

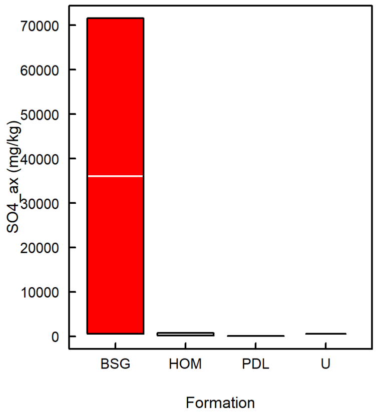
Min = 30
Median = 562
Mean = 10500
Max = 71600
Std dev = 26900
n = 7

BSG	Bowland Shale Formation (2)
HOM	Hodder Mudstone Formation (2)
PDL	Pendleside Limestone Formation (2)
U	Undifferentiated (1)



Blue points are below the median
Red points are at or above the median





Great Scar Limestone Group (GSCL)

Extractable SO4

SO4_ax (mg/kg)

Min = 30
Median = 30
Mean = 30
Max = 30
Std dev = 0
n = 2

KLSL	Kilnsey Formation (2)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Peak Limestone Group (PKLM)

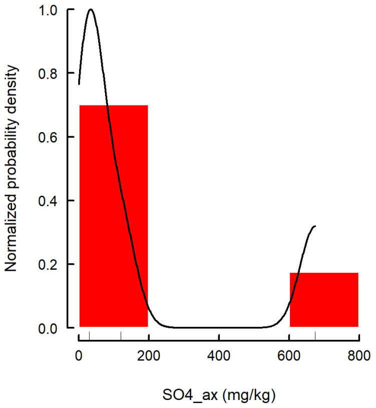
Extractable SO4

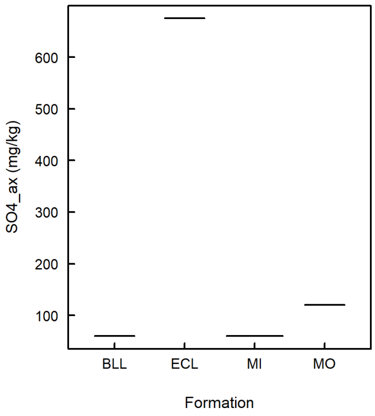
SO4_ax (mg/kg)

Min = 30
Median = 30
Mean = 177
Max = 675
Std dev = 281
n = 5

BLL	Bee Low Limestone Formation (1)
ECL	Ecton Limestone Formation (1)
MI	Milldale Limestone Formation (2)
MO	Monsal Dale Limestone Formation (1)

Blue points are below the median
Red points are at or above the median





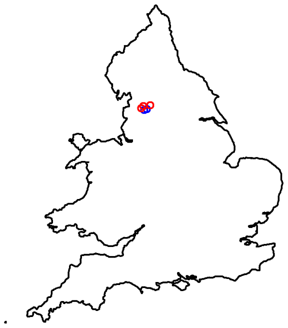
Bowland High Group (BOHI)

Extractable SO4

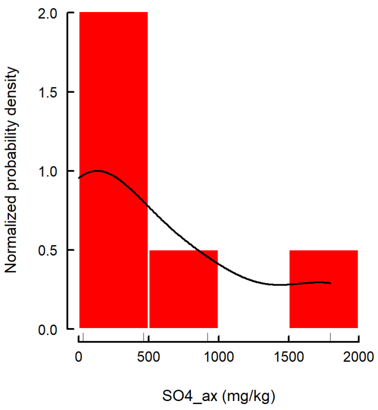
SO4_ax (mg/kg)

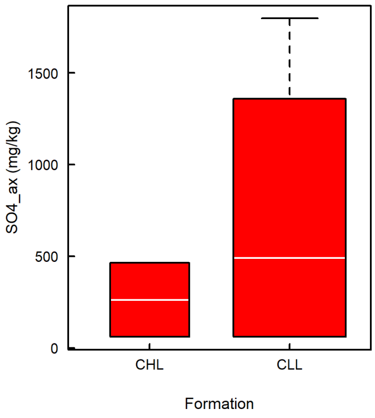
Min = 30
Median = 247
Mean = 546
Max = 1800
Std dev = 709
n = 6

CHL	Chatburn Limestone Formation (2)
CLL	Clitheroe Limestone Formation (4)



Blue points are below the median
Red points are at or above the median





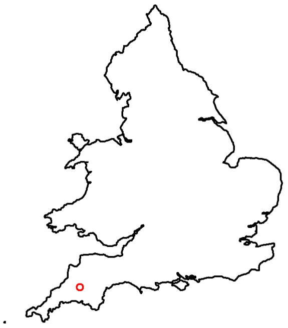
Transition Group (Devonian-Carboniferc

Extractable SO4

SO4_ax (mg/kg)

Min = 30
Median = 30
Mean = 30
Max = 30
Std dev = NA
n = 1

SBT South Brentor Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

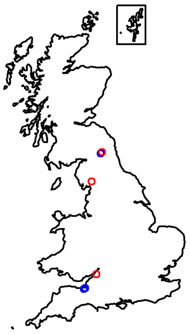
Other Carb. Limestone Supergroup (XC

Extractable SO4

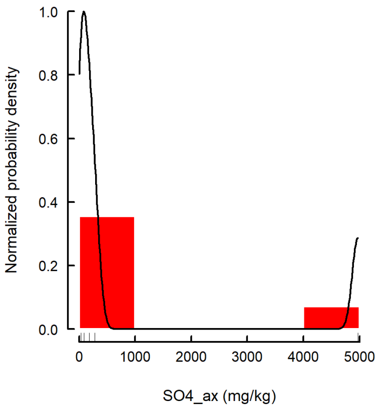
SO4_ax (mg/kg)

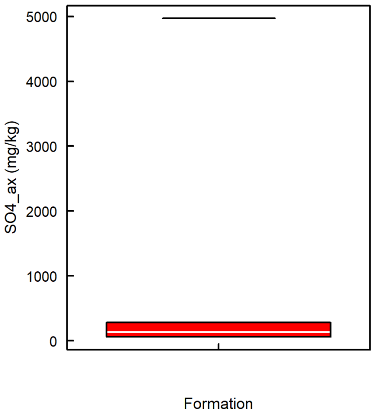
Min = 30
Median = 134
Mean = 929
Max = 4970
Std dev = 1980
n = 6

U Undifferentiated (6)



Blue points are below the median
Red points are at or above the median





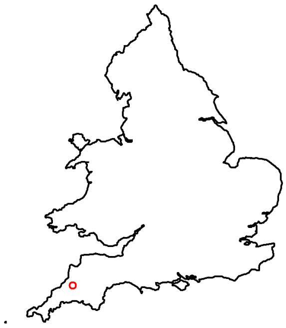
Other Culm Supergroup (XCU)

Extractable SO4

SO4_ax (mg/kg)

Min = 131
Median = 131
Mean = 131
Max = 131
Std dev = NA
n = 1

U Undifferentiated (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

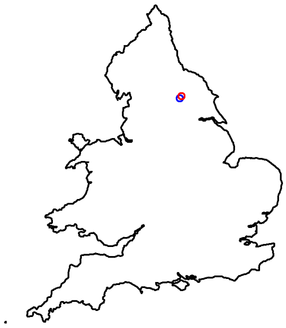
Other Carboniferous (XC)

Extractable SO4

SO4_ax (mg/kg)

Min = 206
Median = 2710
Mean = 2710
Max = 5210
Std dev = 3540
n = 2

U Undifferentiated (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

7.6.7 Devonian

Exmoor Group (EXM)

Extractable SO4

SO4_ax (mg/kg)

Min = 30
Median = 30
Mean = 30
Max = 30
Std dev = NA
n = 1

PLT Pilton Mudstone Formation (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Meadfoot Group (MDT)

Extractable SO4

SO4_ax (mg/kg)

Min = 30
Median = 30
Mean = 30
Max = 30
Std dev = 0
n = 2

U Undifferentiated (2)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

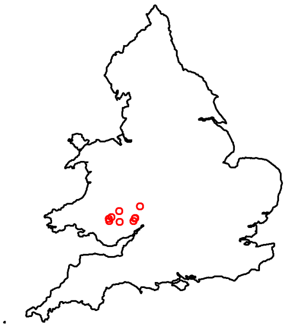
Lower Old Red Sandstone (LORS)

Extractable SO4

SO4_ax (mg/kg)

Min	=	30
Median	=	30
Mean	=	30
Max	=	30
Std dev	=	0
n	=	9

BRS	Brownstones Formation (7)
SMG	St Maughans Formation (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Downton Group (DOW)

Extractable SO4

SO4_ax (mg/kg)

Min	=	189
Median	=	189
Mean	=	189
Max	=	189
Std dev	=	NA
n	=	1

RG Raglan Mudstone Formation (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Other Devonian (XD)

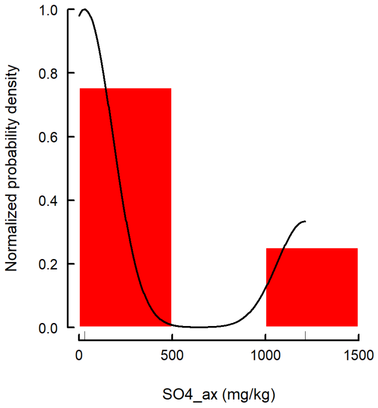
Extractable SO4

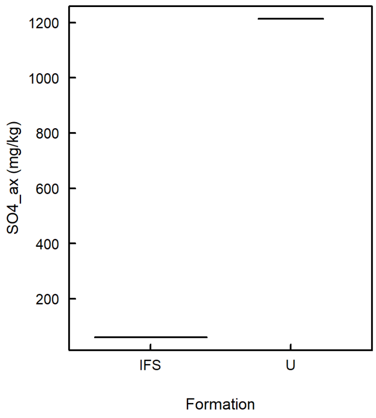
SO4_ax (mg/kg)

Min = 30
Median = 30
Mean = 326
Max = 1210
Std dev = 592
n = 4

IFS Ilfracombe Slates Formation (3)
U Undifferentiated (1)

Blue points are below the median
Red points are at or above the median





7.6.8 Pre-Devonian

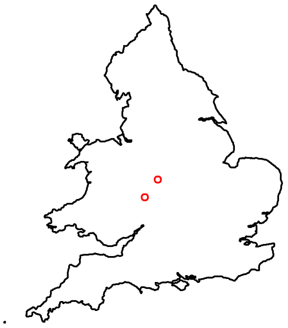
Lower Ludlow Shales Group (LLUS)

Extractable SO4

SO4_ax (mg/kg)

Min = 30
Median = 30
Mean = 30
Max = 30
Std dev = 0
n = 2

U Undifferentiated (2)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Aberystwyth Grits Group (AGF)

