Bournemouth University

School of Applied Sciences

Dissertation

Geochemistry of the Soil and its Effect on Bone

BSc Archaeological, Anthropological and Forensic Sciences

Rosemary Helen Mayne

Student Number: 4332382

2012/2013

Abstract

Understanding the geochemical influences on the level of preservation of skeletal remains is very important for archaeological research. By investigating the different cause and effects that geochemistry has on skeletal remains, predictive models can be put in place to support future research and improve our knowledge of the relationship between soil geochemistry and preservation to set in place necessary conservation models. Twenty-four soil samples were taken from a Durotrigian site in Dorset which was being excavated by Bournemouth University. Each soil sample was taken adjacent of a human or large animal articulated skeletal remain. On site categorical classification of the level of preservation was performed and recorded for each articulated remain. The soil samples were air dried and sieved and then the less than 1mm track was then completely digested using a mix of 6ml HCl and 2ml HNO_3 and a Multiwave 3000 Anton Parr microwave. Digested samples were subsequently filtered and brought to a 50ml volume and then run through an Inductively Couples Plasma Optical Emission Spectrometry (ICP-OES). The pH level of the soil sample along with the heavy metals concentration was then determined. The statistical computer programme SPSS was used along with linear regression lines to obtain correlation co-efficients. The level of bone preservation was found to be in moderate correlation with the pH level of the soil. Due to Ca ions and Al ions having the most influence on pH levels, the ion concentrations were correlated against the pH level to identify any cause and effect relationships. There was a moderate relationship between the pH level and preservation of the skeletal remains. This relationship enabled a working, yet limited, predictive model to be created for using pH as a brief indicator of the *in situ* preservation levels of the remains. Although a working

predictive model was created, pH cannot be solely used to identify possible preservation levels. Ca concentration and pH was found to have a weak relationship in the overall samples, but in fifteen of the samples there was evidence of pH level being in proportionate with Ca concentration. Therefore it is necessary to identify the heavy metal influences on pH.

This study identifies what cause and effect relationships pH and heavy metal concentrations have within soil geochemistry and recognise the detrimental effects they can have within forensic and archaeological contexts and with buried archaeological remains which will threaten the quality of future excavations.

Table of Contents

Table of Figures

Table of Tables

1. Introduction

It is very important for archaeological research to understand the influences that geochemistry has on the preservation of skeletal remains. By researching the influences and the damage they cause, these can be accounted for and suitable controls can be put in place. This understanding of the soil geochemistry's influence on preservation can attribute vital interpretations in forensic and archaeological cases in relation to taphonomy and environmental diagenesis. After archaeologists have established the 'cause and effect' geochemistry has on skeletal remains they can create predictive models to help assess the preservation level and diagenesis of the skeletal remains even before excavation has even taken place and rule out any damage which is not of a taphonomic origin.

Wilson and Pollard (2002) defined diagenesis as "the cumulative physical, chemical and biological processes that alter all archaeological materials in the burial environment; these processes will modify an inorganic object's original chemical and/or structural properties and will govern its ultimate fate, in terms of preservation or destruction". To begin highlighting any possible impact that diagenesis will have on archaeological remains it is necessary to investigate the main factors attributing to diagenesis. The two main factors are the elemental and mineralogical composition of bones and the geochemistry of the soil surrounding.

Soil geochemistry includes examining the pH, heavy metal composition, micro-organism activity, organic matter composition and environmental pollution. This study will be looking solely at the influence that heavy metal composition and pH have on the preservation and decomposition of both human and animal skeletal remains.

Previous research have identified that the level of preservation of skeletal remains in certain soil types but not what factors have caused this difference. From previous studies it is known that within clay type soils the bone condition is very well preserved often cited as looking ‘fresh’, where as in extreme pH soils, such as very chalky or very decalcified gravel, the bones are very damaged (Brothwell, 1981).

Human occupation has been found to mould the geochemical signatures of archaeological sites due to the various habitual activities. Activities such as animal husbandry and other human activities can lead to the deposition of Cu, Cr, Sn and Nd which are regarded as universal indicators of anthropogenic activity (Oonk *et al,* 2008). Rare earth elements (REEs), such as Sc and Y and the lanthanum group, are not deposited from human activities but from the burial of skeletal remains and the following decomposition of bones, teeth, hairs, nails and skin. Other sources of these REEs are from deposits of seaweed, shells, sands and manure which explain these elements are not only found in burial sites but also middens (Cook *et al*, 2006; Entwistle *et al,* 1998). This decomposition of organic materials means that the soils surrounding and in contact with the skeletal remains is constantly changing over time.

Certain elemental ions can cause different damage to skeletal remains in different pH levels due to the soils pH facilitating or disabling the mobility of the ions. The elements P, Fe, Al, Mo, Cu, Zn, Co, Mn, Pb and Ni are immobilized in the pH range of slightly acidic and slightly basic. This helps preserve the skeletal remains within more neutral soils as the ionic exchange between soil and bone is what causes the most damage (Pate *et al,* 1989). This highlights how pH can affect the geochemistry of the soil’s ability to change and influence it greatly.

Certain pH levels, such as slightly basic or acidic conditions, promote the physical preservations of bone whereas extremely basic or acidic conditions cause detrimental effects on archaeological skeletal remains (Nielsen-Marsh *et al*, 2007). Acidic conditions cause bone demineralisation while basic conditions can lead to the deposition of calcium carbonate, these can then greatly damage the bones (Gordon and Buikstra, 1981; Nicholson, 1996; Watson, 1967). The two heavy metals that heavily influence the soil's pH are Al for acidic soils and Ca for the alkaline soils. An increase in either heavy metal will alter the pH over a period of time so it is essential to monitor these heavy metal concentrations due to the effect a small increase of ions can have. Alkalinity of the soil is mainly controlled by the amount of calcite ($CaCO^3$) and reacting with any water present. If there is an increase of Ca^{2+} within a soil then the pH decreases and becomes more alkaline, if there is an increase in CO_2 the soil becomes more acidic (Rowell, 1994).

Bone damage caused by alkaline pH levels can be attributed to the chalky soils found throughout South West England due to the Jurassic coastline depositing marine organism shells, which over time, created the chalk rock-bed. The chalk itself can contribute vastly to the deterioration of remains due to its abrasive nature which causes damage by settling after the burial (Amour-Chelu and Andrews, 1996). As chalk is permeable**,** it can cause the skeletal remains to become eroded and fragile due to leaching (Brothwell, 1981).

It is very important to preserve the bones after excavation and stop any more diagenesis from occurring as this will further damage the vital archaeological artefacts. By acknowledging certain aspects of the soils geochemistry, most notably the pH, this can help identify what aftercare steps are suitable with the cleaning of the skeletal remains and post excavation preservation (Brothwell, 1981).

There is limited research into the area of bone diagenesis caused by environmental factors due to more emphasis being on taphonomic influences. The biggest and most recent dive into this area is the meta-study by Nielsen-Marsh *et al* (2007) where they cluster analysed two hundred and nineteen archaeological bones (One-hundred and twenty-one human and ninety-eight animals) with the accompanying soil samples. The sites where the samples were taken ranged from the time periods of pre-modern to the Mesolithic and were representative of burial environments across Europe. They were able to conclude that numerous environmental factors can be detrimental buried skeletal remains. These geochemical effects have already been identified to threaten buried archaeological artefacts. Nord *et al* (2005) has drawn attention of conservationists to the fact that recently excavated remains are in a poorer condition than previous skeletal remains found in similar soils. This is all down to the soil's geochemical signatures, with emphasis on pH, deteriorating the archaeological artefacts over time. Agriculture has been identified as a main contributor to the fluctuating soil geochemistry which is damaging the buried skeletal remains. This has prompted conservationists to devise *in situ* preservation policies to ensure that any buried skeletal remains are not damaged before they are excavated by environmental factors. By highlighting which soil type causes the most damage to a skeletal remain, the decision to immediately excavate or proceed with *in situ* preservation can be accurately decided (Nielsen-Marsh *et al*, 2007; Nord *et al*, 2005).

By utilising information that is learned about the effects of soil geochemistry many interpretations can be made from skeletal remains. Numerous forensic and archaeological cases have encountered problems with missing bones, whether this is from poor recovery or speeded diagenesis facilitated by the soil's geochemistry. Loss of bones due to speeded diagenesis can cause incorrect assessments to be made. Current archaeozoological research on the abundance of certain species relies solely on the retrieval of bones to calculate the minimum number of individuals present in an area. With small, less dense bones being the most susceptible to the soil's pH influences, inaccurate assumptions on abundances can hinder the progress of research (Nicholson, 1995).

There are many other applications of knowing the effects soil geochemistry within science disciplines. Dating a termite mound in Rhodesia was made possible by Watson (1967) from analysing the skeletal remains buried below the elevation of the surrounding area. Due to the skeletal remains being below the elevation of the mound, it proved that the termite mound was not present at the time of burial. The skeletal remains were found within the alkaline soil and no skeletal remains were found in the surrounding graves where the soil was acidic. Due to the skeletons being well preserved in the alkaline soils they were carbon dated to give the age of the mound, which was around seven hundred years. Without applying the knowledge of soil's geochemistry effects on skeletal remains and by comparing the abundance and preservation levels of control subjects in the surrounding soil, the termite mound would not have been correctly dated.

This introduction has demonstrated the importance of understanding soil geochemistry by highlighting that if this area is not aptly researched quickly and the fundamentals learnt about the soil's geochemical influence, invaluable archaeological remains will be damaged and lost forever. Calculating the cause and effect of heavy metals within soils, in particular the concentration of Al ions (acidic soils) and Ca ions (alkaline soils), will be a major step in grasping the significance of the geochemical influence on bone preservation. The resulting effect of these ions on the soils pH level can be used as a predictive model to discuss whether certain archaeology is at risk of speeded diagenesis and needs to be excavated immediately, or if *in situ* preservation is needed to those that are not at risk. This will undoubtedly save irreplaceable archaeological remains which will help interpret archaeological and anthropological sites.

1.1. Aim and Objectives:

The aim of this study is to identify any possible 'cause and effect' that heavy metals have on pH and the level of bone preservation and contribute to this rarely examined sector of soil geochemistry, and create a prototype of a predictive model for assessing *in situ* bone preservation levels.

The objectives of this study are;

- Isolate an acceptable sample size of articulated skeletal remains from an archaeological site to study.
- Collect soil samples adjacent to the articulated skeletal remains, as these soil types are most relevant to the study due to the period of time they were in contact with the skeletal remains.
- Identify which method is the best for assessing the skeletal remains preservation level in both a quantitative and qualitative manner.
- Identify which method is most suitable to undergo soil digestion to provide the most accurate heavy metal concentrations.

- Form a pH method which will accurately replicate the pH level of the soil within the laboratory to closely match the *in situ* pH level.
- Identify which SPSS subcategory will deduce a correlation co-efficient to identify if there is any relationship between pH and bone preservation, as well as, pH and Ca ion concentration.
- From the results construct and identify any 'cause and effect' relationships between the heavy metal elemental concentrations, pH and skeletal remains.
- Using the results and equations create a working prototype of a predictive model.

2. Methodology

There are many different methods currently available for analysing the samples collected at each stage of this research. This chapter deduces which one is the most appropriate for the study by evaluating and identifying the pros and cons of available methods.

2.1. Sample Collection

Twenty-four soil samples were collected from a Durotrigian site being excavated by Bournemouth University situated near Blandford Forum, Dorset. The soil samples were collected over two days in June 2012. The soil samples were taken from the adjacent area surrounding significant articulated skeletal remains. Out of the twenty-four samples, fourteen were from human burials and ten were from animal remains. The area was photographed before the sample was taken to record the position of the bone and to aid in later identification of the skeletal remains. The context number, feature number and trench area were also recorded to gain an understanding of the grave/skeletal remains' position within the archaeological site (see Table 1).

Table 1: Recorded information of the twenty-four samples collected**.**

Sample Number	Trench/ Area	Context	Feature	Skeletal Remain Type
1	H	1070	1069	Human
2	F	376	181/183-375	Human
13	H	1041	1038	Animal
16	F	342	335	Animal
17	F	342	835	Animal
28	F	OO3	OO2	Human
29	F	OO5	OO4	Human
33	F	191/2-244	394	Animal
39	G	732	731	Animal
42	H	1052	1045	Animal
43	H	1070	1069	Human
44	?	503	502	Human
45a	F	O66	O65	Human
45b	?	540	539	Human
46	?	115	101	Human
47	F	O66	O65	Human
48	?	540	539	Human
49	?	115	101	Human
53	G	739	735	Animal
55	H	1070	1069	Human
59	H	1073	1028	Human
63	F	366	O34	Animal
66	H	OO8	212	Animal
71	?	734	733	Animal

2.2. Soil Analysis

The twenty-four soil samples were air dried for a week before they were sieved using a 1mm sieve. Samples were weighed to 0.25±0.001g and 6ml of 37% HCl and 2ml of 70% HNO_3 added to each sample, using Dispensette®. Samples were microwave digested using a Multiwave 3000 Anton Parr microwave for 40 minutes at 1200W. After digestion the samples were filtered using QT210 filter paper and made up to 50ml volume using analytical grade water. Each sample run was replicated twice. After being digested the samples were run through inductively coupled plasma optical emission spectrometry analysis (ICP-OES). With the ICP-OES analysis eight standards were run first to ensure that the readings were correct.

One of the benefits of using this method of HCl and HNO3 to digest the soil samples is that unlike the *aqua regia* method, the heavy metals concentration is a lot more accurately recorded in the ICP analysis. Previous comparisons of the HCl/HNO3 method and *aqua regia* has shown great discrepancies between the detected heavy metal elements with lower readings being presented from the samples digested via *aqua regia.* This is due to the heavy metal elements within the soil being less affected by the acidic conditions of the *aqua regia* method so therefore complete digestion is not achieved. (Bettinelli, 2000; Hseu *et al,* 2002).