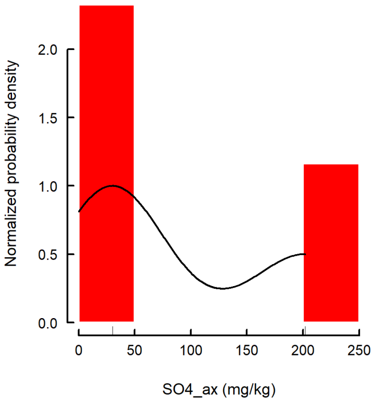
Extractable SO4

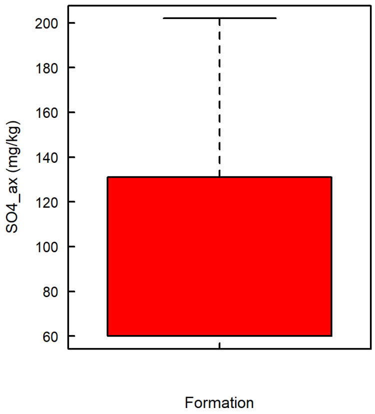
SO4_ax (mg/kg)

Min = 30
Median = 30
Mean = 87.3
Max = 202
Std dev = 99.3
n = 3

MYBA	Mynydd Bach Formation (3)


Blue points are below the median
Red points are at or above the median





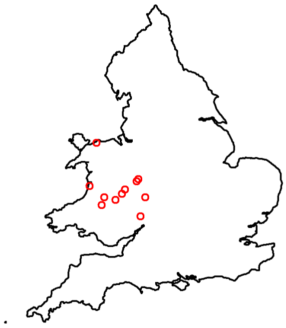
Other Silurian (XS)

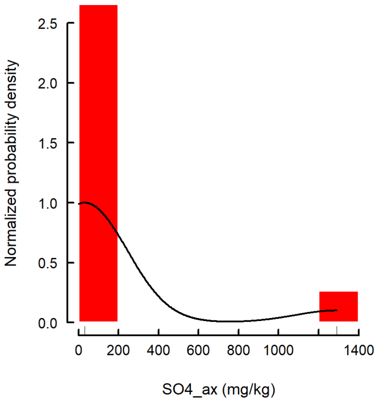
Extractable SO4

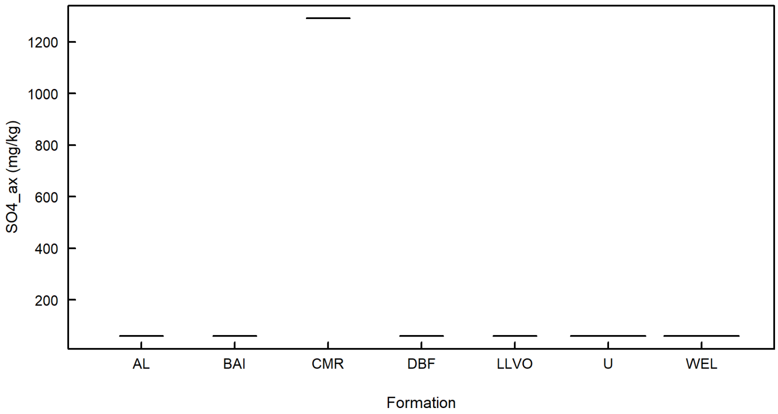
SO4_ax (mg/kg)

Min = 30
Median = 30
Mean = 145
Max = 1290
Std dev = 380
n = 11

AL	Aymestry Limestone Formation (1)
BAI	Bailey Hill Formation (1)
CMR	Cwmere Formation (1)
DBF	Devil'S Bridge Formation (1)
LLVO	Llanwrtyd Volcanic Formation (1)
U	Undifferentiated (3)
WEL	Much Wenlock Limestone Formation (3)


Blue points are below the median
Red points are at or above the median





Builth Volcanic Group (BUVO)

Extractable SO4

SO4_ax (mg/kg)

Min = 30
Median = 301
Mean = 301
Max = 572
Std dev = 383
n = 2

U Undifferentiated (2)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

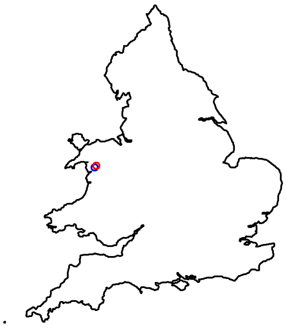
Mawddach Group (MWG)

Extractable SO4

SO4_ax (mg/kg)

Min = 30
Median = 91.5
Mean = 91.5
Max = 153
Std dev = 87
n = 2

FF Ffestiniog Flags Formation (1)
MW Maentwrog Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

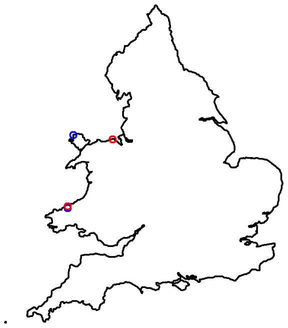
Other Ordovician (XO)

Extractable SO4

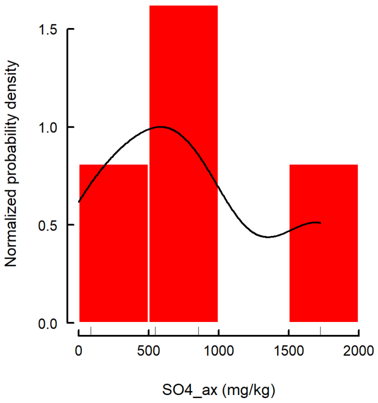
SO4_ax (mg/kg)

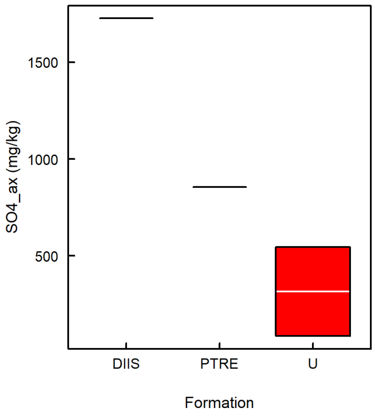
Min = 86
Median = 700
Mean = 803
Max = 1730
Std dev = 692
n = 4

DIIS	Dinas Island Formation (1)
PTRE	Pentre Formation (1)
U	Undifferentiated (2)



Blue points are below the median
Red points are at or above the median





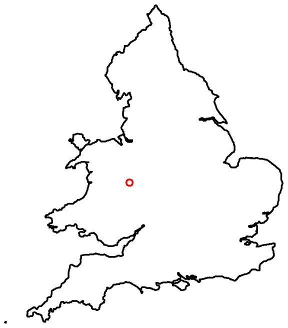
Stretton Group (YST)

Extractable SO4

SO4_ax (mg/kg)

Min = 30
Median = 30
Mean = 30
Max = 30
Std dev = NA
n = 1

SYGP	Synalds Formation (1)



Blue points are below the median
Red points are at or above the median

Not enough data for plotting

Other Pre-Cambrian (XA)

Extractable SO4

SO4_ax (mg/kg)

Min = 30
Median = 30
Mean = 30
Max = 30
Std dev = NA
n = 1

U Undifferentiated (1)

Blue points are below the median
Red points are at or above the median

Not enough data for plotting

8 Mineralogy

8.1 MEASUREMENT OF MINERALOGIAL PARAMETERS

The preliminary consideration of which rock parameters are considered to have major significance for geochemical reactivity suggested three that are, at least to some degree, mineralogical in nature: the clay content, mineral oxide content (i.e. Fe, Mn, Al) and sulphide content. All three can be approached from very different positions when considered in isolation, but all three can be addressed very effectively using modern quantitative X-ray diffraction analysis. The following sections describe the development and range of experimental approaches used to tackle these three parameters individually, before the preferred XRD analysis is described in Section 8.1.4.

8.1.1 Clay content

The term 'clay mineral' is most commonly used to denote a family of hydrous alumino-silicates (more specifically phyllosilicates)' usually with particle sizes <2 µm. They are chemically and structurally similar to other phyllosilicates known as the true and brittle micas. There are many other materials of similar size which are of geological importance, including other silicates such as quartz and zeolites, as well as non-silicates such as the hydroxide, oxyhydroxides, hydrous oxides and amorphous compounds. These are not clay minerals. However, the clay content of rocks and soils is usually methodologically defined in terms of clay-sized material, as the proportion of the material with a given particle size. The particle-size based definition of clay used by the Canadian Soil Survey Committee (CSSC) and the United States Department of Agriculture (USDA) is given in Table 8.1 (Gee and Bauder, 1986).

Table 8.1 Particle size definitions of clay mineralogy

CSSC nomenclature	USDA nomenclature	Mean diameter size range
Clay, fine		<0.2 µm
Clay, coarse		0.2 – 2 µm
	Clay	<2 µm

Particle size analysis can be divided into three different phases; (i) sample treatment, (ii) sample dispersion and (iii) weight contribution of each size fraction of the total sample weight. Each phase comprises several different processes.

PRE-TREATMENTS

Numerous pre-treatments have been developed in order to try to achieve complete aggregate dispersion in samples. The pre-treatments are primarily for the removal of cementing and binding agents such as organic matter, iron oxides, carbonates and soluble salts. A detailed discussion is given by Gee and Bauder (1986).

The effect of organic matter on sample dispersion varies greatly with different soil types. Organic matter acts as a binding agent among particles giving the soil the appearance of having a coarser texture. Organic matter is most commonly removed by oxidation using hydrogen peroxide (H_2O_2). Other oxidants that have been used include sodium hypochlorite (NaOCl), sodium hypobromite (NaOBr) and potassium permanganate ($KMnO_4$) (Gee and Bauder, 1986).

Iron oxides, such as hematite and goethite, can form strong binding agents on soil particles either as discrete crystals or coatings on particle surfaces (Mehra and Jackson, 1960). Iron oxide removal usually involves the reduction and solubilisation of iron using the method of El-Swaify (1980) using sodium dithionite, sodium citrate and sodium bicarbonate (DCB). This procedure consists of multiple washings with the DCB solution until the soil is grey, and subsequent washings with sodium citrate and/or sodium chloride to remove up all iron from the system, saturation of ion-exchange sites with sodium, and flocculation of the samples. Iron oxides are an important part of the mineralogical composition of soils and aquifer material and their removal can change the particle size distribution and lead to erroneous interpretations of other soil chemical properties that are commonly related to particle-size analysis (Kilmer and Alexander, 1949). The procedure should, therefore, be used with caution.

Carbonates are commonly removed from the soil by washing with dilute 0.2 N HCl, 1 N HCl, or an acidified sodium acetate (1 M NaOAC, pH 5) solution. Sodium acetate is recommended because it is not as harsh as HCl and saturates the exchange sites with sodium. Once again caution should be exercised. Limestone and dolomite particles can be removed resulting in a change in particle size distribution and textural classification of the soil (Murray, 2002). The difficulties of measurement of the clay content of carbonate-rich lake sediments after removal of carbonates has also been discussed by Murray (2002).

In alkaline soils, soluble salts of calcium, magnesium, and sodium may be present in concentrations high enough to cause particle flocculation. The addition of sodium-based chemical dispersants further hinders aggregate dispersion by increasing the salt content. Therefore, the salts must be removed prior to sample dispersion. Removal of excess salts can be accomplished by multiple washings with deionised water. Gee and Bauder (1986) suggest the washings should be continued until the leachate salt concentration drops below 10 mM.

MEASUREMENT

The measurement of particle size and hence the clay content are based on the settling of grains in a liquid medium. The rate at which different particles settle is directly related to their size (radius). Falling particles follow Stoke's law in which it is assumed that the particles are smooth and spherical, that they do not interact with each other, that terminal velocity is reached at the start of the settling process, and that the viscosity of the liquid controls the rate of settling. Separation of the various particle sizes can be achieved by homogenisation of the soil suspension and decanting all that remains above a given depth after a given time. Settling times for different fractions are listed in various texts (British Standards Institute, 1998; International Standards Organisation, 1998).