The use of a microwave-assisted digestion method means that the digestion process is fast, simple to conduct and relatively safe due to the use of closed vessels, which in turn protects the user from exposure to heated nitric acid vapours. The use of microwave-assisted digestion also allowed for a shorter time frame between the digestion process and ICP-OES analysis by allowing for large batches of samples to digest all at the same time. The Multiwave 3000 Anton Parr microwave allowed for forty-eight samples to be digested at once, where as traditional methods of dry ashing and using hotplates were limited by the total amount of samples that could be conducted at once by the user. By steering away from the out-dated method of using hotplates with open vessels, meant that volatile elements were not lost from the evaporation of the solution, increasing the accuracy of the ICP-OES results and ensuring that all of the soil's heavy metal concentrations were accurately presented in the analyte.

All of the ICP-OES preparations, filtering of samples and increasing volume, consist of the same filtering method of the solution so there is no difference in the method at that stage. What must be noted is the type of filter paper used to ensure that there is a standard. This study used QT210 filter paper and used analytical grade water to increase the volume. The use of analytical grade water ensured that there was no addition of heavy metals, which will affect the ICP-OES results, due to its highly purified nature.

ICP-OES and ICP-MS have replaced the use of mono-elemental spectrometry, such as FAAS and GFAAS, due to ICP spectroscopic techniques being multi-elemental, which now allows for larger number of analytes to be examined in a much shorter time frame.

Adapting Rowell (1994)'s method, 2±0.05g of the 1mm minus air-dried soil sample was placed into a screw capped bottle and 5ml of distilled water was added. This solution was then hand shook periodically over a 15 minute time period. The suspension was then stirred and the pH was deduced using a pH metre. Each pH reading was conducted thrice times, using distilled water in between to clean the metre. The pH range is for soil samples reduced from 0-14 to 1-12, and it should be noted that the soil pH represents only the pH of a solution in equilibrium with the soil. Rowell (1994)'s method is a standardised procedure which means it can be used to confidently determine a soil's pH and be easily replicated by fellow researchers.

2.3. Bone Preservation and Damage

Utilising a previous method researched by Gordon and Buikstra (1981) to record the level of preservation on each articulated skeletal remains involved categorising the preservation of the bone samples on a scale of 1 to 5. This categorisation was conducted on site alongside with the soil sample collection for the twenty-four articulate skeletal remains. The predetermined categories being:

> Category 1 represents a strong complete bone: Skeletal elements are whole and undamaged.
>
> Category 2 represents fragile bones: Bony elements may be fragmented, but they are completely reconstructable.
>
> Category 3 represents fragmented bone: Skeletal elements are generally cracked and fragmented.
>
> Category 4 represents extremely fragmented bone: Skeletal elements are severely fragmented.
>
> Category 5 represents bone meal or ghost: The bones are reduced to a powdery substance.

Each bone was assessed on two separate occasions to ensure the right category was selected. The bones were also visually examined for certain surface damage caused from the burial. This method by Gordon and Buikstra (1981) has been widely used within the archaeological and anthropological fields for assessing bone preservation in relation of pH in different archaeological studies so ensured that this method is a standardised procedure.

A main alternative method of determining bone preservation levels is the use of bone histology. By cutting thin slices of bone and examining under the microscope for evidence of calcium carbonate, which is found deposited on bones during diagenesis from extreme pH soils.

Another method of assessing the bones state of preservation is the Turner-Walker *et al* (2002) defined method of studying the porosity of the bone using a cluster analysis on the mercury intrusion porosimetry (HgIP) results. These results showed 4 major groups which highlighted different diagenesis mechanisms cause by the soil geochemistry and micro-organism activity. The four groups were;

- Flat traces – well preserved bones.
- Greatest intrusion in ‘s’ porosity – accelerated collagen hydrolysis.
- Greatest intrusion in ‘m’ porosity – microbial attack mechanism.
- Greatest intrusion in ‘l’ porosity – catastrophic mineral dissolution.

Nielsen-Marsh *et al* (2007) utilised this method and analysed these four diagenesis mechanisms against four soil sample types, which were divided into types according to the soils properties. This method is a lot more complex with the use of mercury intrusion porosimetry (HgIP) but provides quantifiable data rather than the qualitative data from the Gordon and Buikstra (1981) method.

Due to the nature of this study and funds/time available, along with level of experience, the use of bone histology along with bone porosity was not practicable so only visual assessment could be undertaken. The fact the skeletal remains used in this study were of archaeological value it would be detrimental to preform histology on them without the available supervision, this meant that the Gordon and Buikstra (1981) method was the most feasible way to assess bone preservation at this level of practice.

2.4. Statistical Analysis

To identify the relationship between the pH and preservation category level, the use of IBM SPSS's scattergram along with linear regression lines will be utilised to correlate any relationship between the two factors and test for significance.

This chapter has demonstrated that the most suitable method of conducting soil digestion in relation to heavy metal concentration is utilising an HCl/HNO_3 acid mix and a microwave-assisted digestion method. This is due to the microwave-assisted digestion method with closed vessels ensuring that no volatile elements are lost, which occurs frequently with the use of hotplates and open vessels. The microwave-assisted digestion method also allows for a large batch of samples to be run at the same time within a short time frame, it is the most time effective and fast way to conduct soil digestions. It also protects the use from risk of exposure to harmful nitric acid vapours which are caused by the heating of HNO_3.

The use of ICP-OES allowed for multi-elemental analysis which is necessary for identifying the 'cause and effect' that multiple heavy metals have on soil geochemistry in the relation to pH level, and their interactions with each other. This also reduced the time necessary for analysis to be conducted, as each sample is analysed for all heavy metal elements in one go, instead of conducting a separate analysis of each individual element.

By adapting Rowell (1994)'s method of using distilled water in equilibrium with the soil sample allowed for the most accurate pH reading which would greatly reflect the true *in situ* pH level.

When it came to identifying and quantitating the level of the skeletal remains' preservation it was concluded the Gordon and Buikstra (1981) method was the most applicable, although not the most ideal or objective, for this level of skill and practice without compromising the important archaeological skeletal remains.

3. Results

This chapter will present the results from each stage of this study respectively.

3.1. Bone Categorisation

For the human skeletal remains the mode level of preservation was Category 1, a strong complete bone (Skeletal remains are whole and undamaged), which was the same for the animal skeletal remains. The mean level of preservation for human remains and animal remains were 1.9 and 1.8, respectively. For both skeletal types their range was between Category 1 and Category 3, with no samples being extremely fragmented or powdered bone (see Table 2).

Table 2: Bone categorisation of the articulated skeletal remains.