The most common technique for particle-size analysis (PSA) of silt and clay fractions is the pipette method. This method is perhaps the standard method to which most other PSA techniques have been compared. Both British standard and ISO methods using this procedure have been published (Schumacher et al., 1995) and the technique is recommended by the USEPA (e.g. Singer et al., 1988). The method consists of bringing the dispersed sample into suspension after removal of coarser sand and silt fractions by wet sieving. Once suspended, an appropriate settling time is allowed and then the resulting suspension is sampled to a specified depth using a pipette of known volume. The extracted aliquot is dried, weighed, corrected for weight contribution of dispersion agent, and converted into weight percent silt or clay. The major disadvantage of this method is that the procedure is very slow.

With advances in electronic and X-ray technologies and improvements in various sensing devices, several new methods have been developed to enhance the speed of PSA. These methods work on the principles of photo extinction of white light (e.g. Beuselinck et al., 1998; Chappell, 1998; Loizeau et al., 1994; Lu et al., 2000; Shillabeer et al., 1992; Vitton and Sadler, 1997), low angled forwards scattering (Fraunhofer diffraction) of laser light (e.g. Singer et al., 1988; Vitton and Sadler, 1997), X-ray absorption (e.g. Pennington and Lewis, 1979), and electrical conductivity (Beuselinck et al., 1998; Buchan et al., 1993; Loizeau et al., 1994; Pennington and Lewis, 1979). Methods employing photoextinction and X-ray absorption techniques are based on particles settling following Stokes' law. Comparisons of these new methodologies with the standard pipette method (Chao and Zhou, 1983) show there are differences in the results obtained although in general there is good agreement. Despite the advantages of increased speed of analysis, the pipette procedure still appears to be the most commonly used method.

The accuracy of the method can be checked on propriety material with standardised particle sizes. The difficulty in specification in the accuracy of the method comes from the type of samples being used and chemical pre-treatments being applied. Reference materials for clay content in the aquifer materials of interest in this work are likely to be difficult to obtain.

8.1.2 Free mineral oxide content

The free mineral oxide content of a geological material is not strictly defined but refers to the crystalline iron and aluminium oxide content of the material that does not include the amorphous iron and manganese oxides. The term 'free' is a reference to the extraction procedure that should be specific for the crystalline Al and Fe (free) oxides and should not extract (bound) Fe and Al by dissolution of primary and clay minerals. Although there have been detailed studies of the specificity of reagents used to extract amorphous Fe and Mn oxides (Schumacher et al., 1995), it is not clear whether there has been rigorous investigation as to whether the reagents used to extract free mineral oxides do not also extract amorphous oxides. Despite this, the results of the free mineral oxide content are treated as being specific and often the ratio of free oxides to amorphous oxides is used to assess the age of soils where weathering processes are thought to increase the crystalline forms of Al and Fe.

A review of the development of extraction methods has been given by Mehra and Jackson (1960) who show that methods used for this analysis have quickly gravitated to two procedures. The most popular of these is the method of Shedrick and McKeague (1975) which uses sodium dithionite, sodium citrate solution buffered to pH 7.3 with sodium bicarbonate. A pH of 7.3 was chosen because the oxidation potential of $Na_2S_2O_4$-$Na_2C_6H_5O_7.2H_2O$ systems buffered with $NaHCO_3$ increases rapidly up to pH 8 while the solubility of Fe_2O_3 decreases rapidly over pH 7. The two curves intersect at about pH 7.3 suggesting that this is the optimum for pH extraction. The other method is that used by the USDA, which involves shaking overnight with citrate-dithionate solution. Mehra and Jackson (1960) found good agreement between this method and that of Neary and Barnes (1993) when used on 14 Canadian soil samples. At the end of the extraction the amount of Al and Fe in solution is determined by AAS or ICP-AES with matrix matched standards. When using either protocol that care must be taken to monitor the shelf life of the $Na_2S_2O_4$ as the reagent deteriorates resulting in low recoveries of Al and Fe. In addition to this, care should be taken in sample preparation as it has been found that over grinding can cause significant errors (Schumacher et al., 1995)

An alternative approach is the use of dilute acid extraction to selectively extract the desired fraction of free metal oxides. Mineral acid extraction has several clear advantages: it is a simple and easy technique, highly pure reagents are commercially available cheaply, subsequent analysis of extracted metals is easy to carry out on acid aqueous matrices by standard instrumental techniques, and if multi-element techniques such as ICP-OES or ICP-MS are used then a full suite of metals can be analysed simultaneously. Using HCl complexes Fe better but using HNO_3 is also very effective and provides a cleaner matrix for analytical instruments.

There are no ISO or BS methods for this determination and no proficiency testing schemes. The USEPA recommends the standard method used by the USDA Schumacher et al. (1995). No formal standard materials exist but Duan et al. (1997) suggest that samples from the Agriculture Canada ECSS round-robin samples could be used as check materials (the availability of these materials is not known).

8.1.3 Pyrite content

The pyrite content of sediments has been investigated as an important part of the studies of the sulphur diagenetic cycle, sulphate reduction and sulphide mineral formation (Canfield et al., 1986). Sulphur is known to exist in a number of forms within sediment materials; sulphates, organo-sulphur compounds, elemental sulphur, acid volatile mono-sulphides and pyrite (Hern, 1984). Methods that use high temperature combustion and oxidation of sulphur species provide information on the total sulphur content but not on the individual sulphur species present (Lord, 1982). An early methodology (Mehra and Jackson, 1960), that was pyrite-specific but time consuming, used a sequential extraction by first removing iron oxide, followed by iron silicate dissolution with hydrofluoric and boric acids and finally extraction of the pyrite with nitric acid and quantification of the iron content by atomic absorption or colorimetric methods. Canfield et al. (1986) described a method whereby reduced sulphur species (pyrite + acid volatile sulphur + elemental sulphur) are decomposed to hydrogen sulphide in hot acidic $CrCl_2$ solution. The evolved hydrogen sulphide was trapped in a zinc acetate solution forming zinc sulphide that was then determined iodimetrically. The method was shown to be specific for reduced sulphur species. More recently Duan et al. (1997) made modifications to this method in which organic extraction and ethanolic hydrochloric acid distillation steps were added prior to the $CrCl_2$ digestion to remove the elemental sulphur and acid volatile monosulphides respectively allowing the specific pyrite content to be quantified.

These methods for pyrite determination are generally regarded as ‘research’ methods and have not been designed for the routine determination of large batches of samples. It has been shown that the results are dependent on sampling techniques (reducible sulphur species can be oxidised in air) and on the age of the pyrite in the material (Duan et al., 1997). It is likely that development of the methodology would have to be carried out to deal with high carbonate content materials (chalk and limestone) as CO_2 out-gassing during reaction with the acids used in the procedures could cause problems. Although there is some evidence that the reproducibility of these methods is acceptable there are no easily available reference materials or proficiency testing schemes to check the accuracy of pyrite determination.

8.1.4 Preferred method of analysis

Although there are multiple methods described for determination of the parameters above, many of them are laborious and expensive to carry out and provide a rather limited range of data. After consideration it was decided not to pursue any of the more traditional methods for quantitative mineralogical analysis. Recent developments in equipment and data processing, both within BGS and at an international level, have made available an attractive alternative approach – quantitative X-ray diffraction (XRD).

The technique has a number of benefits. As a ‘whole sample’ analysis, XRD generates an overall diffraction pattern which corresponds to the combined influence of all the individual materials contained in the sample. Powerful and recently developed software algorithms make it possible to deconvolute that single diffraction pattern into individual mineral contributions. With appropriate calibration those deconvoluted contributions can be quantified.

For the geochemical properties manual, using XRD provided the opportunity to tackle the parameters discussed above from a slightly different perspective. Instead of being obliged needing to determine mineral oxide content or pyrite content singly by the traditional wet methods they could be assessed simultaneously. Instead of determining clay content by particle sizing, the quantities of multiple individual clay minerals could be estimated directly. At the same time, data are generated for many other minerals, which although not included as part of the core parameter set for geochemical parameters are nonetheless informative.

Mineralogical data collected specifically for inclusion in this compilation were therefore measured by X-ray diffraction using the experimental procedures detailed below.

SAMPLE PREPARATION FOR WHOLE-ROCK ANALYSIS

For whole-rock analysis by XRD, a representative portion of milled sample material (ca. 3 g) was micronised under deionised water for 10 minutes to ensure a fine and uniform particle-size.

SAMPLE PREPARATION FOR CLAY MINERALOGY ANALYSIS

Carbonate removal: Where whole-rock analysis indicated that samples contained significant levels of carbonate species i.e. predominantly limestones and chalks, a buffered acid leach was applied in order to facilitate the release of any clay minerals prior to their separation. For each sample, approximately 30 g crushed material was placed in a 500 mL beaker. Approximately 250 mL of buffered sodium acetate/acetic acid (pH 5.3) was then added and the suspension was treated with ultrasound for 3 minutes. The beakers were then placed in a water bath maintained at 60°C for 6 hours and stirred every hour. The suspensions were then treated to further ultrasound for 3 minutes and left to stand overnight. Next morning the supernatant liquid was discarded. The leaching procedure was repeated until no further reaction was detected between the material and buffer. At this point, the material was transferred to a centrifuge bottle and washed three times with distilled water. It was found that for some of the samples, and those from the Chalk in particular, took up to twelve leaches before no further reaction could be detected upon acid addition.

Sulphate removal: The presence of sulphate-bearing species such as gypsum cause clay mineral dispersions to flocculate and prevent accurate size-separation. Therefore, where whole-rock XRD analysis indicated the presence of gypsum, sulphate species were removed from the samples using a modified version of the method proposed by Bodine and Fernalld (1973). Approximately 10 g of the crushed sample material was placed in a plastic bottle with disodium EDTA solution (400 mL, 0.2 M), buffered to pH 11 using NaOH pellets. The suspension was stirred and then placed in a water bath maintained at 100°C for 4 hours. The leaching process was repeated to ensure all traces of sulphate were removed. After leaching, the supernatant was discarded and the residues washed three times.

Clay fraction separation and oriented mount preparation: The carbonate- and gypsum-free residues of between 10 and 30 g crushed clastic material (dependant on lithology; more material being used for clay-poor lithologies such as sandstones) was placed in a 500 mL bottle with approximately distilled water (200 mL) and shaken on a laboratory shaker overnight, treated with ultrasound for 2 minutes before wet sieving on 63 µm. The >63 µm (‘sand’ fraction) material was then dried at 55°C and bagged. The <63 µm suspended material was placed in a 250 mL measuring cylinder with 1 mL 0.1M sodium hexametaphosphate (‘Calgon’) solution to disperse the individual clay particles and prevent flocculation.

After standing for a period determined from Stokes’ Law, a nominal <2 µm (‘clay’) fraction was removed, dried at 55°C and bagged. The remaining 2–63 µm (‘silt’ fraction) material was discarded.

100 mg of the dried <2 μm material was re-suspended in a minimum of distilled water and pipetted onto a ceramic tile in a vacuum apparatus to produce an oriented mount. The mounts were Ca-saturated using 2 mL 0.1M $CaCl_2.6H_2O$ solution, washed twice to remove excess reagent and allowed to dry at room temperature.