Sample Number	Skeletal Remain Type	Bone Categorisation	Sample Number	Skeletal Remain Type	Bone Categorisation
1	Human	1	45	Human	3
2	Human	1	45b	Human	1
13	Animal	3	46	Human	1
16	Animal	1	47	Human	1
17	Animal	2	48	Human	2
28	Human	3	49	Human	2
29	Human	2	53	Animal	3
33	Animal	1	55	Human	3
39	Animal	2	59	Human	3
42	Animal	2	63	Animal	3
43	Human	2	66	Animal	1
44	Human	1	71	Animal	1

Taking in sample size the animal bones were in a worse condition than the human remains (see Figure 1), this would be attributed to how and where they were disposed of. All of the animal skeletal remains were found within middens on the site which contained pottery and other refuse.

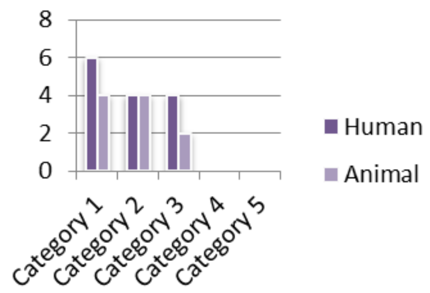

Figure 1: Chart showing the comparison of human and animal remains' level of bone preservation.

The human skeletal remains, apart from two, were found in unique graves dotted around the site. The two samples that were not found in individual graves were samples 28 and 29, which were found in a midden due to being juvenile skeletal remains. Their level of preservation was, 3 and 2, respectively. Sample 28 was among the least preserved skeletal remains within the collection and this has been attributed to the midden burial and that juvenile bones are smaller and more fragile than the adult skeletal remains found within the individual graves so are more susceptible to diagenesis.

3.2. ICP-OES

All concentrations of the elements in the samples were of a detectable level which meant that there was no loss of data. To get the correct concentration (ppm) for each element the equation; (Raw ICP reading x50)/Sample weight, was used on the raw ICP-OES analysis (See Table 3).

When presented with the ICP-OES results main focus was on the four elements; Ca, K, Mg and Na, due to these being the major exchangeable ions which mechanisms and movements are hardly affected by soil pH. Their presence indicates that there was movement of the K, Mg and Na ions from the soil to bone for each sample, and the movement of Ca ions from the bones and into the surrounding soil.

Table 3: ICP-OES concentrations of Ca, K, Mg and Na.

Sample Number	Ca	K	Mg	Na
1	197270	1236	1832	194
2	117707	1498	2297	257
13	148211	3622	3029	327
16	136910	2756	2707	246
17	152791	1749	2261	249
28	162333	2076	2438	271
29	155341	1229	1973	215
33	171741	1139	1750	254
39	78961	1156	1614	181
42	166622	2836	2711	242
43	163866	2688	2598	227
44	150666	1787	2361	188

45	172103	1611	2085	197
45b	149772	1582	2046	167
46	193420	1279	1769	156
47	158155	2032	2330	208
48	148855	1927	2388	198
49	187023	1602	1990	202
53	122728	4366	3732	275
55	165076	1613	2069	199
59	106829	3707	2934	323
63	164301	1415	1784	178
66	103041	1916	2091	255
71	112701	2473	2421	251

Due to each sample having a pH range of 8.2 and 8.8 the concentration of calcium and aluminium were compared (see Figure 2). The samples were found to have higher concentration of calcium in comparison with aluminium. This is to be expected as the soils are alkaline from agriculture soils on a chalk bed.

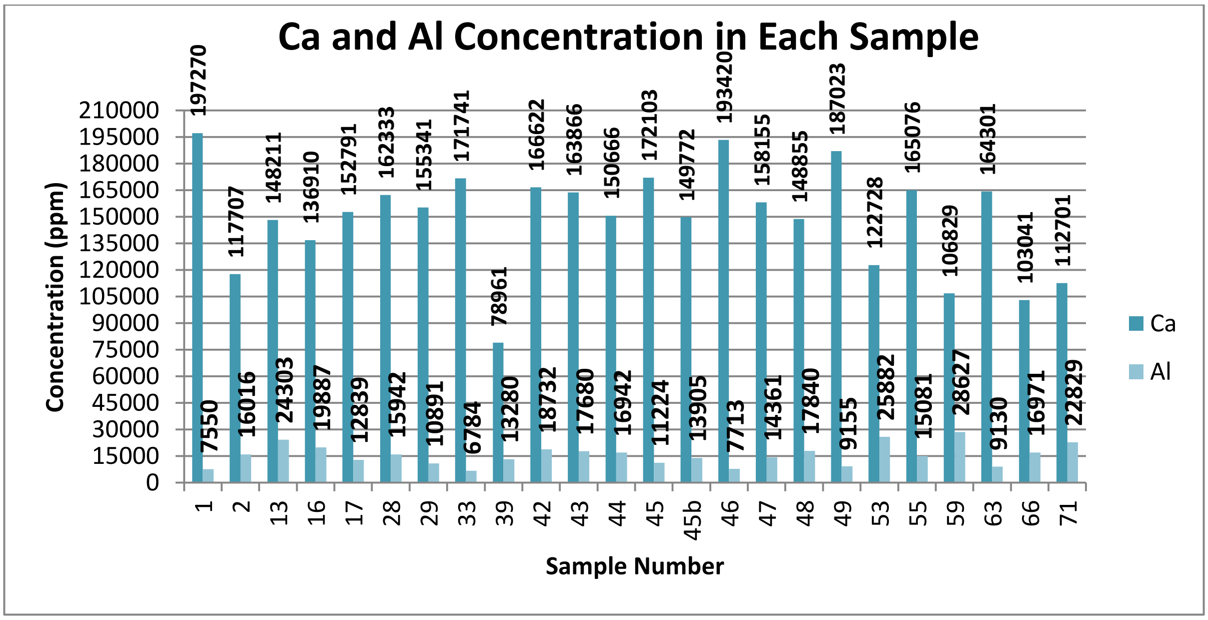

Figure 2: Graph showing the Ca and Al concentration in each of the twenty-four soil samples.

Many samples had higher levels of Mg compared to K, which is expected as these two elements' mobility is facilitated in the same mechanism. Na concentrations are considerably small compared to the Mg and K levels (see Figure 2).