Where less than 100 mg of separated <2 μm material was available, c.20 mg of the material was Ca-saturated using 1M $CaCl_2.6H_2O$ solution. The material was then re-suspended in a minimum of distilled water and pipetted onto a zero-background silicon crystal substrate to produce an oriented mount. The mounts were allowed to dry at room temperature before analysis.

X-RAY DIFFRACTION ANALYSIS

XRD analysis was carried out using a Philips PW1700 series diffractometer equipped with a cobalt-target tube and operating at 45kV and 40mA. Whole-rock powders were scanned from 3-75°2θ at 0.7°2θ/minute. The <2 μm samples were scanned from 2-32°2θ at 0.55°2θ/minute as air-dry mounts, after glycol-solvation and after heating to 550°C for 2 hours. Diffraction data were analysed using Philips X'Pert software coupled to an International Centre for Diffraction Data (ICDD) database running on a PC system.

Following identification of the mineral species present in the samples, mineral quantification was achieved using the Rietveld refinement technique (e.g. Snyder and Bish, 1989) using Siroquant v.2.5 software. This method avoids the need to produce synthetic mixtures and involves the least squares fitting of measured to calculated XRD profiles using a crystal structure databank.

In order to gain further information about the nature of the clay minerals present in the samples, modelling of the XRD profiles was carried out using Newmod-for-Windows™ (Reynolds and Reynolds, 1996) software. Modelling was also used to assess the relative proportions of clay minerals present in the <2 μm fractions by comparison of sample XRD traces with Newmod-for-Windows™ modelled profiles. The modelling process requires the input of diffractometer, scan parameters and a quartz intensity factor (instrumental conditions), and the selection of different sheet compositions and chemistries. In addition, an estimate of the crystallite size distribution of the species may be determined by comparing peak profiles of calculated diffraction profiles with experimental data. By modelling the individual clay mineral species in this way, mineral reference intensities were established and used for quantitative standardization following the method outlined in Moore & Reynolds (1997).

8.1.5 Uncertainty

Relative errors for the quoted mineral concentrations are typically in the region of ±2.5% for concentrations >60 wt%, ±5% for concentrations between 60 and 30 wt%, ±10% for concentrations between 30 and 10 wt%, ±20% for concentrations between 10 and 3 wt% and ±40% for concentrations <3 wt% (Hillier et al., 2001). These figures correspond to a typical absolute uncertainty of ±1.5 wt% across the concentration range.

8.2 SUMMARY AND OVERVIEW OF MINERALOGICAL DATA

The results of whole-rock XRD analysis for the samples are summarised in Table 8.2, split on a stratigraphic basis.

The term 'mica' is used to describe all species that present a c.10Å basal spacing and includes muscovite, biotite, illite and illite/smectite. The term 'chlorite' includes all species that present a c.14Å basal spacing and includes corrensite (an R1 ordered chlorite/smectite). The term 'kaolin' is used to describe all kaolin-group species that typically present c.7.1Å and 3.58Å basal spacings and may include kaolinite and halloysite.

The results of quantitative <2 μm clay mineralogical XRD analyses are summarised in Table 8.3

Carbonate-removal successfully produced clastic fractions from all the carbonate-rich samples (Carboniferous Limestone, Magnesian Limestone, Mercia Mudstone, Lower Lias mudstone, Osmington Oolite, Great Oolite, White Lias and the Chalk) with the exception of one of the samples of Magnesian Limestone. Previous analyses of the Magnesian Limestone have also produced very low clay yields (Gillespie et al., 2001).

Similarly, sulphate-removal successfully produced a clastic fraction from the two Triassic mudstone samples.

Table 8.2 Summary of whole-rock X-ray diffraction analyses. Units of % by mass.

					Silicates						**Carbonates/Sulphates**					**'Clay' mineral**				**Oxides/Sulphides**		
Easting	**Northing**	**Depth (m)**	**Group (Gp)**	**Formation (Fm)**	**Quartz**	**Albite**	**K<Feldspar**	**Cristobalite**	**Tridymite**	**Heulandite**	**Calcite**	**Dolomite**	**Siderite**	**Gypsum**	**Jarosite**	**Mica**	**Chlorite**	**Smectite**	**Kaolin**	**Hematite**	**Anatase**	**Pyrite**
Palaeogene																						
616000	160200	24.0	Thames Gp	Harwich Formation	91.8	2.5	3.5	nd	nd	nd	<0.5	nd	nd	nd	nd	<0.5	<0.5	<0.5	0.7	nd	nd	<0.5
616000	160200	43.0	Montrose Gp	Thanet Fm	87.4	2.5	3.5	nd	nd	nd	1.1	nd	nd	nd	nd	1.6	1.1	0.8	0.7	nd	nd	1.3
616000	160200	12.0	Thames Gp	London Clay Fm	46.5	nd	5.8	nd	nd	nd	nd	nd	nd	nd	nd	23	3.8	4.3	13.9	nd	nd	2.7
591600	165732		Lambeth Gp	Woolwich Fm	85	1.7	3.9	nd	nd	nd	nd	nd	nd	nd	nd	3.1	1.6	1.5	2.4	nd	nd	0.8
616000	160200	33.0	Lambeth Gp	Woolwich Fm	93.7	1.7	2.7	nd	nd	nd	nd	nd	nd	nd	nd	1.7	nd	<0.5	nd	nd	nd	nd
Cretaceous																						
458090	128560	13.7	Chalk Gp	Newhaven Chalk Fm	<0.5	nd	nd	nd	nd	nd	99.3	nd	nd	nd	nd	nd	nd	<0.5	nd	nd	nd	nd
475460	121570		Selborne Gp	Upper Greensand Fm	62.8	<0.5	0.8	6.7	1.9	3.9	10.8	nd	nd	nd	nd	12.6	nd	<0.5	nd	<0.5	nd	nd
517180	206790	35.0	Chalk Gp	Lewes Nodular Chalk Fm	1	nd	nd	nd	nd	nd	97.8	nd	nd	nd	nd	1	nd	<0.5	nd	nd	nd	nd
415900	153710	24.4	Chalk Gp	Lewes Nodular Chalk Fm	<0.5	nd	nd	nd	nd	nd	98.9	nd	nd	nd	nd	0.7	nd	<0.5	nd	nd	nd	nd
636300	167700	21.0	Chalk Gp	Seaford Chalk Fm	0.6	nd	nd	nd	nd	nd	97.7	nd	nd	nd	nd	1.6	nd	<0.5	nd	nd	nd	nd
570300	165750		Chalk Gp	Holywell/New Pit Chalk Fm (Undifferentiated)	0.9	nd	nd	nd	nd	nd	97.9	nd	nd	nd	nd	1	nd	<0.5	nd	nd	nd	nd
415900	153710	48.8	Chalk Gp	New Pit Chalk Fm	0.8	nd	nd	nd	nd	nd	97	nd	nd	nd	nd	2	nd	<0.5	nd	nd	nd	nd
502310	222440	2.3	Chalk Gp	Holywell Chalk Fm	<0.5	nd	nd	nd	nd	nd	96.6	nd	nd	nd	nd	2.2	nd	0.9	nd	nd	nd	nd
415900	153710	96.4	Chalk Gp	Zig Zag Chalk Fm	10	nd	nd	nd	nd	nd	84.1	nd	nd	nd	nd	3.6	2.2	<0.5	nd	nd	nd	nd
502310	222440	27.5	Chalk Gp	Zig Zag Chalk Fm	4	nd	<0.5	nd	nd	nd	91.4	nd	nd	nd	nd	3.4	nd	<0.5	1	nd	nd	nd
557110	363980	39.1	Cromer Knoll Gp	Hunstanton Fm	3.1	0.7	1.7	nd	nd	nd	86.4	nd	nd	nd	nd	4	1.8	<0.5	2.2	nd	nd	nd
524880	127010	18.1	Wealden Gp	Weald Clay Fm	46.1	nd	0.6	nd	nd	nd	nd	nd	nd	nd	nd	20.5	6.4	1.5	24.5	nd	nd	<0.5
Jurassic																						
373420	081720		Corallian Gp	Osmington Oolite Fm	7.7	nd	nd	nd	nd	nd	90.9	nd	nd	nd	nd	0.9	nd	<0.5	nd	<0.5	nd	nd
390910	078510		Ancholme Gp	Kimmeridge Clay Fm	33.9	0.6	2.2	nd	nd	nd	9.8	nd	nd	nd	nd	18.1	1.1	nd	28.3	nd	nd	6
371650	081840		Ancholme Gp	Oxford Clay Fm	40.4	2.6	3.5	nd	nd	nd	13.2	0.5	nd	nd	nd	18.3	3.5	0.9	12.9	nd	nd	4.2
412970	216870	8.0	Great Oolite Gp	Taynton Limestone Fm	1.4	nd	nd	nd	nd	nd	96	nd	nd	nd	nd	2	nd	<0.5	<0.5	nd	nd	nd

					Silicates						**Carbonates/Sulphates**					**'Clay' mineral**				**Oxides/Sulphides**		
Easting	**Northing**	**Depth (m)**	**Group (Gp)**	**Formation (Fm)**	**Quartz**	**Albite**	**K<Feldspar**	**Cristobalite**	**Tridymite**	**Heulandite**	**Calcite**	**Dolomite**	**Siderite**	**Gypsum**	**Jarosite**	**Mica**	**Chlorite**	**Smectite**	**Kaolin**	**Hematite**	**Anatase**	**Pyrite**
426750	210440	12.0	Great Oolite Gp	White Limestone Fm	0.6	nd	nd	nd	nd	nd	95.2	nd	nd	nd	nd	2.5	nd	1	0.7	nd	nd	nd
439520	258540	20.7	Lias Gp		86.2	2.5	1.7	nd	nd	nd	3.2	0.5	nd	nd	nd	3.8	1.4	<0.5	nd	nd	nd	0.6
446870	225860	16.0	Lias Gp	Bridport Sand Fm	41.9	nd	4.9	nd	nd	nd	3.5	0.9	nd	nd	nd	23.1	1.8	1.6	22	nd	nd	<0.5
332970	091210		Lias Gp	Blue Lias Fm	2.3	nd	nd	nd	nd	nd	92	0.5	nd	nd	nd	3	nd	<0.5	0.6	nd	nd	1.3
Triassic																						
309720	085140		Sherwood Sandstone Gp	Otter Sandstone Fm	63.7	nd	24.3	nd	nd	nd	<0.5	nd	nd	nd	nd	7.1	1.1	nd	3.5	<0.5	nd	nd
306120	081650		Sherwood Sandstone Gp	Budleigh Salterton Pebble Beds Fm	90.5	nd	5.5	nd	nd	nd	nd	nd	nd	nd	nd	1.9	nd	nd	1.8	<0.5	nd	nd
357370	328580		Sherwood Sandstone Gp	Helsby Sandstone Fm	83.6	4.6	9.6	nd	nd	nd	<0.5	nd	nd	nd	nd	1.6	nd	<0.5	nd	<0.5	nd	nd
461230	400700	17.0	Sherwood Sandstone Gp	Nottingham Castle Sandstone Fm	86.2	nd	11.2	nd	nd	nd	0.6	nd	nd	nd	nd	0.6	0.8	<0.5	<0.5	<0.5	nd	nd
313130	087360		Mercia Mudstone Gp		45.9	nd	17.6	nd	nd	nd	2.4	4.9	nd	nd	nd	22.6	5.6	nd	nd	1	nd	nd
356530	189520		Mercia Mudstone Gp	Blue Anchor Fm	11.6	1.6	4.5	nd	nd	nd	57.2	9.5	nd	nd	nd	10.3	3.2	nd	nd	nd	nd	2.1
356530	189520		Mercia Mudstone Gp	Blue Anchor Fm	34.2	3.7	11.3	nd	nd	nd	11.7	14.5	nd	nd	nd	17.7	6.4	nd	nd	1	nd	nd
333140	444090	64.5	Mercia Mudstone Gp	Eldersfield Mudstone Fm, Kirkham Mudstone Mb	16.9	2.1	0.7	nd	nd	nd	1.4	13.1	nd	51.8	nd	7.8	6.2	nd	nd	nd	nd	nd
338880	436030	119.0	Mercia Mudstone Gp	Eldersfield Mudstone Fm, Singleton Mudstone Mb	12.4	1.4	3.5	nd	nd	nd	nd	26.3	nd	27	nd	15.5	13.9	nd	nd	nd	nd	nd
324313	388446	30.0	Mercia Mudstone Gp	Tarporley Siltstone Fm	55.3	4.9	2.8	nd	nd	nd	<0.5	8.7	nd	nd	nd	16.6	11.6	nd	nd	nd	nd	nd
Permian																						
424669	507052	60.6	Zechstein Gp		2.5	nd	nd	nd	nd	nd	nd	97.5	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
447738	442014	25.0	Zechstein Gp	Edlington Fm	7	nd	2	nd	nd	nd	62.2	3.5	nd	nd	nd	11.3	13.8	nd	nd	<0.5	nd	nd
372490	294530		No Parent Gp	Bridgnorth Sandstone Fm	84.1	nd	12.9	nd	nd	nd	nd	nd	nd	nd	nd	0.8	<0.5	nd	1.6	<0.5	nd	nd
373850	290320		No Parent Gp	Bridgnorth Sandstone Fm	92.4	nd	6.9	nd	nd	nd	<0.5	nd	nd	nd	nd	<0.5	nd	nd	nd	<0.5	nd	nd
373860	290690		No Parent Gp	Bridgnorth Sandstone Fm	89.4	nd	7.4	nd	nd	nd	<0.5	nd	nd	nd	nd	1.5	nd	nd	1.1	<0.5	nd	nd
363280	328840		No Parent Gp	Bridgnorth Sandstone Fm	97.3	nd	2.2	nd	nd	nd	nd	nd	nd	nd	nd	<0.5	nd	nd	nd	<0.5	nd	nd

					Silicates						**Carbonates/Sulphates**					**'Clay' mineral**				**Oxides/Sulphides**		
Easting	**Northing**	**Depth (m)**	**Group (Gp)**	**Formation (Fm)**	**Quartz**	**Albite**	**K<Feldspar**	**Cristobalite**	**Tridymite**	**Heulandite**	**Calcite**	**Dolomite**	**Siderite**	**Gypsum**	**Jarosite**	**Mica**	**Chlorite**	**Smectite**	**Kaolin**	**Hematite**	**Anatase**	**Pyrite**
Carboniferous																						
418375	433777	20.2	Pennine Coal Measures Gp		45.2	9.5	nd	nd	nd	nd	nd	nd	nd	nd	nd	22.6	9.8	nd	12.9	nd	nd	nd
398380	295665	26.5	Pennine Coal Measures Gp		56	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	16.8	1.8	nd	18.6	nd	nd	1
434520	575640		Pennine Coal Measures Gp		36.9	3.5	1	nd	nd	nd	nd	nd	1.7	nd	nd	25.5	3.9	nd	27.5	nd	nd	nd
402580	351090	12.0	Millstone Grit Gp	Kinderscout Grit	44	nd	<0.5	nd	nd	nd	nd	nd	nd	nd	3.1	22	6.4	nd	17.3	nd	0.5	6.4
411420	348800	19.9	Craven Gp	Ecton Limestone Fm	11.3	nd	nd	nd	nd	nd	84.3	0.5	nd	nd	nd	3.4	nd	nd	0.5	nd	nd	nd
386041	545385	10.6	Namurian Rocks (Undifferentiated)		89.9	nd	nd	nd	nd	nd	nd	nd	0.9	nd	nd	9.2	nd	nd	nd	nd	nd	nd
379080	444490	5.5	Bowland High Gp	Chatburn Limestone Fm	3.6	nd	nd	nd	nd	nd	93.3	1.7	nd	nd	nd	0.9	nd	nd	<0.5	nd	nd	nd
Devonian																						
340204	200852	30.0	Old Red Sandstone SuperGp		48.8	8.9	nd	nd	nd	nd	12.9	0.5	nd	nd	nd	14.5	14.1	nd	nd	nd	nd	<0.5
304260	216360	OC	Old Red Sandstone SuperGp		78.9	11.8	nd	nd	nd	nd	nd	nd	nd	nd	nd	3.5	5.2	nd	nd	0.6	nd	nd
Silurian																						
263050	288120	233.0	Silurian Rocks (Undifferentiated)		61.8	15.9	nd	nd	nd	nd	nd	1.4	nd	nd	nd	12	8.5	nd	nd	nd	nd	<0.5

Notes:

< indicates that the mineral was detected as present, but the signal was too small to quantify; nd indicates that no signal was detected.

Table 8.3 Summary of <2 µm clay mineral X-ray diffraction analyses (% of total clay minerals, by mass).

Easting	Northing	Depth (m)	Group (Gp)	Formation (Fm)	Smectite-Cf	Corrensite-Cf	Illite/Smectite-Cf	Illite-Cf	Kaolinite-Cf	Chlorite-Cf
Palaeogene										
616000	160200	24.0	Thames Gp	Harwich Formation	73	nd	nd	16	5	6
616000	160200	43.0	Montrose Gp	Thanet Fm	78	nd	nd	19	1	3
616000	160200	12.0	Thames Gp	London Clay Fm	62	nd	nd	16	11	10
591600	165732		Lambeth Gp	Woolwich Fm	74	nd	nd	18	3	5
616000	160200	33.0	Lambeth Gp	Woolwich Fm	67	nd	nd	33	nd	nd
Cretaceous										
458090	128560	13.7	Chalk Gp	Newhaven Chalk Fm	100	nd	nd	nd	nd	nd
475460	121570		Selborne Gp	Upper Greensand Fm	53	nd	nd	47	nd	nd
517180	206790	35.0	Chalk Gp	Lewes Nodular Chalk Fm	90	nd	nd	10	nd	nd
415900	153710	24.4	Chalk Gp	Lewes Nodular Chalk Fm	87	nd	nd	11	nd	2
636300	167700	21.0	Chalk Gp	Seaford Chalk Fm	88	nd	nd	12	nd	nd
570300	165750		Chalk Gp	Holywell/New Pit Chalk Fm (Undifferentiated)	80	nd	nd	20	nd	nd
415900	153710	48.8	Chalk Gp	New Pit Chalk Fm	82	nd	nd	18	nd	nd
502310	222440	2.3	Chalk Gp	Holywell Chalk Fm	94	nd	nd	6	nd	nd
415900	153710	96.4	Chalk Gp	Zig Zag Chalk Fm	73	nd	nd	20	nd	7
502310	222440	27.5	Chalk Gp	Zig Zag Chalk Fm	54	nd	nd	25	21	nd
557110	363980	39.1	Cromer Knoll Gp	Hunstanton Fm	64	nd	nd	9	15	11
524880	127010	18.1	Wealden Gp	Weald Clay Fm	9	nd	nd	30	30	30
Jurassic										
373420	081720		Corallian Gp	Osmington Oolite Fm	54	nd	nd	46	nd	nd
390910	078510		Ancholme Gp	Kimmeridge Clay Fm	nd	nd	8	40	41	11
371650	081840		Ancholme Gp	Oxford Clay Fm	3	nd	nd	56	27	14
412970	216870	8.0	Great Oolite Gp	Taynton Limestone Fm	58	nd	nd	25	17	nd

Easting	Northing	Depth (m)	Group (Gp)	Formation (Fm)	Smectite-Cf	Corrensite-Cf	Illite/Smectite-Cf	Illite-Cf	Kaolinite-Cf	Chlorite-Cf
426750	210440	12.0	Great Oolite Gp	White Limestone Fm	26	nd	nd	62	12	nd
439520	258540	20.7	Lias Gp		76	nd	nd	21	nd	3
446870	225860	16.0	Lias Gp	Bridport Sand Fm	4	nd	nd	32	38	26
332970	091210		Lias Gp	Blue Lias Fm	10	nd	nd	40	44	6
Triassic										
309720	085140		Sherwood Sandstone Gp	Otter Sandstone Fm	nd	nd	nd	82	9	9
306120	081650		Sherwood Sandstone Gp	Budleigh Salterton Pebble Beds Fm	nd	nd	nd	88	12	nd
357370	328580		Sherwood Sandstone Gp	Helsby Sandstone Fm	73	nd	nd	25	2	nd
461230	400700	17.0	Sherwood Sandstone Gp	Nottingham Castle Sandstone Fm	57	nd	nd	25	12	7
313130	087360		Mercia Mudstone Gp		nd	nd	nd	92	nd	8
356530	189520		Mercia Mudstone Gp	Blue Anchor Fm	nd	nd	nd	89	nd	11
356530	189520		Mercia Mudstone Gp	Blue Anchor Fm	nd	nd	nd	92	nd	8
333140	444090	64.5	Mercia Mudstone Gp	Eldersfield Mudstone Fm, Kirkham Mudstone Mb	nd	54	nd	35	nd	11
338880	436030	119.0	Mercia Mudstone Gp	Eldersfield Mudstone Fm, Singleton Mudstone Mb	nd	33	nd	49	nd	18
324313	388446	30.0	Mercia Mudstone Gp	Tarporley Siltstone Fm	nd	13	nd	83	nd	3
Permian										
424669	507052	60.6	Zechstein Gp							
447738	442014	25.0	Zechstein Gp	Edlington Fm	nd	45	nd	49	nd	6
372490	294530		No Parent Gp	Bridgnorth Sandstone Fm	nd	nd	71	18	9	2
373850	290320		No Parent Gp	Bridgnorth Sandstone Fm	nd	nd	99	nd	1	nd
373860	290690		No Parent Gp	Bridgnorth Sandstone Fm	nd	nd	88	7	5	nd
363280	328840		No Parent Gp	Bridgnorth Sandstone Fm	17	nd	nd	83	nd	nd

Easting	Northing	Depth (m)	Group (Gp)	Formation (Fm)	Smectite-Cf	Corrensite-Cf	Illite/Smectite-Cf	Illite-Cf	Kaolinite-Cf	Chlorite-Cf
Carboniferous										
418375	433777	20.2	Pennine Coal Measures Gp		nd	nd	18	51	17	15
398380	295665	26.5	Pennine Coal Measures Gp		nd	nd	35	37	21	7
434520	575640		Pennine Coal Measures Gp		nd	nd	12	16	62	11
402580	351090	12.0	Millstone Grit Gp	Kinderscout Grit	nd	nd	44	21	22	13
411420	348800	19.9	Craven Gp	Ecton Limestone Fm	nd	nd	82	15	2	nd
386041	545385	10.6	Namurian Rocks (Undifferentiated)		nd	nd	100	nd	nd	nd
379080	444490	5.5	Bowland High Gp	Chatburn Limestone Fm	nd	nd	nd	83	10	7
Devonian										
340204	200852	30.0	Old Red Sandstone SuperGp		nd	nd	37	38	nd	24
304260	216360	OC	Old Red Sandstone SuperGp		nd	nd	nd	72	nd	28
Silurian										
263050	288120	233.0	Silurian Rocks (Undifferentiated)		nd	nd	nd	62	nd	38

Notes:
< indicates that the mineral was detected as present, but the signal was too small to quantify; nd indicates that no signal was detected.