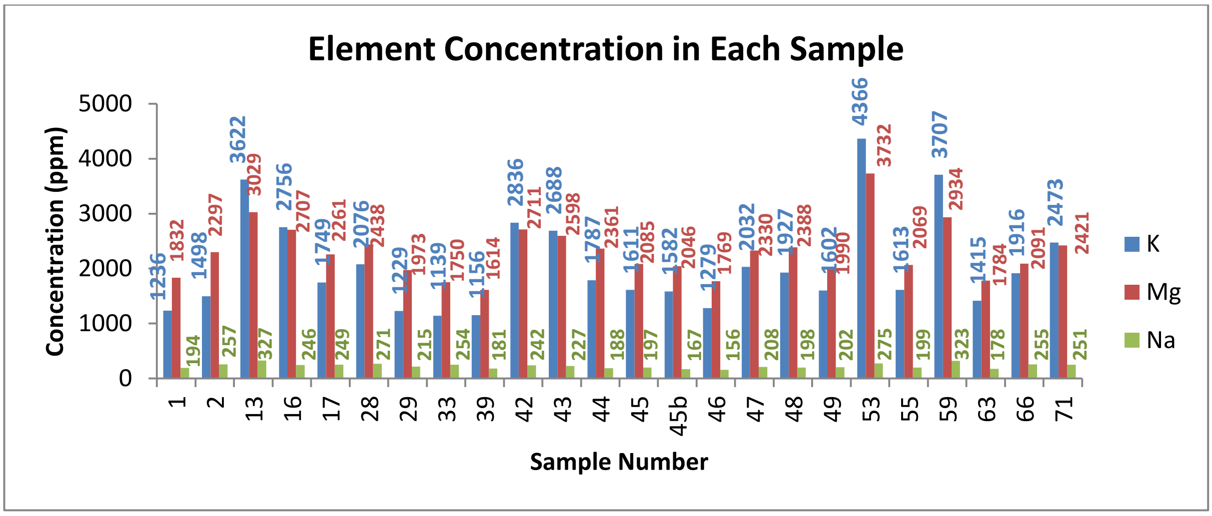

Figure 3: Graph showing the concentration of K, Mg and Na in each of the twenty-four soil samples.

3.3. pH

The pH levels recorded were in the range of 8.1 to 8.8, indicating that each sample, in according with the INRA (1995) classifications, was slightly basic (see Table 3). The mean pH of the soil samples was 8.5. This was expected due to the current use of the site for agriculture purposes and the samples being taken from an area which has a chalk bed.

Table 4: pH levels of the soil samples.

Sample Number	Skeletal Remain Type	pH Level Reading 1	pH Level Reading 2	pH Level Reading 3	pH Average
1	Human	8.2	8.4	8.4	**8.3**
2	Human	8.4	8.2	8.3	**8.3**
13	Animal	8.6	8.6	8.7	**8.6**
16	Animal	8.4	8.4	8.4	**8.4**
17	Animal	8.7	8.4	8.4	**8.5**
28	Human	8.4	8.5	8.4	**8.4**
29	Human	8.1	8.3	8.3	**8.2**

33	Animal	8.3	8.4	8.3	**8.3**
39	Animal	8.6	8.4	8.5	**8.5**
42	Animal	8.5	8.7	8.6	**8.6**
43	Human	8.6	8.6	8.6	**8.6**
44	Human	8.4	8.3	8.3	**8.3**
45	Human	8.8	8.6	8.8	**8.7**
45b	Human	8.4	8.4	8.4	**8.4**
46	Human	8.8	8.7	8.8	**8.8**
47	Human	8.6	8.6	8.6	**8.6**
48	Human	8.5	8.5	8.5	**8.5**
49	Human	8.7	8.7	8.6	**8.7**
53	Animal	8.8	8.6	8.6	**8.7**
55	Human	8.7	8.6	8.6	**8.6**
59	Human	8.6	8.8	8.6	**8.7**
63	Animal	8.7	8.6	8.6	**8.6**
66	Animal	8.4	8.3	8.3	**8.3**
71	Animal	8.1	8.3	8.4	**8.3**

3.4. Statistical Analysis

Utilising SPSS's scattergram subcategory programme, with a linear regression, the correlation coefficient between pH and the preservation category was determined. The correlation coefficient is – R = 0.535 with a R^2 = 0.287, which shows there is a moderate correlation between the pH and the level of bone preservation. This meaning that as the pH decreases and the more basic the soil becomes the skeletal remains become less preserved (See Figure 4). This returned an equation of Preservation Level = 2.669(pH level) – 20.805.

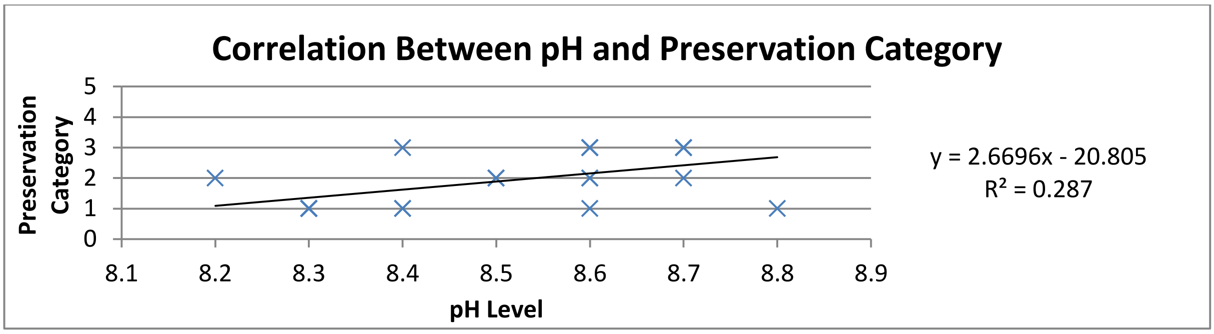

Figure 4: Scattergram of the correlation between pH level and preservation category. Note duplicates have been removed from the graph.

Ca concentration and pH level were also statistically analysed using linear regression. This produced an R of 0.2173 and a R^2 of 0.047, which shows there is a weak relationship between the Ca conc. and the pH level. From this the equation; Ca conc. = (1.703E04 x pH) + 37635.53, was obtained.

After Ca and pH returned an low R number it was decided to correlate the Ca conc. and bone preservation level. It would be predicted that the higher the level of damage to the skeletal remains the more calcium ions there would be in the soil. This correlation produced an incredibly low R^2 of 0.000006735, which shows there is no relationship at all between Ca levels and bone preservation.

As these soil samples are from an agricultural site and therefore alkaline, the concentration of Ca and Al were statistically analysed with linear regression (see Figure 5). This provided us with moderate correlation with a R number of -0.604 and an R^2 of 0.361. This returned an equation of Al concentration= (0.118 x Ca conc.)+33318, which can be applied to future samples.

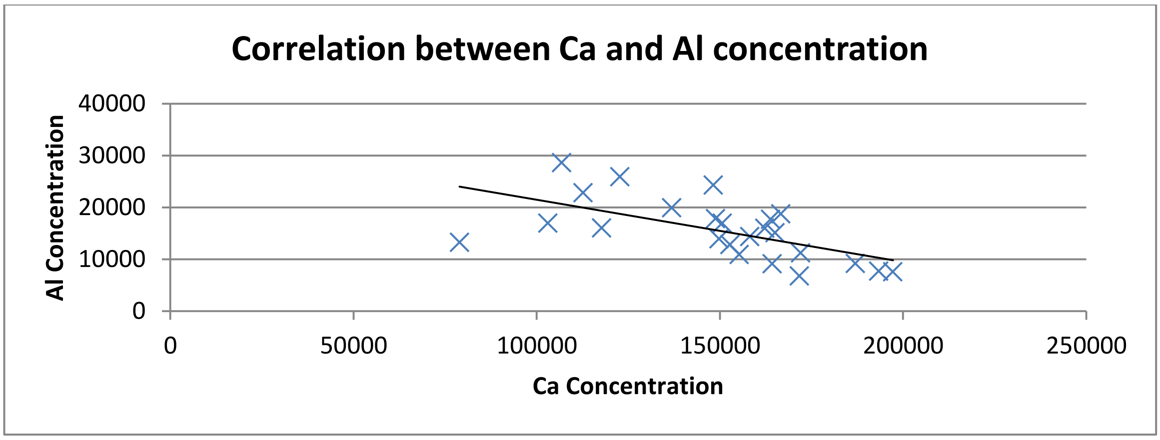

Figure 5: Correlation between the Ca and Al concentrations.

The concentrations of K and Mg were correlated using the SPSS scattergram subcategory together with a linear regression which produced an R^2 of 0.978 and an R of 0.988. This R number showed there was a strong relationship between the concentration of K ions and Mg ions. Therefore the levels of potassium present in the soil is strongly correlated to the amount of magnesium which is expected due to these ions both exchanging from soil to bone in the same facilitated manner from them both being water soluble cations. Due to the same chemical mechanism of diffusion the heavy metal ions K and Mg have within the soil it was expected that they had strong relationship, which this study highlighted.

4. Discussion

In this chapter the main results will be summarised and interpreted with any significance noted. They will then be evaluated to see whether they prove or disprove the hypothesis of the study and confirm/refute previous studies/research. Limitations of this study will be discussed in a separate subheading where suggestions of improvements will be made and future research discussed.

The skeletal remains produced a varied level of preservation within the first three preservation categories; this was to be expected as different grave/midden fillings contain different elemental compositions. This was most certainly the case when comparing the ICP results of the soils collected from human remains and animal remains. The soil samples taken adjacently to the animal remains contained higher concentration of the element Cu which were associated with animal husbandry whereas the soil samples from the human remains had lower concentrations of Al and higher concentration of Ca. The higher concentration of Cu is explained from the decomposition of the waste products of farming, along with the other waste products which are disposed of within the middens that the animal skeletal remains were found (Oonk *et al*, 2008). The two human samples which did not have lower levels of Cu were samples 28 and 29, which were the two juvenile human skeletons that were found disposed of in a midden filled with other refuse. This highlighted that Cu concentrations are not directly caused by the decomposition of animals skeletal remains, but from the other refuse associated with human occupation. The lower levels of Al within the soil samples of the human skeletal remains can be explained from the anthropological side of the burials. When refilling a grave the soil and fill that was removed to accommodate the grave is used, therefore the natural composition of the soil is kept close to the composition as when it was undisturbed. As the archaeological site is based on a chalk bed, many of the graves were cut into the chalk; this increased the natural occurrence of Ca within the soil samples. As the chalk bed consisted of calcium carbonate, it was to be expected that the concentration of Ca was a lot higher than the concentrations of Al within the soil samples.

From statistically analysing certain aspects of the ICP-OES analysis, pH level and bone preservation level, numerous relationships have been identified. The least surprising is the moderate correlation between the pH level and the level of the bone preservation. This relationship means that as the pH level increases the level of level of preservation decreases. This was to be expected as pervious research has highlighted that pH is a contributing factor in the speeded diagenesis of skeletal remains. Gordon and Buikstra (1981)'s original study found a strong correlation between their samples pH and the level of preservation of their samples but this strong correlation only explained 84% of the preservation variation. The stronger correlation Gordon and Buisktra observed has been attributed to the larger sample size and wider range of pH level observed in the soil samples. Although there is moderate relationship between the pH level and bone preservation this, like with Gordon and Buikstra's study, does not explain why many samples in this study which were in a more alkaline soil had better preservation than the less alkaline soils. Many samples fell far from the regression line which had a large standard deviation, but this only proved that pH cannot be the only factor causing speeded diagenesis and therefore it is necessary to investigate the heavy metal composition effects on bone preservation. This further proved that variance of preservation in accordance to soil pH, as observed by Nicholson (1996) and Gordon and Buikstra (1981), cannot be used solely as a predictor of skeletal preservation. As the soil samples used within this study were not wildly varied in their pH level due to being from an agricultural site, it hindered the study as the small alkaline pH range meant that no obvious diagenesis damage, such as the deposition of calcium carbonate, occurred. This is why understanding the heavy metal interactions with the bone and diagenesis mechanisms, such as ion exchange, bone demineralisation, and the deposition of calcium carbonate are the most important variables when it comes to bone.

A surprising relationship observed in this study is the one between Ca concentration and pH. Due to the role of Ca ions within soil geochemistry and it being the main influencing factor on alkaline pH levels, it was hypothesised that there would be a strong relationship between the concentration of Ca and pH. The samples within this study highlighted a weak correlation between the Ca concentration of the soil and pH level. This is surprising as the pH of the soil samples are alkaline so it would be expected that the more alkaline a soil is, the higher the Ca concentration but this is not the case, and therefore a strong correlation (Rowell, 1994). Although there was only a weak relationship between these two variables, this study was able to identify in a few samples that the amount of Ca ions was in fact proportionate to the pH level. Therefore it highlights that Ca concentration certainly has a role in influence pH levels it isn't the sole contributor. Thus to fully understand what the cause and effects heavy metals have on moulding soil pH, it is necessary to investigate their interactions with skeletal remains within small groups or pairs. To further investigate the influence Ca concentration has on pH when paired with other heavy metals, the Ca concentration and Al concentration was analysed for relationships. The soil samples concentration of Ca had a moderate negative correlated to the level of Al. The higher levels of Al within the soil samples showed a decrease in the concentration of Ca ions.

By utilising the equations obtained for each of the moderate/strong relationships, predictive models are made possible. By manipulating the equation they can be used as a predictive model to estimate the pH level or heavy metal concentrations.

An example of this is identifying the estimated preservation level of *in situ* skeletal remains using the preservation level equation found in this study (Preservation = (2.669xpH)-20.805). Thus if we had a soil pH level of 8.9, when applied to this equation we can predict that the level of preservation is 2.9, therefore we expect the bones to be classified as; Skeletal elements are generally cracked and fragmented. Another example is that if we were to have a pH level of 9.2 the equation will produce a preservation level of 3.74, so the skeletal remains would be either cracked and fragmented or severely fragmented. It must be noted that due to the limited pH range found in these samples, and the lack of category 4 and 5 in bone preservation, this preservation equation will not be fully usable in pH levels outside of 8 and 9. Due to the pH level within this study ranging from 8.2 and 8.8, this current application of this equation is very constricted. This is why it is important to further expand this research with multiple archaeological soil samples ranging from 1-12 on the pH scale and skeletal remains showing different levels of diagenesis to ensure the most accurate equation.