9 References

Allen, D J, Brewerton, L J, Coleby, L M, Gibbs, B R, Lewis, M A, MacDonald, A M, Wagstaff, S J, and Williams, A T. 1997. The physical properties of major aquifers in England and Wales. WD/97/34, 312 pp. British Geological Survey and Environment Agency. Keyworth.

Allenking, R M, Butler, B J, and Reichert, B. 1995. Fate of the herbicide glufosinate-ammonium in the sandy, low-organic-carbon aquifer at CFB Borden, Ontario, Canada. *Journal of Contaminant Hydrology*, Vol. 18, 161-179.

Allison, L E. 1960. Wet combustion apparatus and procedure for organic and inorganic carbon in soil. *Soil Science*, Vol. 24, 36-40.

Allison, L E. 1965. Organic carbon. *Methods of soil analysis. Part 2. Chemical and Microbiological Properties*. Black, C A (editor). Agronomy No.9. (American Society for Agronomy.)

Amundson, R G, Trask, J, and Pendall, E. 1988. A rapid method of soil carbonate analysis using gas-chromatography. *Soil Science Society of America Journal*, Vol. 52, 880-883.

Appelo, C A J, and Postma, D. 1993. *Geochemistry, groundwater and pollution*. (Rotterdam: Balkema.)

Banfield, J F, and Hamers, R J. 1997. Processes at minerals and surfaces with relevance to microorganisms and prebiotic synthesis. 81-122. In: *Geomicrobiology: Interactions between Microbes and Minerals. Reviews in Mineralogy,* 35.

Barber, L B. 1994. Sorption of Chlorobenzenes to Cape-Cod Aquifer Sediments. *Environmental Science & Technology*, Vol. 28, 890-897.

Barcelona, M J, and Holm, T R. 1991. Oxidation-reduction capacities of aquifer solids. *Environmental Science & Technology*, Vol. 25, 1565-1572.

Barton, C D, and Karathanasis, A D. 1997. Measuring cation exchange capacity and total exchangeable bases in batch and flow experiments. *Soil Technology*, Vol. 11, 153-162.

Bascomb, C L. 1964. Rapid method for the determination of ction-exchange capacity of calcareous and noncalcareous soils. *Journal of the Science of Food and Agriculture*, Vol. 12, 821-823.

Bekins, B A, Cozzarelli, I M, Godsy, E M, Warren, E, Essaid, H I, and Tuccillo, M E. 2001. Progression of natural attenuation processes at a crude oil spill site: II. Controls on spatial distribution of microbial populations. *Journal of Contaminant Hydrology*, Vol. 53, 387-406.

Bendor, E, and Banin, A. 1994. Visible and near-infrared (0.4-1.1 µm) analysis of arid and semiarid soils. *Remote Sensing of Environment*, Vol. 48, 261-274.

Bendor, E, and Banin, A. 1995. Near-infrared analysis as a rapid method to simultaneously evaluate several soil properties. *Soil Science Society of America Journal*, Vol. 59, 364-372.

Benedetti, M F, van Riemsdijk, W H, Koopal, L K, Kinniburgh, D G, Gooddy, D C, and Milne, C J. 1996. Metal binding by natural organic matter: from the model to the field. *Geochimica et Cosmochimica Acta*, Vol. 60, 2503-2513.

Bengtsson, G, and Ekere, L. 2001. Predicting sorption of groundwater bacteria from size distribution, surface area, and magnetic susceptibility of soil particles. *Water Resources Research*, Vol. 37, 1795-1812.

Benker, E, Davis, G B, and Barry, D A. 1997. Factors controlling the distribution and transport of trichloroethene in a sand aquifer: hydrogeology and results of an in situ transport experiment. *Journal of Hydrology*, Vol. 202, 315-340.

Benner, S G, Hansel, C M, Wielinga, B W, Barber, T M, and Fendorf, S. 2002. Reductive dissolution and biomineralization of iron hydroxide under dynamic flow conditions. *Environmental Science & Technology*, Vol. 36, 1705-1711.

Bergaya, F, and Vayer, M. 1997. CEC of clays: Measurement by adsorption of a copper ethylenediamine complex. *Applied Clay Science*, Vol. 12, 275-280.

Bethke, C. 2006. The Geochemist's Workbench release 6.0. Reference Manual., University of Illinois.

Beuselinck, L, Govers, G, Poesen, J, and Degraer, G. 1998. Grain-size analysis by laser diffractometry: comparison with the sieve-pipette method. *Catena*, Vol. 32, 193-208.

Bodine, M W, and Fernalld, T H. 1973. EDTA dissolution of gypsum, anhydrite, and Ca-Mg carbonates. *Journal of Sedimentary Petrology*, Vol. 43, 1152-1156.

Bolt, G H (editor). 1979. *Soil Chemistry. B. Physico-chemical methods*. Developments in Soil Science. (Elsevier: Amsterdam.)

British Standards Institute. 1995a. Determination of organic and total carbon after dry combustion (elementary analysis). 7755:Soil Quality Section 3.8 1995, British Standard.

British Standards Institute. 1995b. Soil quality: Determination of carbonate content. Volumetric method. BS 7755 Section 3.10, British Standards Institution.

British Standards Institute. 1997. Determination of effective cation exchange capacity and base saturation level using barium chloride solution. 7755:Soil Quality Section 3.3 Amd.1 1997, British Standard.

British Standards Institute. 1998. Determination of particle size distribution in mineral soil material: Method of seiving and sedimentation. 7755:Soil Quality Section 5.4 1998, British Standard.

Broholm, M M, Crouzet, C, and Arvin, E. 1998. Processes underlying remediation of cresote contaminated groundwater in fractured sandstone. Contract EV5V-CT94-0529, Appendix 6 pp. Commission of the European Communities, DG XII. Brussels.

Brubaker, S C, Holzhey, C S, and Brasher, B R. 1992. Estimating the water-dispersible clay content of soils. *Soil Science Society of America Journal*, Vol. 56, 1227-1232.

Brusseau, M L. 1991. Cooperative sorption of organic-chemicals in systems composed of low organic-carbon aquifer materials. *Environmental Science & Technology*, Vol. 25, 1747-1752.

Buchan, G D, Grewal, K S, Claydon, J J, and McPherson, R J. 1993. A comparison of sedigraph and pipette methods for soil particle-size analysis. *Australian Journal of Soil Research*, Vol. 31, 407-417.

Cahill, R A, and Autrey, A D. 1988. Total and inorganic carbon content of 18 National-Bureau-of-Standards and 4 Canadian certified reference materials. *Geostandards Newsletter*, Vol. 12, 39-42.

Canfield, D E, Raiswell, R, Westrich, J T, Reaves, C M, and Berner, R A. 1986. The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales. *Chemical Geology*, Vol. 54, 149-155.

Carey, M A, Finnamore, J R, Morrey, M J, and Marsland, P A. 2000. Guidance on the assessment and monitoring of natural attentuation of contaminants in groundwater. 95, 131 pp. Environment Agency. Bristol.

Carmichael, L M, Smith, T G, and Pardieck, D L. 1999. Site-specific sorption values for mixtures of volatile and semivolatile organic compounds in sandy soils. *Journal of Environmental Quality*, Vol. 28, 888-897.

Caughey, M E, Barcelona, M J, Powell, R M, Cahill, R A, Gron, C, Lawrenz, D, and Meschi, P L. 1995. Interlaboratory study of a method for determining nonvolatile organic carbon in aquifer materials. *Environmental Geology*, Vol. 26, 211-219.

Cerri, G, Langella, A, Pansini, M, and Cappellettii, P. 2002. Methods of determining cation exchange capacities for clinoptilolite-rich rocks of the Logudoro Region in Northern Sardinia, Italy. *Clays and Clay Minerals*, Vol. 50, 127-135.

Chan, C C Y. 1986. Determination of carbonate carbon in 41 international geochemical reference samples by coulometric method. *Geostandards Newsletter*, Vol. 10, 131-134.

Chang, C W, Laird, D A, Mausbach, M J, and Hurburgh, C R. 2001. Near-infrared reflectance spectroscopy-principal components regression analyses of soil properties. *Soil Science Society of America Journal*, Vol. 65, 480-490.

Chao, T T, and Zhou, L. 1983. Extraction techniques for selective dissolution of amorphous iron-oxides from soils and sediments. *Soil Science Society of America Journal*, Vol. 47, 225-232.

Chappell, A. 1998. Dispersing sandy soil for the measurement of particle size distributions using optical laser diffraction. *Catena*, Vol. 31, 271-281.

Chichester, F W, and Chaison, R F. 1992. Analysis of carbon in calcareous soils using a 2 temperature dry combustion infrared instrumental procedure. *Soil Science*, Vol. 153, 237-241.

Ciesielski, H, and Sterckeman, T. 1997. A comparison between three methods for the determination of cation exchange capacity and exchangeable cations in soils. *Agronomie*, Vol. 17, 9-16.

Confalonieri, M, Fornasier, F, Ursino, A, Boccardi, F, Pintus, B, and Odoardi, M. 2001. The potential of near infrared reflectance spectroscopy as a tool for the chemical characterisation of agricultural soils. *Journal of near Infrared Spectroscopy*, Vol. 9, 123-131.

Cozzarelli, I M, Bekins, B A, Baedecker, M J, Aiken, G R, Eganhouse, R P, and Tuccillo, M E. 2001. Progression of natural attenuation processes at a crude-oil spill site: 1. Geochemical evolution of the plume. *Journal of Contaminant Hydrology*, Vol. 53, 369-385.

Crouzet, C, Fléhoc, C, Mouvet, C, and Guaucher, E. 1998. Determination of oxidation and reduction capacities, Fe(II) and Fe(III) contents, and carbonate minerals in aquifer solids. 2 Application to natural solids. R39525, BRGM.

Davis, J A, and Leckie, J O. 1978. Surface ionization and complexation at oxide-water interface. 2. Surface properties of amorphous iron oxyhydroxide and adsorption of metal-ions. *Journal of Colloid and Interface Science*, Vol. 67, 90-107.

Dejong, E, Acton, D F, and Stonehouse, H B. 1990. Estimating the Atterberg Limits of southern Saskatchewan soils from texture and carbon contents. *Canadian Journal of Soil Science*, Vol. 70, 543-554.

Dejong, E, Kozak, L M, and Stonehouse, H B. 1992. Comparison of shrink-swell indexes of some Saskatchewan soils and their relationships to standard soil characteristics. *Canadian Journal of Soil Science*, Vol. 72, 429-439.

DeSimone, L A, Howes, B L, and Barlow, P M. 1997. Mass-balance analysis of reactive transport and cation exchange in a plume of wastewater-contaminated groundwater. *Journal of Hydrology*, Vol. 203, 228-249.

Deutschmann, G, Rummenhohl, H, and Tarrah, J. 1997. The determination of the effective cation exchange capacity of rocks. *Zeitschrift Fur Pflanzenernahrung Und Bodenkunde*, Vol. 160, 151-155.

Duan, W M, Coleman, M L, and Pye, K. 1997. Determination of reduced sulphur species in sediments - an evaluation and modified technique. *Chemical Geology*, Vol. 141, 185-194.

Duquette, M, and Hendershot, W. 1993. Soil surface-charge evaluation by back-titrations. 2. Application. *Soil Science Society of America Journal*, Vol. 57, 1228-1234.

Dzombak, D A, and Morel, F M M. 1990. *Surface Complexation Modeling: Hydrous Ferric Oxide*. (New York: John Wiley & Sons.)

El-Swaify, S A. 1980. Physical and mechanical properties of oxisols. 303-324. In: *Soils of variable charge*. Theng, B K G (editor). (Lower Hutt, New Zealand: New Zealand Society for Soil Science.)

Engleman, E E, Jackson, L L, and Norton, D R. 1985. Determination of carbonate carbon in geological materials by coulometric titration. *Chemical Geology*, Vol. 53, 125-128.

Eriksson, L, and Hermens, J L M. 1995. A multivariate approach to quantitative structure-activity and structure-property relationships. *Chemometrics in Environmental Chemistry - Applications*. Einax, J (editor). 2H. (New York: Springer.)

Evans, P J. 2000. A novel ferric iron bioavailability assay. *Second international conference on remediation of chlorinated and recalcitrant compounds*, Monterey, Batelle Press.

Evans, P J, Jones, A, Liu, C C, and Lovley, D R. 1999. Development of a natural attenuation test kit. *Fifth international in-situ and on-site bioremediation symposium*, San Diego, Batelle Press, 331-336.

Evans, P J, and Koenigsberg, S S. 2001. A bioavailable ferric iron assay and relevance to reductive dechlorination. *Sixth international in-situ and on-site bioremediation symposium*, San Diego, Batelle Press, 209-215.

Ganguly, C, Van Benschoten, J E, and Griffiths, R. 2001. A variable reactivity model for ion binding to environmental sorbents. *Environmental Engineering Science*, Vol. 18, 9-23.

Gee, G W, and Bauder, J W. 1986. Particle size analysis. 383-411. In: *Methods of Soil Analysis, Part 1 Agronomy*. Klute, A (editor). 9.

Gillespie, M R, Kemp, S J, Vickers, B P, Waters, C, and Gowing, C J B. 2001. Cation-exchange capacity of selected lithologies from England, Wales and Scotland. P12-222/TR, 80 pp. Environment Agency. Bristol.

Gillespie, M R, Leader, R U, Higgo, J J W, Harrison, I, Hards, V L, Gowing, C J B, Vickers, B P, Boland, M P, and Morgan, D J. 2000. CEC and Kd determination in landfill performance evaluation. A review of methodologies and preparation of standard materials for laboratory analysis. P340, 67 pp. Environment Agency. Bristol.

Goldberg, S, Lesch, S M, and Suarez, D L. 2000. Predicting boron adsorption by soils using soil chemical parameters in the constant capacitance model. *Soil Science Society of America Journal*, Vol. 64, 1356-1363.

Golder Associates. 2001-2009. LandSim. 2.5. www.landsim.co.uk.

Golder Associates. 2003-2009. ConSim. www.consim.co.uk.

Graf Pannatier, E. 1999. Oxidation capacity of sediments in relation to biodegradation of toluene. *Fifth international in-situ and on-site bioremediation symposium*, San Diego, Batelle Press, 189-194.

Grim, R E. 1968. *Clay mineralogy* (Second edition). (New York: McGraw-Hill.)

Gualtieri, A F, Marchi, E, and Passaglia, E. 1999. Zeolite content and cation exchange capacity of zeolite-rich rocks. *Porous Materials in Environmentally Friendly Processes*, Vol. 125, 707-713.

Hacherl, E L, Kosson, D S, Young, L Y, and Cowan, R M. 2001. Measurement of iron(III) bioavailability in pure iron oxide minerals and soils using anthraquinone-2,6-disulfonate oxidation. *Environmental Science & Technology*, Vol. 35, 4886-4893.

Hefferman, B. 1985. *A handbook of methods of inorganic chemical analysis for forest soils, foliage and water*. (Canberra: CSIRO.)

Hern, J L. 1984. Determination of total sulfur in plant materials using an automated sulphur analyser. *Communications in Soil Science and Plant Analysis*, Vol. 15, 99-107.

Heron, G, Bjerg, P L, Gravesen, P, Ludvigsen, L, and Christensen, T H. 1998. Geology and sediment geochemistry of a landfill leachate contaminated aquifer (Grindsted, Denmark). *Journal of Contaminant Hydrology*, Vol. 29, 301-317.

Heron, G, Christensen, T H, and Tjell, J C. 1994a. Oxidation capacity of aquifer sediments. *Environmental Science & Technology*, Vol. 28, 153-158.

Heron, G, Crouzet, C, Bourg, A C M, and Christensen, T H. 1994b. Speciation of Fe(II) and Fe(III) in contaminated aquifer sediments using chemical-extraction techniques. *Environmental Science & Technology*, Vol. 28, 1698-1705.

Hiemstra, T, and VanRiemsdijk, W H. 1996. A surface structural approach to ion adsorption: The charge distribution (CD) model. *Journal of Colloid and Interface Science*, Vol. 179, 488-508.

Hillier, S, Suzuli, K, and Cotter-Howells, J. 2001. Quantitative determination of Cerussite (lead carbonate) by X-ray powder diffraction and inferences for lead speciation and transport in stream sediments from a former lead mining area of Scotland. *Applied Geochemistry*, Vol. 16, 597-608.

Holmen, B A, and Gschwend, P M. 1997. Estimating sorption rates of hydrophobic organic compounds in iron oxide and aluminosilicate clay-coated aquifer sands. *Environmental Science & Technology*, Vol. 31, 105-113.

International Standards Organisation. 1994. Soil quality -- Determination of effective cation exchange capacity and base saturation level using barium chloride solution. ISO 11260:1994, International Organisation for Standardisation.

International Standards Organisation. 1995a. Soil quality - Determination of organic and total carbon after dry combustion. ISO 10695:1995, International Organisation for Standardisation.

International Standards Organisation. 1995b. Soil quality - Determination of carbonate content - volumetric method. ISO 10693:1995, International Organisation for Standardisation.

International Standards Organisation. 1998. Soil quality - Determination of particle size distribution in mineral soil material - Method by sieving and sedimentation. ISO 11277:1998, International Organisation for Standardisation.

Jackson, L L, and Roof, S R. 1992. Determination of the forms of carbon in geologic materials. *Geostandards Newsletter*, Vol. 16, 317-323.

Jackson, M L. 1958. *Soil chemical analysis*. (New Jersey: Prentice Hall Inc., Englewood Cliffs.)

Jones, G A, and Kaiteris, P. 1983. A vacuum-gasometric technique for rapid and precise analysis of calcium-carbonate in sediments and soils. *Journal of Sedimentary Petrology*, Vol. 53, 655-660.

Jones, H K, Morris, B L, Cheney, C S, Brewerton, L J, Merrin, P D, Lewis, M A, MacDonald, A M, Coleby, L M, Talbot, J C, McKenzie, A A, Bird, M J, Cunningham, J, and Robinson, V K. 2000. The physical properties of minor aquifers in England and Wales. WD/00/4, 234 pp. British Geological Survey and Environment Agency. Keyworth.

Kaira, Y P, and Maynard, D G. 1991. Methods for forest soil and plant analysis. Nor-x-319, 116 pp. Forest.Can.Inf.Rep.

Kerven, G L, Menzies, N W, and Geyer, M D. 2000. Soil carbon determination by high temperature combustion a comparison with dichromate oxidation procedures and the influence of charcoal and carbonate carbon on the measured value. *Communications in Soil Science and Plant Analysis*, Vol. 31, 1935-1939.

Kilmer, V J, and Alexander, L T. 1949. Methods of making mechanical analyses of soils. *Soil Science*, Vol. 68, 15-24.

Kinniburgh, D G, van Riemsdijk, W H, Koopal, L K, Borkovec, M, Benedetti, M F, and Avena, M J. 1999. Ion binding to natural organic matter: Competition, heterogeneity, stoichiometry and thermodynamic consistency. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Vol. 151, 147-166.

Krapiel, A M L, Keller, K, and Morel, F M M. 1999. A model for metal adsorption on montmorillonite. *J. Colloid Interface Science*, Vol. 210, 43-54.

Krom, M D, and Berner, R A. 1983. A rapid method for the determination of organic and carbonate carbon in geological samples. *Journal of Sedimentary Petrology*, Vol. 53, 660-663.

Liu, C L, Wang, M K, and Yang, C C. 2001. Determination of cation exchange capacity by one-step soil leaching column method. *Communications in Soil Science and Plant Analysis*, Vol. 32, 2359-2372.

Loizeau, J L, Arbouille, D, Santiago, S, and Vernet, J P. 1994. Evaluation of a wide-range laser diffraction grain-size analyzer for use with sediments. *Sedimentology*, Vol. 41, 353-361.

Lord, C J. 1982. A selective and precise method for pyrite determination in sedimentary materials. *Journal of Sedimentary Petrology*, Vol. 52, 664-666.

Lovley, D R, Giovannoni, S J, White, D C, Champine, J E, Phillips, E J P, Gorby, Y A, and Goodwin, S. 1993. *Geobacter-metallireducens Gen-Nov Sp-Nov*, a microorganism capable of coupling the complete oxidation of organic-compounds to the reduction of iron and other metals. *Archives of Microbiology*, Vol. 159, 336-344.

Lovley, D R, and Phillips, E J P. 1986a. Availability of ferric iron for microbial reduction in bottom sediments of the fresh-water tidal Potomac River. *Applied and Environmental Microbiology*, Vol. 52, 751-757.

Lovley, D R, and Phillips, E J P. 1986b. Organic-matter mineralization with reduction of ferric iron in anaerobic sediments. *Applied and Environmental Microbiology*, Vol. 51, 683-689.

Lovley, D R, and Phillips, E J P. 1987. Rapid assay for microbially reducible ferric iron in aquatic sediments. *Applied and Environmental Microbiology*, Vol. 53, 1536-1540.

Lu, N, Ristow, G H, and Likos, W J. 2000. The accuracy of hydrometer analysis for fine-grained clay particles. *Geotechnical Testing Journal*, Vol. 23, 487-495.

Matejovic, I. 1993. Determination of carbon, hydrogen, and nitrogen in soils by automated elemental analysis (dry combustion method). *Communications in Soil Science and Plant Analysis*, Vol. 24, 2213-2222.

Matejovic, I. 1997. Determination of carbon and nitrogen in samples of various soils by the dry combustion. *Communications in Soil Science and Plant Analysis*, Vol. 28, 1499-1511.

McBride, M B. 1994. *Environmental chemistry of soils*. (Oxford: Oxford University Press.)