Although using the preservation level equation can provide a provisional estimate of the condition of the skeletal remains, the concentration of the heavy metals should also be estimated and carefully watched. By creating a predictive model of the expected Ca concentrations found for each pH level, with focus on alkaline soils, the Ca concentrations can be closely monitored. This is especially important for monitoring the ever changing concentration of heavy metals within the soils. By manipulating the Ca concentration equation created from the coefficient correlation, Ca conc. = ($1.703E^{04}$ x pH) + 37635.53, to estimate the expected concentration of Ca, or other heavy metals, their influences can be monitored. For example, the pH level of 8.6 is expected to have a Ca concentration of

184,093.5ppm, but if the soil sample was digested and then ICP-OES analysed and produced a Ca concentration of 177,299ppm it would be expected that the soil's pH be around 8.3, this showing that the pH of the soil adjacent to the bone might decrease over time to a lower pH which would increase the preservation level of the bone so *in situ* preservation would be viable. If on the other hand the pH level of the soil was at the time of sampling 8.6 but Ca concentration after analysing was 199,420ppm this would indicate that there might be an increase of pH in the future, causing the soil's pH surrounding to bone to increase to 9.5. This increase to a more alkaline soil will cause calcium carbonate to be deposited on the bones surface causing speeded diagenesis of the skeletal remains, so it would be necessary to excavate as soon as possible to avoid skeletal remains becoming damaged. These examples were for alkaline soils, but if a predictive model was concluded for acidic soils, by estimating the concentration of Al ions as it is the biggest influence for acidic soils, this can have the same application when deciding on which type of conservation is needed. Therefore it is important to not only monitor the soils pH, but also the heavy metal concentrations.

4.1. Limitations

A limitation of this study is that the soil samples collected were all slightly basic only allowing for a small section of the pH scale to be properly studied which means it can only be used as a predictive model of slightly basic/alkaline soils in the range of 8.1 to 8.8 instead of the whole 1-12 pH scale available for soils.

The method used for categorising the bone's level of preservation is also very subjective with only five categories available will cause difficulties if the bone's preservation level is between categories. Or merging the Gordon and Buikstra (1981) method with Nielsen-Marsh (2007)'s HgIP cluster analysis can provide clearer results.

The Rowell (1994) method for obtaining the pH levels has its disadvantage as the soil was collected and dried, then tested off site by the addition of distilled water. This means that the pH reading given is the pH of the soil being in equilibrium with the solution. When the distilled water which has a pH of about 5.6, is added to the soil sample which has a different pH level, the pH of the water changes to be what the soil was originally. Often enough this cannot replicate the exact pH the soil has whilst in the original site but by utilising a standardised procedure the pH level can be confidently established even though the original values are non-replicable so it is recommended that soil pH is conducted on site to obtain the true conditions.

5. Conclusion

Although the studies' soil samples obtained a very limited pH range which greatly limited the application of the equations obtain and creating only a predictive model that could be used on slightly basic soils, it highlighted how these geochemical characteristics can be used to predict the preservation of *in situ* archaeology.

It should be noted that even though in this study there was a moderate correlation between pH level and preservation, pH should not be used as a sole indicator for creating a predictive model on the preservation of skeletal remains *in situ*. The fact that soil has such a varied composition can result in two identical pH soils having such stark difference in level of preservation. This is due to the complicated nature of the individual interactions each heavy metal element has with skeletal remains. To obtain accurate predictive model it is necessary to first understand the role each element, not just as a collective, has within diagenesis when interacting with other elements. When we fully understand this, the true effect geochemistry has on bones will be known and a workable predictive model can be created.

6. Further Research

To further progress in understanding the effects of soil pH has on bones, a wider range of pH should be studied, ranging from extremely basic to extremely acidic. This would mean getting a greater sample size from multiple sites to ensure all pH has suitable number of samples.

Improvements on the categorising of preservation levels will allow for a lot more in depth correlations. Rather than vague grouping into the restricted five options, more options should be in place which address all areas of the bone preservation rather than the level of ‘wholeness’ and flaking. For further studies a minimum of ten options should be in place which will allow for a more precise categorisation and therefore a better understanding of the soils effect. By teaming up elemental content of bones with the bone porosity and cluster analysis a precise predictive model can be deduced due to the quantitative data rather than the subjective qualitative data from using only visual assessment.

Acknowledgements

Thanks to Paul Cheetham for the inspiration to research this topic and pushes in the right direction with this dissertation, as well as allowing the research to focus on skeletal remains excavated on the Bournemouth University's yearly archaeological dig.

A huge thank you to Karen Walmsley for the supervision of the laboratory work, as well as the much needed guidance and knowledge for the future. Also to Damien Evans for putting up with the soil samples sitting in the lab for a lot longer than they should have.

And finally, thank you to Bournemouth University's School of Applied Sciences for enabling this study from the use of the facilities on campus which were vital for this piece of research.

References

Amour-Chelu, M., Andrews, P. 1996. Studies of the Buried Bone from Overton 1992 Excavation: 11.2 Surface Modification of Bone. *The experimental earthwork project*. England: York, Council for British Archaeology.

Bettinelli, M., Beone, G.M., Spezia, S., Baffi, C. 2000. Determination of heavy metals in soils and sediments by microwave-assisted digestion and inductively coupled plasma optical emission spectrometry analysis. *Analytica Chemica Acta*. 424, 289-296.

Brothwell, D.L. 1981. *Digging Up Bones: The Excavation, Treatment and Study of Human Skeletal Remains*. New York: Cornell University Press.

Cook, D.E., Kovacevich, B., Beach, T., Bishop, R. 2006. Deciphering the inorganic chemical record of ancient human activity using ICP-MS: a reconnaissance study of late Classic soil floors at Cancuén, Guatemala. *Journal of Archaeological Science*. 33 (5), 628-240.

Entwistle, J.A., Abrahams, P.W., Dodgshon, R.A. 1998. Multi-Element Analysis of Soils from Scottish Historical Sites. Interpreting Land-Use History Through the Physical and Geochemical Analysis of Soil. *Journal of Archaeological Science*. 25, 53-68.

Gordon, C.C., and Buikstra, J. E., 1981, Soil pH, bone preservation, and sampling bias at mortuary sites. *American Antiquity*. 46 (1), 566–71.

Hseu, Z., Chen, Z., Tsai, C., Tsui, C., Cheng, S., Liu, C., Lin, H. 2002. Digestion methods for total heavy metals in sediments and soils. *Water, Air and Soil Pollution.* 141, 189-205.

INRA. 1995. Référentiel pédologique. *Association Française d'étude des sols*. INRA, 332.

Moor, C., Lymberopoulou, T., Dietrich, V.J. 2001. Determination of Heavy Metals in Soils, Sediments and Geological Materials by ICP-AES and ICP-MS. *Mikrochimica Acta*. 136, 123-128.

Nicholson, R. 1996. Bone Degradation, Burial Medium and Species Representation: Debunking the Myths, and Experiment-based Approach. *Journal of Archaeological Science*. 23 (4), 513-533.

Nielsen-Marsh, C.M., Smither, C.I., Jans, M.M.E., Nord, A., Kars, H., Collins, M.J. 2007. Bone diagenesis in the European Holocene II: taphonomic and environmental considerations. *Journal of Archaeological Sciences. 3*4 (9), 1523-1531.