McKeague. 1978. *Manual on soil sampling and methods of analysis* (2nd edition). (Ottawa: Canadian Society of Soil Science.)

Meeussen, J C L. 2003. ORCHESTRA: An object-oriented framework for implementing chemical equilibrium models. *Environmental Science & Technology*, Vol. 37, 1175-1182.

Mehra, O P, and Jackson, M L. 1960. Iron oxide removal from soils and clays by a dithionate citrate system with sodium bicarbonate. *Clays and Clay minerals*, Vol. 7, 317-327.

Metson. 1956. Methods of chemical analysis for soil survey. *New Zealand Department of Science, Industry Resouces and Soil Bureau Bulletin*, Vol. 12, 208.

Milne, C J, Kinniburgh, D G, and Tipping, E. 2001. Generic NICA-Donnan model parameters for proton binding by humic substances. *Environmental Science & Technology*, Vol. 35, 2049-2059.

Milne, C J, Kinniburgh, D G, Van Riemsdijk, W H, and Tipping, E. 2003. Generic NICA-Donnan model parameters for metal-ion binding by humic substances. *Environmental Science & Technology*, Vol. 37, 958-971.

Moore, D M, and Reynolds, R C. 1997. *X-Ray diffraction and the identification and analysis of clay minerals* (2nd edition). (New York: Oxford University Press.)

Murphy, M A, and Salvador, A. 1999. International Subcommission on Stratigraphic Classification of IUGS International Commission on Stratigraphy - International Stratigraphic Guide - An Abridged Version. *Episodes*, Vol. 22, 255-271.

Murray, M R. 2002. Is laser particle size determination possible for carbonate- rich lake sediments ? *Journal of Paleolimnology*, Vol. 27, 173-183.

Neal, R H, and Younglove, T. 1993. The use of a dry combustion infrared instrumental technique to determine total and organic-carbon in California soils. *Communications in Soil Science and Plant Analysis*, Vol. 24, 2733-2746.

Neary, A J, and Barnes, S R. 1993. The effect of sample grinding on extractable iron and aluminum in soils. *Canadian Journal of Soil Science*, Vol. 73, 73-80.

Nelson, D W, and Sommers, L E. 1962. Total carbon, organic carbon, and organic matter. 65-68. In: *Methods of soil analysis*, (2nd Edition edition). Miller, R H, and Keeney, D R (editors). Agronomy 9.

Nelson, R E. 1982. *Methods of Soil Analysis, Part 2*. (Madison,WI: American Society for Agronomy.)

Nieuwenhuize, J, Maas, Y E M, and Middelburg, J J. 1994. Rapid analysis of organic-carbon and nitrogen in particulate materials. *Marine Chemistry*, Vol. 45, 217-224.

Osman, M A, and Suter, U W. 2000. Determination of the cation-exchange capacity of muscovite mica. *Journal of Colloid and Interface Science*, Vol. 224, 112-115.

Pacey, N R. 1989. Organic-matter in Cretaceous chalks from Eastern England. *Chemical Geology*, Vol. 75, 191-208.

Parkhurst, D L, and Appelo, C A J. 1999. User's guide to PHREEQC (version 2)- A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. Water Resources Investigations Report 99-4259, 312 pp. United States Geological Survey.

Peck, L C. 1964. Systematic analysis of Silicates. USGS Bulletin 1170, 89 pp. United States Geological Survey.

Pennington, K L, and Lewis, G C. 1979. A comparison of electronic and pipet methods for mechanical analysis of soils. *Soil Science*, Vol. 128, 280-284.

Petersen, L W, Moldrup, P, Jacobsen, O H, and Rolston, D E. 1996. Relations between specific surface area and soil physical and chemical properties. *Soil Science*, Vol. 161, 9-21.

Rafai, H S, Newell, C J, Gonzales, J R, Dendrou, S, Kennedy, L, and Wilson, J T. 1998. Bioplume III. Natural attentuation decision support system. User's manual. EPA/600/R-98/010, US EPA.

Ran, Y, Xiao, B H, Fu, J M, and Sheng, G Y. 2003. Sorption and desorption hysteresis of organic contaminants by kerogen in a sandy aquifer material. *Chemosphere*, Vol. 50, 1365-1376.

Reynolds, R C, and Reynolds, R C. 1996. *Description of Newmod-for-Windows™. The calculation of one-dimensional X-ray diffraction patterns of mixed layered clay minerals*. (Hanover, NH: R C Reynolds Jr.)

Rhoades, J D. 1982. Cation exchange capacity. 149-158. In: *Methods of Soil analysis, Part 2. Agronomy*, (2nd edition). Page, A L (editor). 9.

Roden, E E, and Lovley, D R. 1993. Dissimilatory Fe(III) reduction by the marine microorganism desulfuromonas-acetoxidans. *Applied and Environmental Microbiology*, Vol. 59, 734-742.

Roden, E E, and Urrutia, M M. 2002. Influence of biogenic Fe(II) on bacterial crystalline Fe(III) oxide reduction. *Geomicrobiology Journal*, Vol. 19, 209-251.

Roden, E E, and Zachara, J M. 1996. Microbial reduction of crystalline iron(III) oxides: Influence of oxide surface area and potential for cell growth. *Environmental Science & Technology*, Vol. 30, 1618-1628.

Rowell, D L. 1997. *Soil science: Methods and applications* (5 edition). (Longman.) ISBN 0 582 087848.

Ryan, J N, and Gschwend, P M. 1991. Extraction of iron-oxides from sediments using reductive dissolution by titanium(III). *Clays and Clay Minerals*, Vol. 39, 509-518.

Schollenberger, C J. 1927. A rapid approximation method for determining soil organic matter. *Soil Science*, Vol. 24, 65-68.

Schumacher, B A, Neary, A J, Palmer, C J, Maynard, D G, Pastorek, L, Morrison, I K, and Marsh, M. 1995. Laboratory methods for soil and foliar analysis in long-term enviromental monitoring programs. EPA/600/R-95/077, 178 pp. United States Environment Protection Agency.

Shapiro, L. 1975. Rapid analysis of silicate, carbonate, and phosphate rocks - revised edition. USGS Bulletin 1401, 76 pp. Inited States Geological Survey.

Shedrick, B H, and McKeague, J A. 1975. A comparison of extractable Fe and Al data using methods followed in the U.S.A. and Canada. *Canadian Journal of Soil Science*, Vol. 55, 77-78.

Shillabeer, N, Hart, B, and Riddle, A M. 1992. The use of a mathematical-model to compare particle-size data derived by dry-sieving and laser analysis. *Estuarine Coastal and Shelf Science*, Vol. 35, 105-111.

Singer, J K, Anderson, J B, Ledbetter, M T, McCave, I N, Jones, K P N, and Wright, R. 1988. An assessment of analytical techniques for the size analysis of fine-grained sediments. *Journal of Sedimentary Petrology*, Vol. 58, 534-543.

Skinner, M F, Zabowski, D, Harrison, R, Lowe, A, and Xue, D. 2001. Measuring the cation exchange capacity of forest soils. *Communications in Soil Science and Plant Analysis*, Vol. 32, 1751-1764.

Snyder, J D, and Trofymow, J A. 1984. A rapid accurate wet oxidation diffusion procedure for determining organic and inorganic carbon in plant and soil samples. *Communications in Soil Science and Plant Analysis*, Vol. 15, 587-597.

Snyder, R L, and Bish, D L. 1989. Quantitative analysis by X-ray powder diffraction. 101-145. In: *Modern Powder Diffraction*. Bish, D L, and Post, J E (editors). *Reviews in Mineralogy,* 20. (Washington D. C.: Mineralogical Society of America.)

Steventon-Barnes, H. 2000. Solid organic matter in UK aquifers: its role in sorption of organic compounds. PhD thesis, University College London.

Stuart, M E, and Vickers, B P. 1989. Determination of cation exchange capacity in calcium-rich samples. WI/89/4, 9 pp. British Geological Survey. Keyworth.

Stumm, W, Kummert, R, and Sigg, L. 1980. A ligand-exchange model for the adsorption of inorganic and organic-ligands at hydrous oxide interfaces. *Croatica Chemica Acta*, Vol. 53, 291-312.

Sudduth, K A, and Hummel, J W. 1993. Soil organic-matter, CEC, and moisture sensing with a portable NIR spectrophotometer. *Transactions of the Asae*, Vol. 36, 1571-1582.

Sutherland, R A. 1998. Loss-on-ignition estimates of organic matter and relationships to organic carbon in fluvial bed sediments. *Hydrobiologia*, Vol. 389, 153-167.

Tipping, E. 1998. Humic ion-binding Model VI: an improved description of the interactions of protons and metal ions with humic substances. *Aquatic Geochemistry*, Vol. 4, 3-48.

Tipping, E, Lofts, S, and Sonke, J E. 2011. Humic Ion-Binding Model VII: a revised parameterisation of cation-binding by humic substances. *Environmental Chemistry*, Vol. 8, 225-235.

Tuccillo, M E, Cozzarelli, I M, and Herman, J S. 1999. Iron reduction in the sediments of a hydrocarbon-contaminated aquifer. *Applied Geochemistry*, Vol. 14, 655-667.

Venables, W, and Ripley, B. 2002. *Modern Applied Statistics with S* (4th edition). (Springer.) ISBN 0387954570.

Vitton, S J, and Sadler, L Y. 1997. Particle-size analysis of soils using laser light scattering and X-ray absorption technology. *Geotechnical Testing Journal*, Vol. 20, 63-73.

Walczak, B, and Massart, D L. 2001a. Dealing with missing data Part I. *Chemometrics and Intelligent Laboratory Systems*, Vol. 58, 15-27.

Walczak, B, and Massart, D L. 2001b. Dealing with missing data: Part II. *Chemometrics and Intelligent Laboratory Systems*, Vol. 58, 29-42.

Walkley, A. 1947. A critical examination of a rapid method for determining organic carbon in soils - effect of variartions in digestion conditions and of inorganic soil contituents. *Soil Science*, Vol. 65, 251-263.

Walkley, A, and Black, I A. 1934. An examination of the Degtjareff method for determining organic matter, and a proposed modification of the chromic acid titration method. *Soil Science*, Vol. 37, 29-38.

Wang, D L, and Anderson, D W. 1998. Direct measurement of organic carbon content in soils by the Leco CR-12 Carbon Analyzer. *Communications in Soil Science and Plant Analysis*, Vol. 29, 15-21.

Weliky, K, Suess, E, Ungerer, C A, Muller, P J, and Fischer, K. 1983. Problems with accurate carbon measurements in marine-sediments and particulate matter in seawater - a new approach. *Limnology and Oceanography*, Vol. 28, 1252-1259.

WRIGHT, A F, AND BAILEY, J S. 2001. Organic carbon, total carbon, and total nitrogen determinations in soils of variable calcium carbonate contents using a Leco CN-2000 dry combustion analyzer. *Communications in Soil Science and Plant Analysis*, Vol. 32, 3243-3258.

ZHAO, B J, LAM, M T, BACK, M H, GAMBLE, D S, AND WANG, C. 1997. Soil cation exchange capacity measurements using ultrafiltration techniques: Comparison of different metal ions as substitutes. *Communications in Soil Science and Plant Analysis*, Vol. 28, 161-171.