Nord, A.G., Tronner, K., Mattsson, E., Borg, GCh., Ullén, I. 2005. Environmental threats to buried archaeological remains. *AMBIO: A Journal of the Human Environment*. 34, 256–262

Oonk, S. Slomp, C.P., Huisman, D.J., Vriend, S.P. 2009.Effects of site lithology on geochemical signatures of human occupation in archaeological house plans in the Netherlands. *Journal of Archaeological Science.* 36 (6), 1215-1228.

Pate, F.D., Hutton, J.T., Norrish, K. 1989. Ionic exchange between soil solution and bone: toward a predictive model. *Applied Geochemistry*. 4, 303-316.

Rowell, D.L. 1994. *Soil science: Methods and Applications*. Harlow, Essex: Longman Scientific and Technical.

Turner-Walker, G., Nielsen-Marsh, C.M., Syversen, U., Kars, H., Collins M.J. 2002. Sub-micron spongiform porosity is the major ultra-structural alteration occurring in archaeological bone. *International Journal of Osteoarchaeology*, 12 (6), 407–414

Watson, J.P. 1967. A Termite Mound in an Iron Age Burial Ground in Rhodesia. *Journal of Ecology.* 55 (3), 663-669.

Wilson L., Pollard M. 2002. Here today, gone tomorrow? Integrated experimentation and geochemical modeling in studies of archaeological diagenetic change. *Acc Chem.* 35, 644–5.

Appendices

Evaluative Supplement

From working on this project and researching into this link between geochemistry and archaeology, I have realised that there is still a lot of work to do within this area. It was very interesting to investigate something that has not been widely researched as each research paper took on its own identity whilst researching the cause and effect link. But as there wasn't much direct research into this area, apart from two studies; Gordon and Buikstra (1891) which first highlighted the relationship and then Nielsen-Marsh et al (2007) who developed and expanded this field, it meant that finding previous research into the diagenesis of skeletal remains in relation to environmental factors was very hard to come by. Most of the studies I was able to find focused on taphonomic damage to skeletal remains and completely ignored the environmental damage. This caused many setbacks when conducting this study.

My literature review showed a promising start highlighting and complimenting the Gordon and Buikstra method of conducting on site bone preservation categorisation. I then chose this for my method of assessing bone damage. However when critiquing it for my methodology section I found numerous problems with this, the main one being how subjective it was. By using a qualitative method and using only five categories, it greatly affected my results as well as this methods replicability. It was simple to use, and very vague, but at this level of study I was not able to use histology, which was my first choice of methodology, to create quantifiable results. As I found this method to be very subjective, whilst assessing on site I ensured that each bone was assessed to the best of my ability. A problem occurred with my results when all of my twenty four samples fell into the first three categories, this greatly affected my statistical analysis. This problem was identified post excavation, at that point the skeletal remains had undergone cleaning and storage – this would alter their preservation levels from what was recorded in situ, therefore I could not re-evaluate them using a more precise methods. If I was to undergo a project like this I would opt to use histology to obtain quantifiable data as well as creating more categories with a point system. By assigning certain damage with a numerical system and tallying the points, it will create accurate preservation levels instead of assigning to five vague categories.

As I was unable to conduct my pH readings on site I had to create a method that would create an accurate reproduction of the in situ pH level. For this I utilised Rowell's 1994 method of adding distilled water to my soil samples and ensuring the soil was in equilibrium with the added water. For future research I would conduct my pH readings on site to ensure that the pH levels were truly reflecting of the conditions the skeletal remains was under.

Another setback occurred after the pH readings were taken. This was due to all of the soil samples being within the pH range of 8.2 and 8.8, this meant that any predictive models created from my data could only be truly applied to soil samples found in pH levels between 8 and 9. This greatly affected the predictive models relevance to other soils. It is in my interest, if I further my research into this area, to utilise the meta-study approach Nielsen-Marsh et al utilised by focusing on more than one archaeological site ensuring that my samples will have a larger pH range and different soil types and geochemistry. It would have been result changing if my soil samples had a larger pH range as a preliminary predictive model could be created which would cover the whole of the pH range and then be shaped into a full and usable predictive model with any further research. Whereas now any further research will greatly change the conclusion and results drawn from this project.

Reading Nielsen-Marsh's study really opened my eyes to numerous methods I could apply to my future work. Their use of cluster analysing the ICP results along with using mercury intrusion porosimetry (HgIP) allowed for objective and quantifiable data to be achieved. Their use of two-hundred and ninety-eight samples allowed for numerous soil types to be analysed for their individual characteristics.

What disappointed me with this project is that I wasn't able to establish any strong cause and effect relationships between any of the heavy metal concentrations. The only moderate relationship I achieved in this study was the correlation between pH level and bone preservation level. This showed that the higher the pH level the less preserved the skeletal remains will be. Many samples fell far from the regression line which had a large standard deviation, but this only proved that pH cannot be the only factor causing speeded diagenesis and therefore it is necessary to investigate the heavy metal composition effects on bone preservation.

From undertaking this project I have learnt to completely critique any methods, such as my method of bone assessment, I choose in the future before data collection begins to avoid situations where the results obtained are less informative than they should be, and to ensure that every piece of data I collect is concise, usable and worthwhile.

Planning this project allowed me to set time constraints and allow for any inconveniences which may crop up. I originally booked to complete my soil digestion in September 2012, but when the time approached the microwave that was used for this process was out of order. This meant that my results, discussion and conclusion sections of my dissertation were put on hold for longer than expected due to the start of this new school year. This caused my laboratory work to be undertaken a few months away from the deadline, which greatly increased the stress and pressure of getting my dissertation done. But I am thankful for this as it's shown me to always expect the unexpected when conducting independent research, and that everything is not going to go ahead like the original plan. I now know for the future to ensure that any sample collection, laboratory work and analysis are done as soon as possible to allow for a smooth transition from one section to the other.

This project also allowed me to explore many different areas of research and broaden my knowledge and focus away from just being pigeonholed into researching forensic or archaeological science. I was able to learn about the conservational and archaezoological aspects of this research which really made me understand that certain research is not only valuable to one area of science, but in fact to all areas when applied correctly and in context.

Interim Interview Comments

Student Research Project Interview – Agreed Comments Form

Student Name: Rosemary Helen Mayne	Programme: BSc Archaeological, Anthropological and Forensic Sciences
Date: June 2012	IRP Geochemistry of the soil and its effects on bones.
Supervisor Name: Paul Cheetham	

Interim meeting was conducted on site where it was discussed that soil samples were only going to be taken from large articulated animal skeletal remains as well as human burials.
Individual bones are not to be included due to uncertainty if damage was taphonomic in nature or environmental.
Bone assesment of damage will be conducted on site to ensure no loss of sample data in the post excavation process.
Soil samples are going to be pH tested off site using a suitable methodology.

Two copies of this form are needed – student to retain one copy the other is to be handed in to the student admin office C237.

Student Signature: RMayne	Supervisor Signature: P.N. Cheet